Long- and short-term changes in sulfate deposition: Effects of the 1990 Clean Air Act Amendments

GENE E. LIKENS, THOMAS J. BUTLER & DONALD C. BUSO
Institute of Ecosystem Studies, Millbrook, NY 12545

Abstract. Annual, volume-weighted concentrations of SO_4^{2-} in bulk precipitation have declined steadily (-0.44 μmol/liter-yr) since 1965 at the Hubbard Brook Experimental Forest (HBEF), NH in response to decreases in regional SO_2 emissions ($r^2 = 0.74$). Similar declines in concentrations have occurred in wet-only precipitation at HBEF and at nearby sites since 1978. However, decreases in SO_4^{2-} concentrations following passage of the U.S. Clean Air Act Amendments in 1990, were not unusual from the perspective of long-term data from the HBEF. Statistically significant declines (-5.6 mol/ha-yr) in bulk deposition of SO_4^{2-} also have occurred since 1965 in relation to decreases in SO_2 emissions ($r^2 = 0.57$), but annual variations in deposition also are strongly related to amount of precipitation and other factors.

Introduction

The causes, distribution and effects of acid rain have been debated in North America since 1972 (Likens et al. 1972). Federal regulations to control air pollution in the United States were initiated in 1963, and significantly strengthened and enlarged in 1970 (e.g. Masters 1998), but the 1990 Amendments to the Clean Air Act (CAAA) were the first time a national legislative initiative focused specifically on the acid rain problem in the United States. Acid rain is the popular term used to describe the atmospheric input of anthropogenic acids and acidifying substances to the Earth's surface. These acids are formed in the atmosphere from the oxidation and hydrolysis of SO_2 and NO_x, which currently are emitted primarily from the combustion of fossil fuels and smelting (e.g. Likens et al. 1972; Likens 1992; Weathers & Likens 1998).

Actual effects of the 1990 CAAA were not realized until 1995 when implementation of Phase I caused a decline in U.S. annual SO_2 emissions equivalent to about 40% of the overall reduction targeted by the 1990

CAAA. This decline was not continued and national emissions increased slightly during 1996 and 1997 (Environmental Protection Agency 1998). Implementation of Phase II of the 1990 CAAA intends to cap national SO_2 emissions from utilities at 8.1 Mg $\times$ 10^6/yr by 2010, representing a reduction of about 50% from 1980 utility emissions. Assuming other SO_2 emission sources remain at 1997 levels, total SO_2 emissions would be 14.7 Mg $\times$ 10^6/yr (Environmental Protection Agency 1998). It is anticipated that these reductions in emissions will reduce the impacts of acid rain on sensitive ecosystems in the eastern United States and Canada. Emissions of SO_2 undoubtedly would have increased significantly without the 1990 CAAA. The large reductions in SO_2 also provide an opportunity to evaluate the effects of this major 'manipulation' on emission/deposition relationships. Moreover, these realized and expected changes raise the important question: Have reductions in SO_2 emissions as a result of the 1990 CAAA resulted in a commensurate or unusual decrease in SO_4^{2-} concentrations in precipitation or in deposition? Much smaller reductions in NO_x emissions were mandated by the 1990 CAAA and are not considered here.

An SO_2 emission source region based on two years of 15-hr air-mass, back trajectories, for all days and for precipitation-only days, was established for the Hubbard Brook Experimental Forest (HBEF). Emissions from 12 states within these back trajectories comprise this source region for the HBEF (see details in Figure 1 and Butler et al. 2000). This air-mass, back trajectory analysis suggests that emissions of SO_2 from southern Ontario also can contribute as an emission source for the HBEF (Butler et al. 2000), but continuous annual data on Canadian emissions are limited (Environment Canada 1998) and so are not included in this analysis. If SO_2 emissions from Ontario were included, they would represent 19%, 14%, 8%, and 10% of the total emissions affecting the HBEF for 1980, 1990, 1994, and 1995 to 1997, respectively. The impact of Canadian SO_2 emissions has little effect on the relationship between emissions and SO_4^{2-} concentrations for the 1990s when the record is most complete. For example, there was a 20% decline in SO_2 emissions between the periods 1991–1994 and 1995–1997 for the source region used in Figure 1. If Ontario were included in this source region, the decline would be 19% between these two time periods.

