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# CHESAPEAKE BAY AIRSHED EXCHANGE BUDGET

*Convenors: Dr. Joel Baker and Mr. Paul Miller*

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ATMOSPHERIC NITROGEN DEPOSITION TO THE CHESAPEAKE BAY

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*Abstract:* Nitrification of Chesapeake Bay is well established as a major threat to the health of these waters, but the role of the atmosphere as a source of reactive nitrogen to the Bay remains as a critical unanswered question. Anthropogenic emissions dominate among sources of reactive nitrogen in the lower atmosphere over the Chesapeake Bay watershed, both for oxidized nitrogen (nitric acid, particulate nitrate, oxides of nitrogen) and reduced nitrogen (ammonia and ammonium). The flux of these species, and even their concentrations, are at present not known well enough to produce reliable estimates of the impact of atmospheric pollutants on the Bay.

At the University of Maryland, we have made a few preliminary measurements of reactive nitrogen species in the air over the Chesapeake Bay watershed and are building a program on Regional Atmospheric Measurements, Modeling and Prediction (RAMMP). A year-long study of NO and NO<sub>y</sub> (the sum of NO, NO<sub>2</sub>, HNO<sub>3</sub>, PAN, NO<sub>3</sub>, and other minor species) in Shenandoah National Park (SNP) showed that reactive nitrogen peaks in winter (mean = 4.0 ppb) were completely out of phase with wet deposition of nitrate. We also measured total airborne nitrate (HNO<sub>3</sub> + NO<sub>3</sub><sup>-</sup>) for a brief (3-wk) period. If we assume that the mixing ratios are typical of the entire watershed, the observed mean nitrate to NO<sub>y</sub> ratio of 20% is representative of the annual average, and the mean deposition velocity is 0.02 m/sec, then about 4 x 10<sup>9</sup> g N/yr are deposited directly onto the Bay, and about 55 x 10<sup>9</sup> g N/yr are deposited onto the Bay watershed. This would be a significant fraction of the total N deposition.

In August and September 1993, we measured NO, NO<sub>x</sub> (NO + NO<sub>2</sub>), and NO<sub>y</sub> at the University of Maryland's Wye River site on Maryland's Eastern Shore. Mixing ratios were higher than in SNP (mean NO<sub>y</sub> = 7.7 ppb) and were strongly dependent on the origin of the air, with greatest concentrations arising with winds from the Baltimore or Washington areas. NO<sub>x</sub> to NO<sub>y</sub> ratios averaged around 60% meaning that a large fraction of the reactive, even near urban areas, is in the form of nitrates.

Work in progress (in collaboration with the National Oceanic Atmospheric Administration's Air Resources Laboratory) includes direct measurements of the flux of NO and nitrate with the eddy correlation technique, and new high-speed and high-resolution measurements of ammonia. To extrapolate from individual measurements to regional-scale effects, we are developing a mesoscale chemical/meteorological model. By constraining the model to agree with existing observations, we hope to be able to predict more accurately the role of atmospheric processes in the health of the Bay.

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LONG-TERM NITROGEN DEPOSITION ON THE RHODE RIVER WATERSHED

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**Abstract:** We have continuously measured, on an event basis, bulk precipitation fluxes of nitrate for 21 years, ammonium for 17 years, and total nitrogen for 18 of those years. The long-term volume-weighted mean concentrations of nitrate, ammonium, and organic nitrogen were 502, 289, and 333  $\mu\text{g N per liter}$ , respectively. Fluxes of nitrate have increased over the last 20 years and have varied from 3.26  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1974 to 8.86  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1989, and averaged 5.56  $\text{kg N ha}^{-1} \text{yr}^{-1}$ . Ammonium fluxes increased as well, with a minimum of 1.72  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1980 and a maximum of 4.44  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1991, and averaged 3.18  $\text{kg N ha}^{-1} \text{yr}^{-1}$ . Organic nitrogen was more variable and, if anything, declined. It varied from a low of 1.79  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1990 to a maximum of 6.73  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1978 and averaged 3.62  $\text{kg N ha}^{-1} \text{yr}^{-1}$ . Fluxes of nitrate, ammonium, and organic nitrogen all peaked in the spring. Fluxes of nitrate and organic nitrogen were lowest in the fall, while ammonium flux was lowest in the winter. The sum of overland storm and groundwater fluxes of all three fractions of nitrogen from cropland-dominated, pasture-dominated, and forested watersheds all peaked in the spring and were lowest in the fall. Watershed discharge fluxes of organic nitrogen were 87%, 21%, and 41% of bulk precipitation fluxes, respectively, for cropland, pasture, and forest. Watershed discharges of inorganic nitrogen were 51%, 9%, and 3% of precipitation fluxes, respectively, for cropland, pasture, and forest.

INTRODUCTION

Atmospheric deposition of nitrate, ammonium, and organic nitrogen has been an often overlooked component of the nitrogen budget of ecosystems. Atmospheric deposition is composed of both wet deposition in rainwater and dry deposition. The dry component consists of sedimenting particles, and aerosols and molecules trapped from the air by impaction on surfaces of plants, soil, water, etc. This dry deposition is difficult to measure and few accurate data exist for the Chesapeake Bay region. However, the techniques for measuring wet deposition and bulk precipitation are well established and are relatively easy. The main difference between the sampling techniques for wet and bulk precipitation is that the wet-only collector is closed between rainstorms, while the bulk sampler is open all of the time. Thus, the bulk collector samples both wet deposition in rainwater and sedimenting dry particulates between storms. In our experience there are few significant differences in the chemical, composition of samples taken by the

two methods side by side (Jordan et al. in press).

In the Chesapeake Bay region, acidic atmospheric deposition has deleterious effects on watersheds and freshwater ecosystems (Correll and Ford 1982, Correll et al. 1984, Weller et al. 1986, Correll et al. 1987, Baker et al. 1991). In addition, enrichment of precipitation with nitrate and ammonium contributes to eutrophication of tidal waters (Correll and Ford 1982, Jordan et al. 1983, Correll 1987, Fisher and Oppenheimer 1991) and possibly the coastal ocean (Pearl 1985, 1993, Fanning 1989).

Our measurements of wet and bulk deposition at the Rhode River site on the western shore of the Bay near Annapolis, Maryland, from 1973 to the present are the longest set of data for the Chesapeake Bay region. Here we report detailed results for the volume and nitrogen content of bulk precipitation. For further data on other components and statistical trend analyses, see Jordan et al. (in press). We also compare these nitrogen input fluxes with long-term discharge fluxes from

Rhode River subwatersheds with different land uses (Correll 1977, 1981, Correll et al. 1992). This study is part of an overall long-term airshed/watershed/estuary study of the Rhode River, a tributary system of Chesapeake Bay (Jordan et al. 1991a, 1991b, Correll et al. 1992).

## METHODS

Precipitation volume was measured with a Belfort weight-recording rain gauge and with a standard weather-bureau manual rain gauge. Bulk precipitation samples for chemical analysis were collected with a 28 cm diameter polyethylene funnel on a polyethylene bottle mounted on a 13 m high tower near the rain gauges. After each event or combination of events of more than 5 mm of precipitation, samples were collected and the sampler was cleaned. Nine hundred and thirty seven samples were collected. Samples were stored at 4°C until analysis and analyses, for ammonium and TKN were made within 5 days, nitrate within 2 weeks, or else the samples were frozen.

Three watersheds, drained by small first-order streams, were sampled (Correll 1977). One (no. 110) was a mature deciduous forest that had never been clearcut and another (no. 109) was two-thirds row crops and one-third riparian forest and had been in agricultural use since at least 1846 (Vai thiyanathan and Correll 1992). The third (no. 111) was a pasture used for beef cattle grazing. Watershed discharges were measured with sharp-crested V-notch weirs and volume-integrated samples representative of the chemical composition of the discharge were taken for laboratory analysis of nutrient composition (Correll 1977, 1981). Aliquots of streamwater were pumped from the stream channel when a fixed increment of flow had occurred. These aliquots were composited for one-week intervals in plastic bottles with sulfuric acid preservative. The watersheds are all underlain by the Marlboro clay, an impervious aquiclude near sea level, and the weir foundations extend down to this layer. Thus, both overland storm flows and shallow groundwater originating within the watershed are forced to flow through the weir.

Analytical techniques for nitrate were changed over time, but whenever techniques were changed a series of samples were analyzed by both the old and new techniques to test comparability. Triplicate analyses were routinely performed on about 10% of the samples to assess analytical precision. Nitrate was initially analyzed by colorimetry after cadmium amalgam reduction to nitrite (APHA

1976), and later with a Dionex ion chromatograph and a Technicon auto-analyzer (method no. 696-82W). Ammonium was analyzed by the hypochlorite oxidation technique (American Public Health Association 1976). Total Kjeldahl nitrogen was digested according to Martin (1972), and the resultant ammonium was distilled and analyzed by Nesslerization (American Public Health Association 1976). The concentration of total organic nitrogen was calculated as the difference between TKN and ammonium. The concentration of total nitrogen was calculated as the sum of TKN and nitrate.

## RESULTS

### Annual Bulk Precipitation

The annual volume of rainfall from 1974 through 1993 averaged 111.7 cm (table 1), somewhat above the long-term mean of 108.6 cm for the vicinity of the Rhode River between 1817 and 1977 (Hignan and Correll 1982). Years in which rainfall was more than 20% below the long-term mean were 1977, 1980, and 1986. Years when rainfall was more than 20% above the mean were 1975, 1979, and 1989. None exceeded the extremes in the 160-year record.

Volume-weighted annual nitrate concentrations averaged 502  $\mu\text{g N l}^{-1}$  (table 1) and increased over the 20-year period (figure 1). Nitrate concentrations were more than 20% below the 20-year mean in 1974, 1975, and 1979 and were more than 20% above the mean in 1978, 1986, and 1989. Rates of nitrate deposition in bulk precipitation averaged 5.56  $\text{kg N ha}^{-1} \text{yr}^{-1}$  and peaked at 8.86  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1989 (table 1, figure 2). Volume-weighted annual ammonium concentrations averaged 289  $\mu\text{g N l}^{-1}$  (table 1) and also increased over the 16-year period (figure 1). Ammonium concentrations were more than 20% below the 16-year mean in 1979, 1980, and 1982 and were more than 20% above the mean in 1986, 1991, and 1992. Rates of ammonium deposition in bulk precipitation averaged 3.18  $\text{kg N ha}^{-1} \text{yr}^{-1}$  and peaked at 4.44  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1991 (figure 2). The mean for organic nitrogen deposition for the 13 complete years measured was 3.62  $\text{kg N ha}^{-1} \text{yr}^{-1}$  (table 1). Organic nitrogen deposition was much more variable than nitrate or ammonium ranging from a low of 1.79  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1990 to a high of 7.63  $\text{kg N ha}^{-1} \text{yr}^{-1}$  in 1991 (figure 2). Total nitrogen deposition for the 17 years measured averaged 11.8  $\text{kg N ha}^{-1} \text{yr}^{-1}$  (table 1).

Table 1. Volume-weighted annual mean bulk precipitation data for the Rhode River site.

Year	Volume (cm)	Nitrate		Ammonium		Organic N (kg N/ha)	Total N (kg N/ha)
		(ug N/l)	(kg N/ha)	(ug N/l)	(kg N/ha)		
1974	106.1	308	3.26				7.97
1975	133.3	295	3.93				9.34
1976	119.2	410	4.89				10.4
1977	82.4	447	3.69				9.34
1978	119.7	633	7.58	264	3.16	6.73	17.5
1979	164.5	375	6.17	174	2.87	3.81	12.9
1980	85.9	498	4.27	200	1.72	2.89	8.88
1981	90.9	491	4.46	316	2.87	5.22	12.6
1982	114.1	455	5.19	224	2.56	2.40	10.1
1983	130.1	578	7.52	257	3.34	4.07	14.9
1984	126.5	494	6.25	338	4.28	3.13	13.7
1985	96.6	563	5.44	289	2.79	1.95	10.2
1986	86.5	614	5.32	358	3.10	2.34	10.8
1987	112.6	524	5.90	292	3.29		
1988	98.0	530	5.19	278	2.72		
1989	146.6	604	8.86	242	3.55		
1990	110.0	503	5.53	341	3.75	1.79	11.1
1991	105.0	590	6.19	423	4.44	7.63	18.3
1992	106.7	561	5.99	363	3.87	2.45	12.3
1993	98.6	573	5.65	262	2.58	2.61	10.8
Mean	111.7	502	5.56	289	3.18	3.62	11.8

#### Seasonal Bulk Precipitation

Mean winter (December-February) precipitation for the 21 years of our study was 25.9 cm, higher than the 24.6 cm 160-year mean volume for winter precipitation (Higman and Correll 1982). Years during this study in which precipitation was over 30% below this long-term mean were 1977, 1980, and 1981, while 1978, 1979, 1984, 1987, and 1994 were more than 30% above this mean (table 2). The winter of 1979 exceeded the maximum volume recorded during the 160 years prior to 1978 (Higman and Correll 1982). Winter nitrate concentrations for the 21 seasons of our study averaged 512 ug N l<sup>-1</sup> (table 2). Years in which nitrate concentrations were more than 30% below the mean were 1974, 1975, 1979, and 1987, while concentrations were more than 30% above the mean in 1978 and 1989. In winter nitrate deposition averaged 1.29 kg N ha<sup>-1</sup> season<sup>-1</sup>, peaking in 1978 at 3.06 kg N ha<sup>-1</sup> season<sup>-1</sup>. Winter ammonium concentrations and deposition rates were lower than for the other seasons. For 17 winters ammonium concentrations averaged 197 ug N ha<sup>-1</sup> season<sup>-1</sup> (table 2). Concentrations were more than 30% below this mean in 1978, 1979, and 1980, while in 1986, 1989, and 1990 concentrations were

more than 30% above the mean. Mean ammonium deposition rates were 0.484 kg N ha<sup>-1</sup> season<sup>-1</sup> and peaked in 1994 at 0.627 kg N ha<sup>-1</sup> season<sup>-1</sup>. Organic nitrogen and total nitrogen deposition rates averaged 0.365 and 2.07 kg N ha<sup>-1</sup> season<sup>-1</sup>, respectively (table 2).

During the 21 spring seasons of our study precipitation volume averaged 28.4 cm (table 2), slightly above the long-term average of 28.0 cm (Higman and Correll 1982). In 1973, 1977, 1985, 1986, and 1987, precipitation was more than 30% below the long-term mean, while in 1978, 1983, 1984, and 1989 it was more than 30% above the long-term mean. Mean spring nitrate concentrations, at 569 ug N l<sup>-1</sup>, were the highest of any season (table 2). Spring nitrate concentrations were more than 30% below the mean in 1973, 1974, and 1975, while in 1986 and 1987 they were more than 30% above the mean (figure 3). Spring deposition of nitrate averaged 1.54 kg N ha<sup>-1</sup> season<sup>-1</sup> with peaks in 1984 and 1989 of 2.77 and 2.78 kg N ha<sup>-1</sup> season<sup>-1</sup>, respectively. Spring ammonium concentrations averaged the highest of any season at 419 ug N l<sup>-1</sup> (table 2). In 1978, 1979, 1980, 1983, and 1993 spring ammonium concentrations were more than 30% below the average, while they were more than 30% above the mean in 1986, 1987, and 1991 (Fig. 4). Ammonium

Table 2. Volume-weighted mean seasonal bulk precipitation for the Rhode River site.

Winter	Volume (cm)	Nitrate (ug N/l) (kg N/ha)	Ammonium (ug N/l) (kg N/ha)	Organic N (kg N/ha)	Total N (kg N/ha)		
1974	30.4	313	0.950		1.56		
1975	26.8	340	0.910		1.47		
1976	28.9	535	1.54		2.46		
1977	11.5	456	0.525		0.817		
1978	41.8	732	3.06	132	0.552	0.719	4.33
1979	49.6	326	1.61	117	0.579	0.447	2.64
1980	12.9	461	0.593	132	0.170	0.263	1.03
1981	13.9	458	0.636	212	0.294	0.175	1.11
1982	25.2	610	1.54	207	0.522	0.354	2.41
1983	26.1	646	1.69	220	0.574	0.790	3.05
1984	34.4	494	1.70	144	0.495	0.234	2.43
1985	17.9	596	1.07	219	0.391	0.0781	1.54
1986	19.2	584	1.12	274	0.525	0.236	1.88
1987	39.2	347	1.36	152	0.596	0.265	2.22
1988	27.0	451	1.22	197	0.531		
1989	17.7	842	1.49	322	0.571		
1990	18.2	562	1.02	267	0.485	0.0612	1.57
1991	23.3	473	1.10	226	0.528	0.490	2.12
1992	20.3	520	1.06	180	0.366	0.215	1.64
1993	24.4	527	1.29	172	0.418	0.529	2.23
1994	34.4	471	1.62	182	0.627	0.623	2.87
Mean	25.9	512	1.29	197	0.484	0.365	2.07
Spring							
1973	14.8	388	0.576				1.21
1974	31.7	298	0.946				3.36
1975	32.6	362	1.18				3.08
1976	20.0	533	1.06				2.63
1977	18.4	576	1.06				3.23
1978	40.0	506	2.02	206	0.823	2.88	5.73
1979	27.9	435	1.22	251	0.701	1.04	2.96
1980	30.6	515	1.57	211	0.646	1.27	3.49
1981	28.4	518	1.47	457	1.30	3.29	6.06
1982	23.6	528	1.24	326	0.768	0.720	2.73
1983	48.7	444	2.16	276	1.34	1.18	4.68
1984	40.9	677	2.77	539	2.21	1.54	6.52
1985	19.4	536	1.04	474	0.918	0.941	2.90
1986	10.8	128	1.21	697	0.749	0.597	2.56
1987	19.1	956	1.82	548	1.04	1.46	4.33
1988	22.9	616	1.41	479	1.10		
1989	43.5	639	2.78	311	1.35		
1990	34.1	420	1.43	414	1.41	0.892	3.73
1991	30.5	630	1.92	743	2.27	5.70	9.89
1992	24.2	738	1.78	528	1.28	0.475	3.53
1993	34.5	503	1.74	243	0.839	0.893	3.47
Mean	28.4	569	1.54	419	1.17	1.63	4.00

Table 2. (continued)

Summer	Volume (cm)	Nitrate (ug N/l (kg N/ha)	Ammonium (ug N/l) (kg N/ha)	Organic N (kg N/ha)	Total N (kg N/ha)		
1973	24.8	438	1.09		1.89		
1974	23.9	350	0.834		2.02		
1975	38.9	264	1.03		3.03		
1976	38.0	316	1.20		3.31		
1977	23.4	508	1.19		3.30		
1978	21.8	538	1.17	506	1.10	1.32	4.72
1979	39.3	538	2.11	272	1.07	1.37	4.19
1980	19.9	641	1.28	280	0.558	1.28	2.77
1981	30.0	449	1.35	258	0.773	1.26	3.39
1982	37.8	430	1.62	255	0.964	1.26	3.45
1983	24.4	716	1.75	408	0.995	1.26	4.34
1984	27.9	452	1.26	381	1.06	1.26	3.15
1985	20.2	492	0.993	435	0.877	1.23	2.46
1986	34.6	463	1.60	288	0.995	1.23	3.39
1987	25.0	574	1.43	313	0.782		
1988	22.0	630	1.39	340	0.749		
1989	52.5	539	2.83	174	0.913		
1990	41.4	602	2.49	358	1.48	0.263	4.61
1991	26.7	767	2.04	367	0.980	0.158	4.12
1992	31.2	467	1.46	364	1.14	0.310	3.37
1993	11.0	897	0.987	407	0.448	0.404	1.80
Mean	29.3	527	1.48	338	0.931	0.971	3.30
Fall							
1973	18.1	183	0.330				0.701
1974	20.1	266	0.534				1.03
1975	35.0	231	0.807				1.76
1976	32.4	335	1.08				2.02
1977	29.0	313	0.910	127	0.369	0.452	1.99
1978	16.2	820	1.33	423	0.684	0.449	2.69
1979	47.7	257	1.23	109	0.519	0.446	3.06
1980	22.5	368	0.827	153	0.343	0.435	1.59
1981	18.6	542	1.01	270	0.502	0.414	2.00
1982	27.6	284	0.783	111	0.307	0.383	1.55
1983	31.0	623	1.93	138	0.427	0.339	2.86
1984	23.3	221	0.515	222	0.516	0.279	1.56
1985	39.2	599	2.35	153	0.601	0.180	3.29
1986	22.0	628	1.38	377	0.831	0.177	2.93
1987	29.4	435	1.28	293	0.862		
1988	26.1	452	1.18	132	0.345		
1989	32.9	534	1.76	217	0.714	0.186	3.31
1990	16.3	358	0.585	228	0.372	0.182	1.17
1991	24.5	460	1.12	270	0.661	0.189	2.13
1992	31.0	545	1.69	352	1.09	0.197	3.76
1993	28.7	572	1.64	305	0.875	0.117	3.34
Mean	27.2	430	1.16	228	0.590	0.295	2.25