Cloud and fog water also could contribute additional deposition of S, but such events are few at HBEF and concentrations of S tend to be relatively low (Weathers et al. 1988). Estimates of dry deposition of S for the HBEF have been attempted by various methods, but with poor agreement in results (Likens et al. 1990b; Lovett et al. 1992, 1997). Inputs of S by dry deposition may be about 20 to 40% of bulk deposition inputs, but because of the uncertainty will not be considered further here.
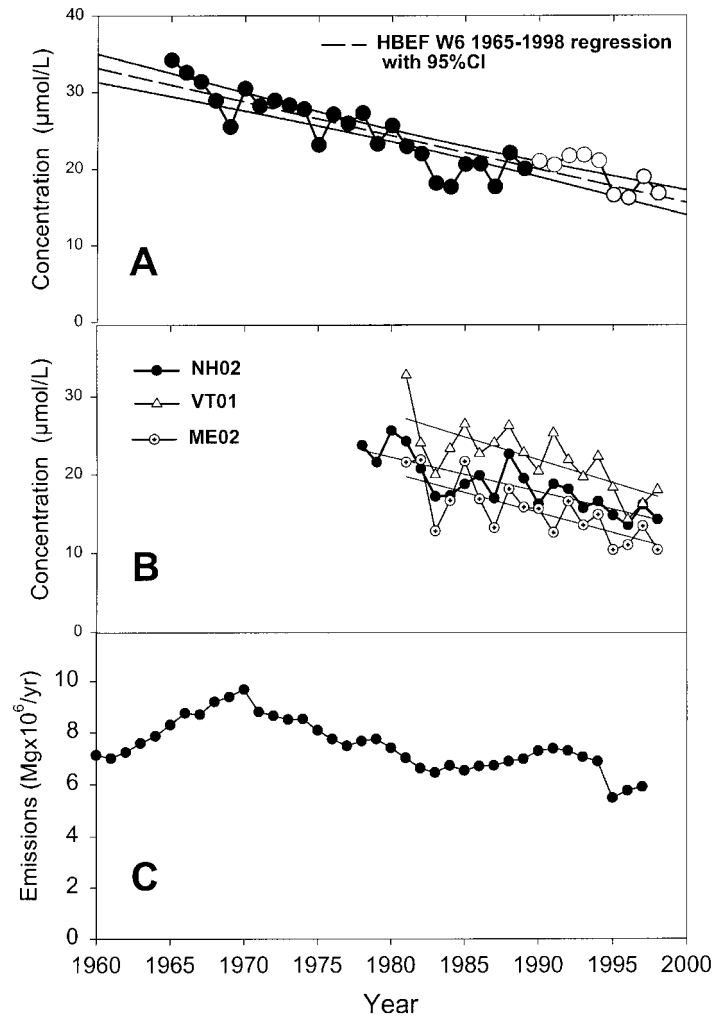
Figure 1. **A.** Long-term linear regression for annual SO_4^{2-} concentrations in bulk precipitation (calendar-year) for Watershed 6 of the Hubbard Brook Experimental Forest (HBEF) with 95% confidence intervals (see Table 1 for regression statistics). The gray circles indicate years after passage of the 1990 CAAA and open circles indicate Phase I of the 1990 CAAA; **B.** Linear regressions for wet-only annual SO_4^{2-} concentrations in precipitation (NADP/NTN data: NADP 1999; http://nadp.sws.uinc.edu) at HBEF (——●——) from 1978–1998 (slope = −0.44; r^2 = 0.66), at Bridgeton, ME (——○——) from 1981–1998 (slope = −0.51; r^2 = 0.55), and at Underhill, VT (——△——) from 1981–1998 (slope = −0.59; r^2 = 0.55); **C.** Annual SO_2 emissions from the (CT, DE, MA, MD, NH, NJ, NY, OH, PA, VA, VT, WV) source area based on 15-hr air-mass, back-trajectory analysis (see Butler et al. 2000 for details on back-trajectory analysis).

Long-term records

We have measured the concentration and calculated the deposition (concentration times amount of water) of SO_4^{2-} in bulk precipitation at the Hubbard Brook Experimental Forest (HBEF) in the White Mountains of central NH since June of 1964 (Likens & Bormann 1995). This represents the longest, continuous record of precipitation chemistry in North America, and thus provides a long-term perspective on changes that may have occurred as a result of the 1990 CAAA. As a result, these data provide an unusual opportunity to help guide implementation of Phase II of the Amendments and the pending reauthorization of the Clean Air Act itself.