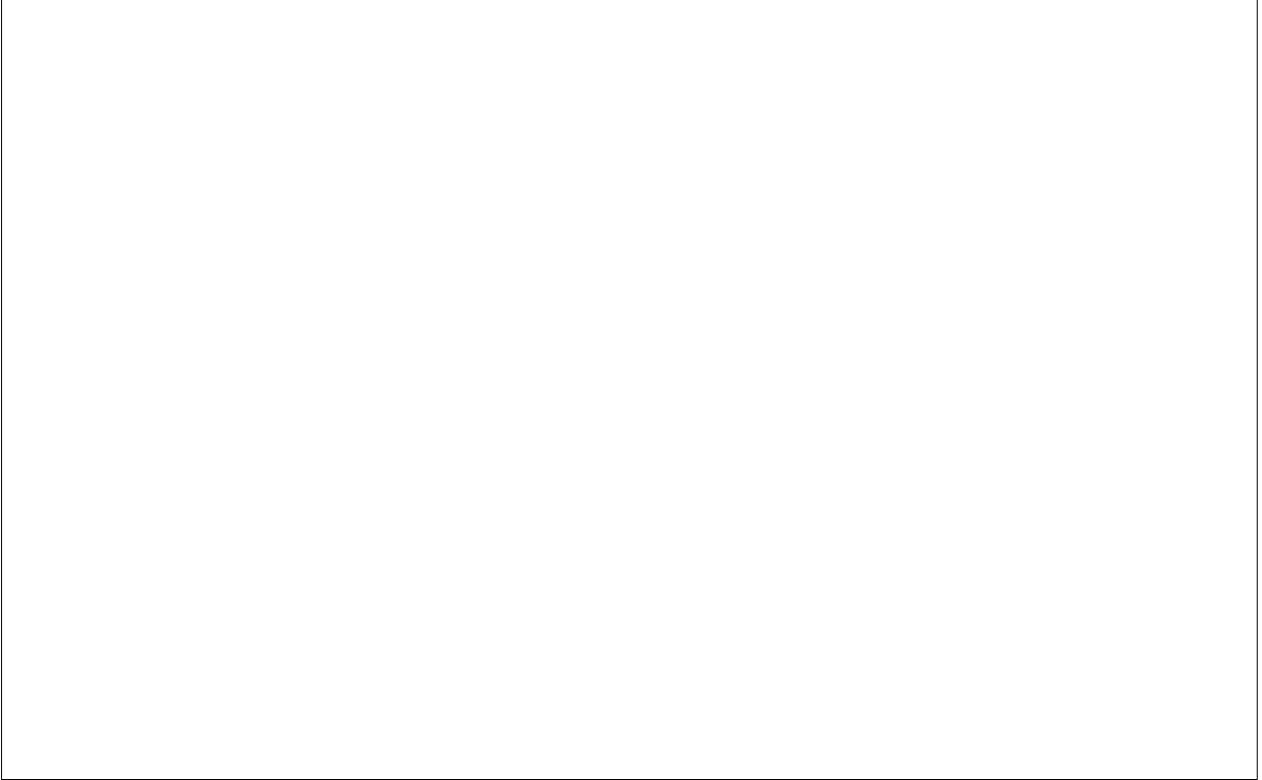


Figure 1. Long-term variations in annual volume-weighted mean nitrate and ammonium concentrations in bulk precipitation at the Rhode River, site. Solid points are nitrate means.



Figure 2. Long-term variations in annual atmospheric deposition of nitrate and ammonium in bulk precipitation at the Rhode River, site. Solid points are nitrate means.

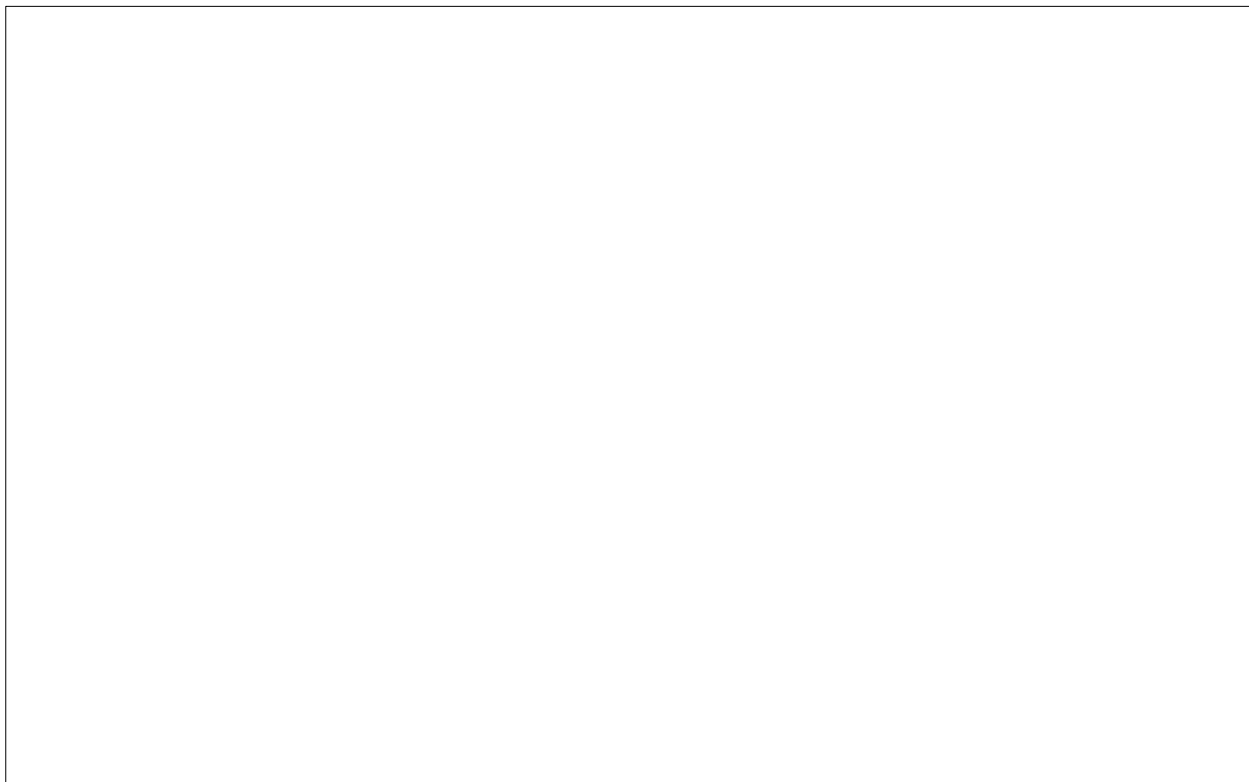


Figure 3. Interannual variations in annual volume-weighted nitrate concentrations in bulk precipitation at the Rhode River site. Solid points are spring means and open squares are fall means.

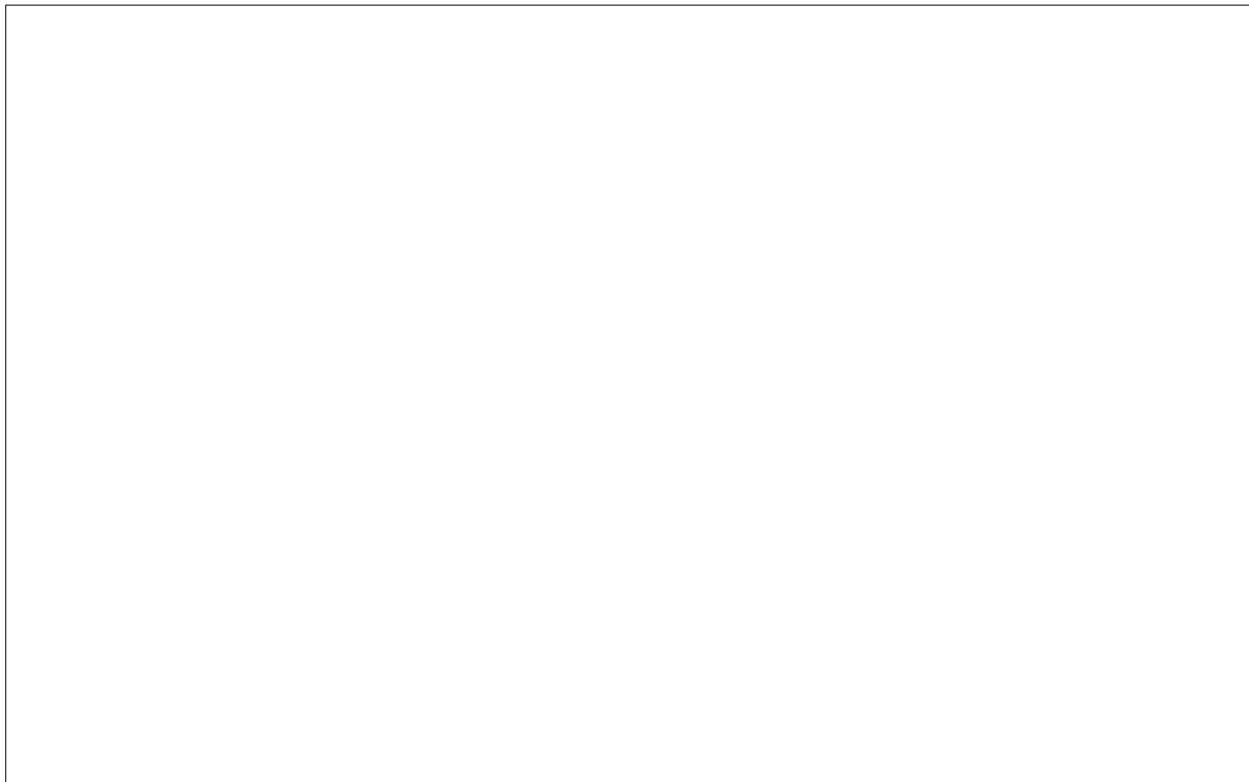


Figure 4. Interannual variations in volume-weighted ammonium concentrations in bulk precipitation at the Rhode River site. Solid points are spring means and open squares are fall means.

deposition in spring averaged  $1.17 \text{ kg N ha}^{-1} \text{ season}^{-1}$  with peaks in 1984 and 1991 of  $2.21$  and  $2.27 \text{ kg N ha}^{-1} \text{ season}^{-1}$ , respectively. Deposition of organic nitrogen and total nitrogen also was highest in the spring and averaged  $1.63$  and  $4.00 \text{ kg N ha}^{-1} \text{ season}^{-1}$ , respectively (table 2).

During the 21 summer seasons of our study, the volume of precipitation averaged  $29.3 \text{ cm}$  (table 2), somewhat below the 160-year of  $31.4 \text{ cm}$  (Higman and Correll 1982). In 1978, 1980, 1985, and 1993, precipitation was more than 30% below the long-term mean, while in 1989 and 1990 it was over 30% above the mean. Summer nitrate concentrations averaged  $527 \text{ ug N l}^{-1}$ . Summer nitrate concentrations were more than 30% below the mean in 1974, 1975, and 1976, but were more than 30% above the mean in 1983, 1991, and 1993 (table 2). Nitrate deposition in summer averaged  $1.48 \text{ kg ha}^{-1} \text{ season}^{-1}$ , with a peak of  $2.83 \text{ kg N ha}^{-1} \text{ season}^{-1}$  in 1989. Summer ammonium concentrations averaged  $338 \text{ ug N l}^{-1}$ . In 1989, ammonium concentration was more than 30% below the mean, while in 1978 it was more than 30% above the mean. Summer deposition of organic nitrogen and total nitrogen averaged  $0.971$  and  $3.30 \text{ kg N ha}^{-1} \text{ season}^{-1}$ , respectively (table 2).

Fall precipitation had a mean volume of  $27.2 \text{ cm}$  during the 21 falls of our study, considerably higher than the 160-year of  $24.5 \text{ cm}$  (Higman and Correll 1982). Precipitation in the fall was over 30% below the long-term mean in 1978 and 1990, but more than 30% above this mean in 1975, 1976, 1979, 1985, and 1989 (table 2). Mean fall nitrate concentrations and deposition rates were lower than for any of the other seasons. Nitrate concentrations were more than 30% below the mean of  $430 \text{ ug N l}^{-1}$  in 1973, 1974, 1975, 1979, 1982, and 1984, while concentrations were more than 30% above this mean in 1978, 1983, 1985, 1986, and 1993 (figure 3). Nitrate deposition in the fall averaged  $1.16 \text{ kg N ha}^{-1} \text{ season}^{-1}$ , but ranged from  $0.330$  to  $2.35 \text{ kg N ha}^{-1} \text{ season}^{-1}$  in 1973 and 1985, respectively. Fall ammonium concentrations were over 30% below the average of  $228 \text{ ug N l}^{-1}$  in 1977, 1979, 1980, 1982, 1983, 1985, and 1988, but were more than 30% above this mean in 1978, 1986, 1992, and 1993 (figure 3). Ammonium deposition in the fall averaged  $0.590 \text{ kg N ha}^{-1} \text{ season}^{-1}$  and ranged from  $0.31$  to  $1.09 \text{ kg N ha}^{-1} \text{ season}^{-1}$  in 1982 and 1992, respectively. Fall deposition of organic nitrogen and total nitrogen averaged  $0.295$  and  $2.25 \text{ kg N ha}^{-1} \text{ season}^{-1}$ , respectively.

#### Comparisons of Bulk Precipitation Deposition with Watershed Discharges

At the Rhode River site, precipitation inputs to the watershed as bulk precipitation usually exceeded watershed outputs in overland stormflow and groundwater for nitrate, ammonium, and organic nitrogen (table 3). The cropland-dominated watershed had by far the highest discharges per area for all nitrogen fractions, but these fluxes only exceeded bulk precipitation input fluxes for nitrate in the spring for organic nitrogen in the winter and summer. Average annual nitrogen discharge from the cropland-dominated watershed was still less than precipitation input despite the large input of fertilizer nitrogen (Peterjohn and Correll 1984) to the croplands.

Forest area yield discharges were lowest in all seasons for nitrate, in the winter and fall for ammonium, and in the winter for organic nitrogen (table 3). Annual discharges of nitrate from forest were only 21% of those from pasture and 3.5% of those from cropland. Annual discharges of ammonium from forest slightly exceeded those from pasture, but were only 30% of those from the cropland-dominated watershed. In the spring and summer, ammonium discharges from forest were 29% and 6% above those from pasture, respectively, but only 42% and 18% of those from cropland, respectively. Forest discharges of organic nitrogen were relatively high compared to those of inorganic nitrogen, but did not exceed bulk precipitation fluxes for any season (table 3). Forest annual discharges of organic nitrogen were only 41% of the input flux in bulk precipitation.

Pasture discharges of nitrate and organic nitrogen per area were intermediate between those for the cropland-dominated watershed and for forest, but were lowest of the three land use categories for ammonium and total nitrogen (table 3).

#### DISCUSSION

In general, the rate of deposition of nitrogen in bulk precipitation is higher than watershed nitrogen discharges per hectare (table 3). This might lead one to conclude that atmospheric wet deposition falling directly on the surface waters of the estuary are larger than nonpoint sources of nitrogen in land discharges. However, one must remember that the watershed has more surface area than the estuary. For example, the Rhode River watershed has six times the surface area of the Rhode River (Correll 1977, Jordan et al. 1991a).

Table 3. Comparison of long-term mean Rhode River watershed bulk precipitation nitrogen inputs with nitrogen discharges from three land use categories. All values are in kg of nitrogen per hectare. Measurements spanned 16 complete years for the cropland and forest watersheds and 14 years for the pasture watershed.

A. Nitrate Season	Precipitation Inputs	Watershed Outputs		
		Cropland	Pasture	Forest
Winter	1.29	1.28	0.324	0.0281
Spring	1.54	1.98	0.310	0.0948
Summer	1.48	0.569	0.0259	0.0133
Fall	1.16	0.127	0.0111	0.00469
Total for Year	5.56	3.90	0.649	0.138
B. Ammonium				
Winter	0.484	0.112	0.0531	0.0284
Spring	1.17	0.205	0.0675	0.0870
Summer	0.931	0.163	0.0282	0.0298
Fall	0.590	0.0288	0.0129	0.0098
Total for Year	3.18	0.524	0.154	0.157
C. Organic-N				
Winter	0.365	0.490	0.243	0.176
Spring	1.63	1.25	0.360	0.681
Summer	0.971	1.20	0.126	0.364
Fall	0.295	0.147	0.0603	0.216
Total for Year	3.62	3.16	0.763	1.47
D. Total-N				
Winter	2.07	1.88	0.620	0.233
Spring	4.00	3.44	0.738	0.863
Summer	3.30	1.94	0.180	0.407
Fall	2.25	0.304	0.0843	0.230
Total for Year	11.8	7.58	1.57	1.77

The watershed of Chesapeake Bay is almost 15 times larger than the combined surface area of the Bay and its tidal tributaries (Correll 1987).

Even when one takes the relative areas of the watershed into account, however, in most years the Rhode River receives more inorganic nitrogen in bulk precipitation falling directly on the tidal waters than it receives in watershed discharges (Correll and Ford 1982). However, Chesapeake Bay has proportionally more watershed than does Rhode River. The importance of atmospheric deposition as a source of nitrogen for the watershed of the Bay was emphasized by Fisher and Oppenheimer (1991) in an analysis that included two key assumptions. First, it was assumed that atmospheric dry deposition of nitrogen was equal

to wet deposition. Because there were essentially no measurements of dry deposition in the region, this might be a fair assumption. Second, it was assumed that nitrogen deposited on forested watershed areas was not retained very effectively. This was not so for the coastal plain forest we studied (e.g., Weller et al. 1986 and table 3), but may be a better assumption for some areas of the watershed that are within the Appalachian Plateau physiographic province. For example, the Fernow Experimental Forest in the Appalachian Plateau on the upper Potomac River watershed in West Virginia was much less effective at retaining nitrogen than was the forest we studied. Over a 13-year period ending in 1990, precipitation at the Fernow forest averaged 149.4 cm and contained

Table 4. Comparison of Rhode River bulk precipitation composition with other long-term wet deposition study sites on or adjacent to the Chesapeake Bay watershed. Volume-weighted mean annual nitrate and ammonium concentrations ( $\mu\text{g N l}^{-1}$ ).

Collection Site	Years Included	Nitrate	Ammonium
Rhode River, MD	1974-1993	502	289
Fernow Exp. Forest, WV	1978-1990	366	156
Tunkhannock, PA	1979-1987	365	187
Ithaca, NY	1977-1987	417	230
Penn. State Univ., PA	1977-1987	41	245
Univ. Virginia, VA	1977-1987	356	200
Lewes, DE	1979-1987	283	186

$156 \mu\text{g N l}^{-1}$  of ammonium nitrogen and  $366 \mu\text{g N l}^{-1}$  of nitrate nitrogen. Stream discharge from the control forested watershed contained an average of  $87 \mu\text{g N l}^{-1}$  of ammonium nitrogen and  $771 \mu\text{g N l}^{-1}$  of nitrate nitrogen (Adams et al. 1994). If the only effect of the watershed were to evaporate and transpire water vapor, leaving the nutrient salts behind, the mean stream concentration of ammonium and nitrate nitrogen would have been  $336 \mu\text{g N l}^{-1}$  and  $791 \mu\text{g N l}^{-1}$ , respectively, in that stream discharge averaged 69.3 cm per year. This suggests that this forest was retaining only 74% of the ammonium and 3% of the nitrate from the wet precipitation, assuming that there was no dry deposition. For comparison, nitrate retention calculated in a similar manner for the Rhode River forest was 97.5% (table 3).

Wet deposition varies spatially throughout the Chesapeake watershed. The wet deposition at the Fernow Experimental Forest was about the same as our measurements at the Rhode River site. The volume of precipitation was 34% higher at Fernow and the nitrate content was 37% lower than at Rhode River. The Utility Acid Precipitation Study Program (American Public Health Association 1989) reported long-term (1979-87) means of 365 and  $187 \mu\text{g N l}^{-1}$  for nitrate and ammonium, respectively, at Tunkhannock in north-eastern Pennsylvania. The U. S. Department of Energy (1989) has reported wet deposition from 1977 through 1987 for Ithaca, New York (just north of the boundary of the Bay's watershed), Pennsylvania State University, and the University of Virginia. Data from 1979 through 1987 were also reported from Lewes, Delaware (just east of the boundary of the lower Bay watershed) (U. S. Department of Energy 1989). Nitrate concentrations from these four sites ranged from  $283 \mu\text{g N l}^{-1}$  at Lewes to  $441$

$\mu\text{g N l}^{-1}$  at Pennsylvania State University. Ammonium concentrations ranged from  $186 \mu\text{g N l}^{-1}$  at Lewes to  $245 \mu\text{g N l}^{-1}$  at PA State University. Our long-term means for nitrate and ammonium of  $502 \mu\text{g N l}^{-1}$  and  $289 \mu\text{g N l}^{-1}$  are somewhat higher than the six other sites (table 4).

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TRENDS IN PRECIPITATION CHEMISTRY THROUGHOUT THE EASTERN UNITED STATES

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*Abstract:* Trend analyses were conducted on weekly precipitation volume and chemistry data collected at National Atmospheric Deposition Program (NADP) monitoring sites from 1980 through 1992. These data were accumulated into bi-monthly precipitation totals and volume-weighted mean concentrations. Trends in ionic concentrations at each site were evaluated with a general linear least squares model using log-transformed concentration data. The normality of the residuals was evaluated using a Shapiro-Wilk test. The constancy of error variance about the estimated trends was examined by testing whether the mean absolute value of residuals differed significantly ( $p < 0.05$ ) among years. A mean annual concentration value was estimated for each ion for 1980 and 1992 to determine how much the ionic composition of precipitation changed from the beginning to the end of the trend analysis period. Of the 41 sites in operation within the eastern US from 1980-1992, 15 exhibit significant ( $p < 0.05$ ) decreasing sulfate concentration trends. No site exhibits an increasing sulfate concentration trend. Nitrate concentrations are decreasing at 4 sites. None of the sites exhibit increasing or decreasing ammonium concentration trends. With respect to base cation trends, calcium, magnesium, potassium, and sodium concentrations are generally decreasing throughout the region. From an acidity point of view, only 8 of the 41 sites exhibit increasing (less acidic) pH trends. Decreasing pH trends are not evident at any site. Of the 8 sites with increasing pH trends, all have corresponding significant ( $p < 0.05$ ) decreasing sulfate concentration trends. The lack of statistically significant increasing pH trends at many sites with decreasing sulfate trends is attributable to decreasing base cations concentrations in precipitation in the region. Although regional sulfur and nitrogen oxide emissions are generally decreasing, correlation with decreasing sulfate and nitrate concentrations in precipitation is difficult to assess owing to the influence of "local" emission sources.

INTRODUCTION

It has only been within the past 15 years that atmospheric deposition has been recognized as a significant nonpoint-source of pollution to terrestrial and aquatic ecosystems in the United States. Its importance as a source of nitrogen to the Chesapeake Bay was first realized in 1988 with the publication of two reports, one by Fisher et al. (1988) and the other by Tyler (1988). These independent studies estimated that in 1984 atmospheric deposition of nitrogen was 25% or more of the total nitrogen load to the Bay. In a similar study, Williams and Lynch (1989) estimated that atmospheric contributions of nitrate-nitrogen to the Bay in 1984 at  $2.3 \times 10^7$  kg, somewhat higher than the estimate by Fisher et al. (1988), but within the range reported by Tyler (1988). Other reports have emphasized the importance of acidic deposi-

tion to the Bay and its tributaries and its impact on aquatic fauna and flora.

Given the potential significance of atmospheric deposition, especially nitrogen deposition, to the Bay, it would appear that successful restoration of the Bay will occur only if atmospheric contributions are taken into consideration. Fortunately, the Clean Air Act Amendments of 1990 specifically require reductions in the emissions of both nitrogen and sulfur oxides from fossil fuel combustion. Such reductions should impact the Bay and its tributaries by reducing both nitrogen and acidic deposition. However, the magnitude of these reductions is unknown and can be determined only through evaluation of existing data and continued monitoring of atmospheric deposition to the basin. The most significant source of data on atmospheric deposition to the Bay is available

from the National Atmospheric Deposition Program/National Trends Network (NADP/NTN). This national network was initiated in 1978, although the majority of sites were not in operation until the early 1980s. Additional data are available from the nine-site Pennsylvania Atmospheric Deposition Monitoring Network. This network was established in 1982 and is supported by the Pennsylvania Department of Environmental Resources.

One means of detecting changes in deposition to the Bay is to conduct trend analyses. The most recent comprehensive summary of temporal trends in precipitation chemistry in the United States was reported in the National Acid Precipitation Assessment Program (NAPAP) report on deposition monitoring. Sisterson et al. (1990) applied a Kendall seasonal *tau* test for trend detection in the presence of constant-length cycles or seasonal effects (see Hirsch et al. 1982). Sen's median slopes (Gilbert 1987) were calculated to estimate the magnitude of changes in concentrations and depositions for sites meeting predetermined data completeness criteria (Olsen et al., 1990; Sisterson et al. 1990).

The NAPAP trends analysis addressed two time periods: a 39-site (24 NADP/NTN sites), nine-year data set (1979-87) and a 148-site (76 NADP/NTN sites), six-year data set (1982-1987). Statistically significant ( $p < 0.05$ ) trends were found at a higher proportion of sites for all ions, except  $\text{NO}_3^-$ , in the 9-year data set than in the 6-year period. This suggested that the largest changes occurred early in the data record from 1979 to 1982. Except for  $\text{NO}_3^-$  and  $\text{K}^+$ , the absolute magnitudes of the median percentage changes were larger for the nine-year period, as well. For the ions most affecting pH ( $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{Ca}^{2+}$ ), the strongest evidence for change was in the base cation,  $\text{Ca}^{2+}$ . Calcium decreased at 38 of the 39 sites over the 1979-87 period; at 13 sites these changes were significant ( $p < 0.05$ ). Sulfate decreased at 35 of the 39 sites; at seven sites these changes, all down, were significant ( $p < 0.05$ ). Nitrate,  $\text{NH}_4^+$ , and  $\text{H}^+$  ions exhibited a more even split of increasing and decreasing changes (Sisterson et al. 1990). These results lead the authors to conclude that the acidity of precipitation did not decrease because of the decrease in cations.

In a more recent article, Hedin et al. (1994) reported steep declines in base cation concentrations in precipitation in the United States Annual volume-weighted mean concentrations of  $\text{SO}_4^{2-}$

and base cations (defined as the sum of non-sea-salt  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ , and  $\text{K}^+$ ) were calculated using data from 32 NADP/NTN sites (1979 or 1980 to 1990), nine Multi-state Atmospheric Power Production Pollution Study (MAP3S) sites (1978-88), and the Hubbard Brook Experimental Forest (HBEF) (1965-89). A regression of these annual means against time in years yielded trend estimates for  $\text{SO}_4^{2-}$  and cations ( $\text{NH}_4^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ). At Hubbard Brook and at NADP/NTN sites in the Northeast, Southeast, and Midwest, both  $\text{SO}_4^{2-}$  and base cations decreased and the trends were significant ( $p < 0.05$  or  $p < 0.001$ ). At the nine MAP3S sites,  $\text{SO}_4^{2-}$  decreases were also statistically significant; however, base cations decreased at only five sites, none of which were statistically significant. Hedin et al. (1994) concluded that recent declines in both base cation and  $\text{SO}_4^{2-}$  have offset one another in varying proportions in many regions in the northern hemisphere.

In this study, a 13-year record (1980-92) of high quality weekly precipitation chemistry data from the NADP/NTN (National Atmospheric Deposition Study, 1980-1992) are examined for trends in pH and the major anions and cations affecting the free acidity of precipitation in the eastern United States. A least squares general linear model (SAS Institute, 1988) is used to evaluate the size and significance of the trends in log-transformed ion concentrations. The focus is on site-by-site trends in individual anion and cation concentrations at sites that met the data completeness criteria. The stoichiometric relationships of the trends in cation and anion concentrations to free hydrogen ion concentrations are evaluated to determine why precipitation pH did or did not change significantly over the 13-year period.

## METHODS

For use in trend analyses, weekly precipitation volume and chemistry observations from each NADP/NTN site were accumulated into bi-monthly precipitation totals and volume-weighted mean concentrations of  $\text{H}^+$  (from laboratory pH),  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{K}^+$ , and  $\text{Na}^+$ . Only valid weekly observations of 35 ml, or more, were used to calculate bi-monthly volume-weighted mean concentrations. These samples had adequate volume for a complete set of analyses without dilution (National Atmospheric Deposition Program 1990). Sites and bi-monthly records were selected for the trend analyses

according to the following completeness criteria:

- 1 Only those monitoring sites having weekly precipitation chemistry records from January 1980 through December 1992 were considered. Further, at least 75 % of the precipitation recorded from 1980 through 1992 had to have valid chemical analyses in order for the site's data to be accepted for trend analyses.
- 2 For a bi-monthly record to be accepted, at least 90 percent of the precipitation recorded during that period must have had a valid analysis for each ion.
- 3 During each bi-monthly period, at least 50% of the weekly samples having sufficient volume to analyze (> 35 ml) must have had a valid analysis for each ion.

Trends in the ionic concentrations in precipitation at each site having suitable data were evaluated using a two-stage, least squares general linear model (SAS Institute 1988). The form of the model for both stages was,

$$\log(C_y) = b_0 + b_y y + \sum_{s=1}^6 b_s I_s$$

where  $C_y$  = estimated concentration of a given ion at time  $y$ .

$b_0$  = intercept

$b_y$  = slope of the long-term log-concentration trend.

$y$  = mid-point of the bi-monthly observation period expressed as decimal years. For example,  $y$  for a May-June 1990 observation was coded as  $90 + (5/12)$  or 90.4167.

$b_s$  = adjustment to estimate for bi-monthly period,  $s$ . The array of 6  $b_s$  coefficients accounts for the seasonal variation in precipitation chemistry.

$I_s$  = an element of an array of 6 indicator variables set to 1 for bi-monthly period,  $s$ , and set to 0, otherwise.

Log-transformed concentrations were used because they have a more nearly normal distribution (Dana and Easter 1987). After initially fitting the model to a site's concentration data (expressed as micro-equivalents/L) for a given ion, studentized residuals were calculated. Any bi-monthly observation having a studentized residual >3.5 in absolute value were eliminated from the data set and a second calculation of the model coefficients was performed using the remaining

observations. This "automated" outlier removal was implemented because the large number of sites and ions under consideration prohibited intensive investigation of potential anomalies in the precipitation records corresponding to each outlier. The selected cut-off value applied to the studentized residuals would be exceeded by chance at a rate less than 0.001 under the assumption of normally distributed residuals of constant variance.

In order to illustrate how the ionic composition of precipitation has changed from 1980 through 1992 and how these changes have affected the  $H^+$  concentration, a mean annual concentration value ( $\mu\text{eq/L}$ ) was estimated for each ion for 1980 and 1992. The arrays of mean annual concentration estimates for 1980 and 1992 were contrasted to determine how the predicted changes in the ionic balance of precipitation accounted for the occurrence of significant trends in pollutant concentration. The interpretations of ionic balance are based on the assumption that  $H^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ , and  $NH_4^+$  account for all of the cations and that  $SO_4^{2-}$ ,  $Cl^-$  and  $NO_3^-$  account for all of the anions present in precipitation. In order to assess the relationship between anion and cation changes and changes in  $H^+$  concentrations, an ion balance was calculated according to the equation:

$$\Delta H^+ = \Delta \text{anions} - \Delta \text{cations}$$

where

$$\Delta H^+ = H^+_{1980} - H^+_{1992}$$

$$\Delta \text{anions} = (SO_4^{2-} + NO_3^- + Cl^-)_{1980} - (SO_4^{2-} + NO_3^- + Cl^-)_{1992}$$

$$\Delta \text{cations} = (Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4^+)_{1980} - (Ca^{2+} + Mg^{2+} + K^+ + Na^+ + NH_4^+)_{1992}$$

## RESULTS

### Trend Analysis

Results of the linear trend analyses for each site and ion are presented in table 1. Twenty-one NADP/NIN sites located in the eastern portion of the United States met the above completeness criteria and were included in this analysis. Of the 21 sites, 11 sites (52%) exhibit significant ( $p < 0.05$ ) decreasing  $SO_4^{2-}$  concentration trends from 1980 through 1992. None of the sites exhibit increasing trends. Although nearly the same number of sites with significant trends occurred in the northern and southern regions, the percentage of sites with significant trends was much greater in the south-

east (67% versus 42%). In addition,  $\text{SO}_4^{2-}$  trends at sites in the southern portion of the eastern United States were statistically more significant than in the northern portion of this region.

In comparison, only six sites (28.6%) exhibit significant ( $p < 0.05$ ) H<sup>+</sup> trends, all of which are decreasing (table 1). The number of significant sites is equally divided between the northeastern and southeastern regions. Of the 11 sites with significant ( $p < 0.05$ ) decreasing  $\text{SO}_4^{2-}$  trends, only five sites had concurrent decreasing H<sup>+</sup> concentration trends (table 2). Two of the sites are located in New York (NY08 and NY10); the remaining sites are all located in North Carolina (NC25, NC34, and NC35).

Of all the cations and anions in precipitation,  $\text{NO}_3^-$  and  $\text{NH}_4^+$  exhibit the least amount of change over the 13-year study period. Significant ( $p < 0.05$ )  $\text{NO}_3^-$  concentration trends are evident at only three sites (14.3%), all of which are decreasing. NY08 is the only site in the Northeast to exhibit a significant  $\text{NO}_3^-$  trend; in the Southeast, significant ( $p < 0.05$ ) trends are evident at NC03 and NC25. With regards to  $\text{NH}_4^+$ , only two sites (9.5%) in the Eastern United States exhibit significant ( $p < 0.05$ ) trends. In the northeast,  $\text{NH}_4^+$  concentrations are decreasing at NY20, while at NC41 in the southeast,  $\text{NH}_4^+$  concentrations have increased the past 13 years.

$\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations show the most consistent widespread decline of any of the ionic species in precipitation (table 1). Over 85% of the sites (18) have significant ( $p < 0.05$ ) decreasing  $\text{Ca}^{2+}$  concentrations, while 90.5% of the sites (19) exhibit significant decreasing  $\text{Mg}^{2+}$  concentrations. This general decreasing pattern is consistent and uniform in both the Northeast and Southeast. The only sites where  $\text{Ca}^{2+}$  concentration trends are not significant ( $p < 0.05$ ) are NY52, PA29, and VA13; the only sites where  $\text{Mg}^{2+}$  trends are not significant are PA29 and FL11. Potassium concentrations exhibit significant, widespread decline in the Northeast (10 of 12 sites). However, in the Southeast, the opposite is true. Only 2 of 9 sites in the Southeast (FL11 and NC35) have significant ( $p < 0.05$ ) decreasing  $\text{K}^+$  trends. Although statistically not significant,  $\text{K}^+$  concentrations at VA13 are increasing.

Seventy-five percent of the sites (8) in the Northeast exhibit statistically significant decreasing  $\text{Cl}^-$  concentration trends. In contrast, only 2 sites (22.2%) have significant decreasing  $\text{Cl}^-$  trends in the Southeast. For the most part,  $\text{Na}^+$  concentrations exhibit a similar decreasing concentration pattern. No site exhibits an increasing  $\text{Na}^+$  or  $\text{Cl}^-$  concentration pattern.

The results of a separate trend analysis that included nine sites from the Pennsylvania monitoring network and seven NADP/NTN sites not included in the above analysis because the sites were initiated after 1980 are shown in table 3. For the most part, the trend results follow closely those from sites with the longer record. Significant decreasing trends ( $p < 0.05$ ) at the two Maryland sites (MD03 and MD13) are evident for only  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{K}^+$  (except MD03). This same pattern is evident at other NADP/NTN sites, including NJ99, VA00 (except  $\text{Ca}^{2+}$ ), VA28 (except  $\text{K}^+$ ), WV04, PA29 (except  $\text{Ca}^{2+}$  and  $\text{K}^+$ ), and PA72. The WV04 sites is the only other NADP/NTN site in the region with a significant decreasing  $\text{SO}_4^{2-}$  concentration trend. With respect to the Pennsylvania Network sites (PA01 through PA09, table 3), significant ( $p < 0.05$ ) decreasing trends are evident for H<sup>+</sup> (4 sites),  $\text{SO}_4^{2-}$  (2 sites),  $\text{NO}_3^-$  (3 sites),  $\text{Ca}^{2+}$  (4 sites), and  $\text{K}^+$  (2 sites), and  $\text{Mg}^{2+}$  (9 sites). None of the sites exhibit significant trends for  $\text{Cl}^-$  and  $\text{Na}^+$ . An increasing trend in  $\text{NH}_4^+$  concentrations is evident at the Gettysburg site (PA02).

#### Regression Analysis

It has been widely reported that the H<sup>+</sup> concentrations in precipitation are largely the result of sulfuric and nitric acids, which in turn are by-products of photochemical oxidation of  $\text{SO}_2$  and  $\text{NO}_x$  oxides released to the atmosphere during combustion of fossil fuels (Venkatram et al. 1990). To verify this association, stepwise least squares regression analysis was performed on the NADP/NTN data to identify the most important ions associated with free H<sup>+</sup> in precipitation. The results of this regression analysis are presented in table 4. Without exception,  $\text{SO}_4^{2-}$  concentrations are positively correlated with H<sup>+</sup> and explained, for the most part, the largest percentage of variation in H<sup>+</sup> concentrations.  $\text{NO}_3^-$  concentrations are generally the second most important ion associated with free acidity, and like  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  concentrations are also positively correlated with H<sup>+</sup> at all sites except VA13.  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  concentrations are the third and fourth ions most often associated with H<sup>+</sup> concentrations. Unlike  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations,  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  are negatively associated with H<sup>+</sup> at all sites except ME09 ( $\text{NH}_4^+$ ) and VA13 ( $\text{NH}_4^+$ ). The remaining ions are sporadically associated with H<sup>+</sup>; some of these associations are positive (i.e.,  $\text{Cl}^-$  at six sites) and negative (i.e.,  $\text{Na}^+$  at 10 sites). When combined in the regression models,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ,  $\text{Ca}^{2+}$ , and  $\text{NH}_4^+$  and to a lesser

extent some of the remaining ions, explain on average 94% of the variation in  $H^+$  in the Northeast and 90% of the variation in the Southeast.

The occurrence of relatively poor regression model  $R^2$ 's to predict  $H^+$  concentrations in precipitation at the two Florida sites is most likely the result of bicarbonate ( $HCO_3^-$ ) influence on free acidity. In an open system, such as rain,  $CO_2$  can combine with water to form  $H_2CO_3$ , which in turn can dissociate to  $H^+$  and  $HCO_3^-$ .  $HCO_3^-$  can also dissociate to  $H^+$  and  $CO_3^{2-}$ . Because of these reactions,  $HCO_3^-$  can influence  $H^+$  concentrations in precipitation. The degree of  $HCO_3^-$  influence on free acidity is pH dependent, and can account for less than 1% of the free acidity at pH 4.65 or lower. Consequently,  $HCO_3^-$  influence on  $H^+$  concentrations is most likely to occur at those sites where the mean annual precipitation pH is 4.65 (22.38  $\mu eq/l$ ) or higher. Based on the mean  $H^+$  concentrations ( $\mu eq/l$ ) in precipitation at the 21 NADP/NTN monitoring sites from 1980 through 1992 (table 5),

$HCO_3^-$  influence on free acidity is most likely to occur at FL11 and to a lesser extent at FL03.

#### Stoichiometric Relationships

A comparison of the predicted changes in  $H^+$  concentrations between 1980 and 1992 with the sum of the predicted changes in anions ( $Cl^-$ ,  $SO_4^{2-}$ ,  $NO_3^-$ ) and cations ( $Ca^{2+}$ ,  $Mg^{2+}$ ,  $K^+$ ,  $Na^+$ ,  $NH_4^+$ ) are shown in Table 6. Although space does not permit site by site comparisons, two sites (NC03 and NC25) are discussed to illustrate the importance of changes in base cations on  $H^+$  concentrations in precipitation. Both sites experienced similar declines in anion concentrations since 1980 (19.49  $\mu eq/l$  and 18.64  $\mu eq/l$  respectively), most of which can be attributed to lower  $SO_4^{2-}$  concentrations (13.25  $\mu eq/l$  and 14.25  $\mu eq/l$ , respectively). The predicted changes in cation concentrations at NC03 is -12.31  $\mu eq/l$  and at NC25 -6.92  $\mu eq/l$ . The decrease in cations at NC03 was large enough to

Table 1. Linear trends in ionic concentrations of precipitation collected at NADP monitoring sites from 1980 through 1992. Trends were assessed after removing seasonal (bi-monthly) variation from log-transformed concentration data. Positive Trends: + =  $p < 0.1$ , ++ =  $p < 0.05$ , +++ =  $p < 0.001$  Negative Trends: - =  $p < 0.1$ , -- =  $p < 0.05$ , --- =  $p < 0.001$ .

Table 2. Coincidence of significantly ( $p < 0.05$ ) decreasing sulfate and hydrogen ion concentrations from 1980 through 1992.

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Table 3. Linear trends in ionic concentrations of precipitation collected at NADP and Pennsylvania network monitoring sites placed in operation after 1980. Positive Trends: + =  $p < 0.1$ , ++ =  $p < 0.05$ , +++ =  $p < 0.001$  Negative Trends: - =  $p < 0.1$ , -- =  $p < 0.05$ , --- =  $p < 0.001$ .

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Table 4. Stepwise least squares regression of hydrogen ion concentrations against concentrations of other dominate ions in precipitation collected from 1980 through 1992. All concentrations were log-transformed.

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Table 5. Mean ion concentrations ( $\mu\text{eq/l}$ ) of precipitation collected at NADP monitoring sites from 1980 through 1992. Means are calculated from log-transformed concentrations.

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offset much of the decrease in acid anions at this site. As a result, the  $-6.77 \mu\text{eq/l}$  change in  $\text{H}^+$ , which is almost equal to the difference between the sum of the predicted changes in cation and anion concentrations ( $-7.18 \mu\text{eq/l}$ ), was not statistically significant despite the significant decrease in  $\text{SO}_4^{2-}$  concentrations. At NC25,  $\text{H}^+$  decreased by  $9.36 \mu\text{eq/l}$ , which is close to the predicted difference in the sum of the cations and anions ( $-11.73 \mu\text{eq/l}$ ). At NC25, the decrease in cations was insufficient to offset the large decrease in anion concentrations. As a result, a significant decrease in  $\text{H}^+$  was observed at this site.

Within the northeast, a decrease in  $\text{SO}_4^{2-}$  accounted for approximately 80% of the mean decrease in anion concentrations ( $11.24 \mu\text{eq/l}$ ). This decrease was partially offset by a  $6.63 \mu\text{eq/l}$  decrease in cation concentrations, mostly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ . The net impact on free acidity within the northeast was a predicted decrease in  $\text{H}^+$  of  $4.10 \mu\text{eq/l}$ , which compares very well to the predicted net difference between the sums of the cation and anion changes of  $-4.62 \mu\text{eq/l}$ . A similar scenario is evident in the southeast as well, although the mean predicted changes in anions ( $-15.01 \mu\text{eq/l}$ ), cation ( $-6.83 \mu\text{eq/l}$ ), and  $\text{H}^+$  ( $-5.75 \mu\text{eq/l}$ ) concentrations are larger. The predicted changes in  $\text{H}^+$  in the southeast did not compare as favorably to the differences between the sums of the changes in cations and anions. The reason for this appears to be related to the two Florida sites. The actual change in  $\text{H}^+$  concentrations at these sites are most likely influenced by  $\text{HCO}_3^-$ , particularly at FL11.

#### SUMMARY

There is clear evidence that  $\text{SO}_4^{2-}$  concentrations in precipitation decreased throughout the Eastern United States between 1980 and 1992 and that approximately half of the trends (11 of 21 sites) are statistically significant ( $p < 0.05$ ). Concurrent with the  $\text{SO}_4^{2-}$  trends have been significant decreasing patterns in most of the cations in precipitation, especially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  concentrations. With respect to  $\text{NO}_3^-$  concentrations, only a few sites (3) exhibit significant trends; ammonium concentrations have changed the least over the 13-year period; significant ( $p < 0.05$ ) trends are evident at only two sites (1 increasing and 1 decreasing). Given the very strong positive relationship between  $\text{H}^+$  concentrations and  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations and the negative association with  $\text{Ca}^{2+}$  and  $\text{NH}_4^+$  at all NADP/NTN sites in the eastern United States, it would be safe to

assume that the combined effects of the changes in cation and anion concentrations would be to offset one another to varying degrees as suggested by Hedin et al. (1994). In fact, the results of this study suggest this to be the case, because only 5 of the 11 sites with significant decreasing trends in  $\text{SO}_4^{2-}$  have concurrent decreasing trends in  $\text{H}^+$ . The trend results from this study are consistent with those published by Sisterson et al. (1990), Hedin et al. (1994), Sirois, (1993), Oehlert (1993), and Baier and Cohn, (1993), among others. However, it is important to recognize that considerable intra-regional variability exists. Indeed, such variability is even evident at the state level where multiple sites exist (i.e., North Carolina). In addition, although it may be safe to assume that general decreasing patterns in cations, particularly  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ , have significantly affected  $\text{H}^+$  concentrations in precipitation throughout the eastern United States, we should not ignore changes in  $\text{NH}_4^+$ ,  $\text{Na}^+$ ,  $\text{NO}_3^-$ , and  $\text{Cl}^-$  concentrations. Based on the stepwise regression analysis in this study,  $\text{NH}_4^+$  and  $\text{NO}_3^-$  concentrations and to a lesser extent the  $\text{Na}^+$  and  $\text{Cl}^-$  can be individually very important in determining  $\text{H}^+$  trends at any given site.

It is apparent from the results of this study that nitrogen deposition to the Chesapeake Bay and its tributaries has not changed significantly since 1980. Whether reductions in the emission of nitrogen oxides, as mandated in the Clean Air Act Amendments of 1990, will significantly reduce nitrogen deposition to the Bay is unclear and can be quantified only through continued monitoring of atmospheric deposition in the Chesapeake Bay watershed.

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CRITICAL LOADS A MANAGEMENT TOOL FOR THE CHESAPEAKE BASIN

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*Abstract:* Critical loads represent maximum allowable deposition rates of sulfate, and nitrate below which continued acidification of target receptors is not expected to occur. Critical loads to 73 watersheds across Maryland were estimated using steady state (PROFILE) and dynamic (Regional MAGIC) stream chemistry models. Model inputs included factors such as biological endpoints, soil mineralogy and texture, net long term uptake of base cations and nitrogen to vegetation, annual precipitation and runoff, and deposition of sulfur and nitrogen. The critical load estimates were used in optimization analyses to identify efficient and equitable sulfur dioxide (SO<sub>2</sub>) control strategies that satisfy environmental quality targets at receptor locations. Emission control strategies included 10 million tons per year SO<sub>2</sub> reductions in the United States, uniform percentage reduction scenarios, and state-level sensitivity analyses. The results show a full range of critical loads from very low values in sensitive catchments in western Maryland and the coastal plain to high values in central Maryland and the Piedmont.

INTRODUCTION

In late 1988, Governor William Schaefer, of Maryland appointed a Work Group on Acid Deposition to evaluate then-current knowledge of acid deposition and its effects in Maryland. He gave the group three charges:

- Should Maryland develop an acid deposition control program?
- What form should it take to be most effective?
- Are there complementary actions the state should take?

In its 1989 report, the work group recommended that the State should, among other recommendations:

- Continue support for federal legislation,
- Explore a regional approach to emissions reductions, and
- Implement a Maryland program if Congress fails to enact national reductions, and achieve reductions necessary to protect resources.

This latter recommendation led the Maryland Department of Natural Resources to implement the Maryland Critical Loads Project. Critical loads represent maximum allowable deposition rates of sulfate and nitrate below which continued acidification of target receptors is not expected to occur. A stepwise procedure was used to calculate the critical loads:

- Define biological/ecological indicator.
- Define critical limits or water quality requirements (min. pH, Ca, max, Al).
- Derive alkalinity requirement.
- Calculate required alkalinity supply rate.
- Calculate critical load

Models that are used to calculate critical loads must consider the factors that influence a watershed's response to deposition. These factors include vegetation, topography, land use, soils; bedrock, weathering, hydrology, permeability, CEC, sulfate absorption, and base cations. Proceeding through the steps of the critical load calculation procedure, we selected important fishes in Maryland as the biological indicators.

An extensive review of the published literature identified critical pH values for the indicator species:

Species	Critical pH
Brook trout	5.3
White sucker	5.6
Smallmouth bass	5.8
Blueback herring	6.5

These critical pH values represent the in-stream limits that must not be exceeded by means of

stream acidification in response to continued acid deposition.

To derive the alkalinity (or acid neutralizing capacity [ANC] that corresponds to the critical pH limits, calculate the alkalinity supply rate from the watershed, and calculate the critical load, several other steps were performed. Seventy-three watersheds across Maryland were identified from sites sampled during the 1987 Maryland Synoptic Stream Chemistry Survey (MSSCS). The MSSCS was a stratified random sample of 559 stream reaches from a list frame of 1:250,000-scale reaches. The MSSCS strata generally conformed to Maryland's physiographic province boundaries. Available geological, soils, land use, and other data necessary for model input were compiled.

Two critical loads models were used in this study. PROFILE, a steady state model developed at the Lund Institute of Technology in Sweden, was applied to each of the 73 individual watersheds to estimate their critical load of sulfur and their responses to future deposition scenarios. The MAGIC model, a dynamic model developed at the University of Virginia, was applied in a regional mode to examine regional stream chemistry responses to future deposition scenarios.

PROFILE was used iteratively for each of the 73 watersheds. The model was run with current deposition initially to establish the long-term steady state stream chemistry. The sulfate deposition was then adjusted iteratively until the steady-state stream chemistry matched the critical stream pH. That deposition represents the critical load for the site.

Regional MAGIC can be used to estimate the relative response of stream acid-base chemistry to different deposition levels. Regional MAGIC runs were made at a series of sulfur dioxide (SO<sub>2</sub>) deposition levels from 0.25 to 2 x current, for all eight regions in Maryland. The percentage of stream reaches with pH values less than the critical pH was estimated for each of the eight regions. Using regional MAGIC, the critical load can be operationally defined as some proportion of the stream reaches within a region which is deemed appropriate for protection from damage from acidification.

The critical load estimates derived from PROFILE and Regional MAGIC were used to analyze various SO<sub>2</sub> emission reduction strategies at national, regional, and state scales. Optimization methods were used because they can explicitly include critical loads by identifying control strategies that meet specific loading limits. Optimiza-

tion analysis provides an efficient screening method for undesirable attributes, and allows efficient exclusion of inferior strategies, and it provides a high degree of flexibility in defining the attributes of emission reduction strategies. Linear programming was used for these analyses. The decision variables were the SO<sub>2</sub> and NO<sub>x</sub> removal levels at each source. The basic linear programming (LP) model was:

$$\text{MINIMIZE } \sum_k E_k(1-R_k)t_{jk} + BC_j \leq D_j$$

This translates to the statement that we desire to minimize the aggregate annual emission reduction over all source regions such that the deposition at an individual receptor (from man-made and natural sources) is less than or equal to the critical load.

Major elements of the emission reductions analyses were:

- Yearly source-specific SO<sub>2</sub> emissions and pollutant removal cost functions were obtained
- Transport estimates (i.e., transfer coefficients) of emissions from each source to deposition at every receptor were obtained from the Ontario Ministry of Environment (MOE) long-range atmospheric transport model.
- Critical load estimates for each receptor (output from PROFILE and Regional MAGIC).

The emissions sources included in the modeled domain were:

- Two hundred and thirty-one utility and industrial sources in the US & Canada (≈ 19 kt SO<sub>2</sub>/yr)
- Eleven "large" Maryland point sources (> 19 kt SO<sub>2</sub>/yr).
- Three hundred and twenty-eight area sources (in 90 states or province, remainder in Maryland). The emissions reductions strategies evaluated were:
  - 10 million tons per year SO<sub>2</sub> reduction
  - 10 million tons variants
  - Uniform reductions
  - "State-level" sensitivities
  - "Source-level" sensitivities
  - Optimized cost minimization
  - Bound deposition changes owing to allowance trading
  - Critical loads as hard upper bound
  - Identify core sources and receptors

Some of the key results were as follows. The statewide median critical load for sulfur deposition is about 96 kg SO<sub>2</sub>/ha/yr. The median total SO<sub>2</sub> deposition is 48-60 kg/ha/yr. About 25% of

the stream reaches statewide have critical loads less than the current median SO<sub>2</sub> deposition and may be subject to episodic acidification.

Based on results from the PROFILE model runs, watershed, regional, and statewide responses in stream chemistry to future deposition were very similar across the emission reduction scenarios. Under constant deposition, ANC and pH will decline to levels less than present. Only the 90% and 10 million ton scenarios result in appreciable improvement in stream chemistry over constant deposition. The 50% U.S. and 90% and 50% regional reductions result in only marginal to moderate differences in response. The 90% Maryland-only scenario is not significantly different from constant deposition.

The regional responses in stream chemistry to deposition scenarios projected by Regional MAGIC compare well to those from PROFILE. Responses to the 90% U.S. and 10 million ton scenarios are much greater than would be expected under other scenarios. Regions 1 (western Maryland), 7 and 8 (the southern coastal plain) stand out as areas with very low critical loads and watersheds in which critical loads could not be achieved via any of the emissions reductions strategies. These watersheds (and others in the population they represent) might be candidates for evaluating mitigation options.

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EFFECTS OF ACIDIC DEPOSITION ON THE HYDROCHEMISTRY OF BEAR BRANCH, A SMALL FORESTED WATERSHED ON CATOCTIN MOUNTAIN, NORTH-CENTRAL MARYLAND

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*Abstract:* The hydrology and hydrochemistry of small watersheds on Catoctin Mountain, Maryland, were investigated from 1990 to 1993 by the U. S. Geological Survey, in cooperation with the Maryland Department of the Environment and the Maryland Department of Natural Resources. One watershed, Bear Branch, is a perennial headwater stream with a drainage area of 98 hectares. The watershed is forested, with approximately 90% deciduous and 10% coniferous trees and is used as parkland. The watershed is sensitive to acidic deposition because it is underlain by bedrock composed of quartz and other relatively nonreactive minerals. During the study, the quantity and quality of water entering and exiting the watershed, including precipitation, throughfall, soil water at two depths (10 to 15 cm below land surface and 45 to 60 cm below land surface), shallow groundwater, and streamwater during base flow and stormflow were analyzed. Water samples collected from the watershed were analyzed for dissolved concentrations of  $H^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ , total Al, total Fe,  $Cl^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ , and  $SiO_2$ ; for acid-neutralizing capacity; and for stable isotopes of hydrogen and oxygen.

Hydrologic data indicate that the watershed is strongly affected by changes in the seasonal rates of evapotranspiration, with higher streamflows during the winter and spring and lower streamflows during the summer and fall. Of the approximately 114 cm of precipitation that enter the watershed each year, approximately 44 cm of water (38%) exit the watershed as streamflow. Approximately 31% of annual streamflow consists of stormflow.

Geochemical data indicate that the acidic precipitation that enters the watershed is mildly buffered as it comes in contact with watershed materials. In general, base cation concentrations rise and the water becomes higher in acid-neutralizing capacity as it travels through the watershed. The chemical and isotopic compositions of streamwater during base flow are similar to those of near-stream shallow groundwater. During storms, the streamwater is episodically acidified and its chemical and isotopic compositions change significantly from those of base flow. The episodic acidification and changes in hydrochemistry indicate that throughfall and shallow soil water are significant sources (up to 50%) of streamwater during storm runoff. Mass-balance calculations indicate that the watershed retains dissolved  $NO_3^-$  and  $SO_4^{2-}$  on an annual basis. While the streamwater has measurable concentrations of dissolved  $NO_3^-$  and  $SO_4^{2-}$  throughout the year, net export of these constituents occurs only during periods of high discharge.

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ATMOSPHERIC WET DEPOSITION OF TRACE ELEMENTS OF THE CHESAPEAKE BAY

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*Abstract:* The atmospheric wet deposition of selected trace elements (Al, As, Cd, Cu, Fe, Mn, Pb, Se, and Zn) has been examined at three Chesapeake Bay sites as a component of the Chesapeake Bay Atmospheric Deposition (CBAD) Study. Precipitation was sampled on a weekly integrated basis using a modified wet-only collector in conjunction with a rigorous trace element handling protocol.

Wet depositional fluxes for each site were directly calculated as the product of the elemental concentration and the corresponding measured precipitation depth. For the two-year period from January 1991 through December 1992, the annual wet fluxes ( $\mu\text{g m}^{-2}\text{ yr}^{-1}$ ) averaged for the three sites were: Al (12,600), As (57), Cd (82), Cu (300), Fe (12,000), Mn (1,200), Pb (520), Se (134), and Zn (3,000). Except for Al, Fe and to a lesser extent Mn, most elements appear to have a dominant noncrustal source. Consistent spatial gradients in the flux of some of the elements are evident, as well as apparent temporal trends. Several anthropogenic elements (As, Cd, Se) display seasonal trends, characterized by summer maxima that parallel the major acid components ( $\text{H}^+$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$ ).

Compared with concurrent estimates of dry deposition, the relative input via wet flux is less for crustal elements (Al, Fe), but comparable for anthropogenically enriched elements (Pb, Se, Cd). The atmospheric loadings of certain elements of environmental concern (Pb, Zn, As, Cd) appear to be important when compared with estimated fluvial inputs.