Annual atmospheric concentrations and inputs of S to the HBEF are measured as volume-weighted concentrations in bulk precipitation (Likens & Bormann 1995; Buso et al. 2000). Details about the forest ecosystem and methods and procedures related to collection and analysis of atmospheric deposition are given in Likens & Bormann 1995 and Buso et al. 2000. Traditionally, a bulk collector has been used for the long-term record at the HBEF. Martin et al. (2000) found no difference in SO_4^{2-} concentrations between wet-only and bulk collections during 1979–1989 at HBEF. Because of hydrologic considerations, a water-year (1 June–31 May) has been used to aggregate annual data for the HBEF (Likens & Bormann 1995; Federer et al. 1990). However, because data on emissions are compiled and used on a calendar-year basis, data for SO_4^{2-} concentrations and deposition in bulk precipitation are given here on a calendar-year basis. Annual precipitation averaged 142.5 cm $\pm$ 188 (SD) during 1965–1998 (147.6 cm $\pm$ 197 (SD) during 1990–1998) with approximately 1/3 as snow, and was uniformly distributed throughout the year at HBEF.

Long-term data on SO_4^{2-} concentrations in bulk precipitation show a steady decline since 1965 (Figure 1(a); Table 1). It is also clear from these data that the large decreases in SO_2 emissions since 1995 following implementation of the 1990 CAAA are correlated with decreased SO_4^{2-} concentrations in bulk precipitation (Figure 1). However, from a long-term perspective, no *unusual* decline in SO_4^{2-} concentrations in bulk precipitation at HBEF has occurred since 1990 or 1995. In fact, the departure in concentrations in 1983 and 1984 from the long-term trend was larger than anything observed following the passage of the 1990 CAAA (Figure 1(a)). Likens et al. (1990a) analyzed these data on a water-year basis and found that the extremely low values in 1983–1984 were due to small amounts of precipitation occurring during the summer months when SO_4^{2-} concentrations normally peak and to more high-volume, low ionic-strength storms of coastal origin during the fall, winter and spring.

Table 1. Linear regression statistics for annual SO_4^{2-} concentrations in bulk precipitation at Watershed 6 of the Hubbard Brook Experimental Forest for different periods since 1965.

Period	n (years)	Slope (μmol/liter-yr)	r^2	p-value
1965–1998	34	−0.44	0.80	<0.001
1965–1994	30	−0.44	0.74	<0.001
1965–1989	25	−0.58	0.82	<0.001
1983–1994	12	+0.30	0.46	0.016
1990–1998	9	−0.63	0.55	0.022
1995–1998	4	+0.35	0.13	0.63

Annual SO_4^{2-} concentrations in bulk precipitation at HBEF are strongly correlated with annual SO_2 emissions (Figure 2). This finding suggests that further reductions or increases in SO_2 emissions should result in additional decreases or increases in SO_4^{2-} concentrations in bulk precipitation.

Atmospheric bulk deposition of SO_4^{2-} varies greatly from year to year depending upon the interaction of many variables, e.g. differences in SO_2 emissions, amount and timing of rain or snow, oxidant levels, air-mass trajectories, SO_4^{2-} concentrations, etc. Nevertheless, annual bulk deposition of SO_4^{2-} has declined significantly (slope = −5.6 mol/ha-yr; $p < 0.001$; $r^2 = 0.60$) at the HBEF since 1965 (Table 2), and a statistically significant relationship exists between annual bulk deposition and annual SO_2 emissions (slope = 51.2 mol/ha-Mg $\times 10^6$; $p < 0.001$; $r^2 = 0.57$; Table 2). Annual bulk deposition of SO_4^{2-} values were also dependent upon amount of precipitation (slope = 0.14 mol/ha-cm; $p = 0.029$, $r^2 = 0.14$; Table 2). For example, even though SO_2 emissions declined sharply (20.5%) in 1995, precipitation amount was about average, and as a result bulk deposition was not uniquely low (Table 2). Conversely, bulk deposition of SO_4^{2-} during 1987 was the lowest on record; SO_4 concentrations were low and amount of precipitation was below average (Table 2). Amount of annual precipitation during 1973 and 1996 was large and approximately equal (182 cm; Table 2), however, bulk deposition of SO_4^{2-} during 1996 was only 57% of that in 1973. Moreover, even though SO_2 emissions from the source area declined by 1.13 m ton, or more than 16%, between 1994 and 1996, 1996 was one of the wettest years on record at HBEF and as a result, bulk deposition of SO_4^{2-} during 1996 was about 11% higher than 1994 and 20% higher than in 1995. Such changes illustrate the complexities in relating emissions and meteorology to annual deposition.
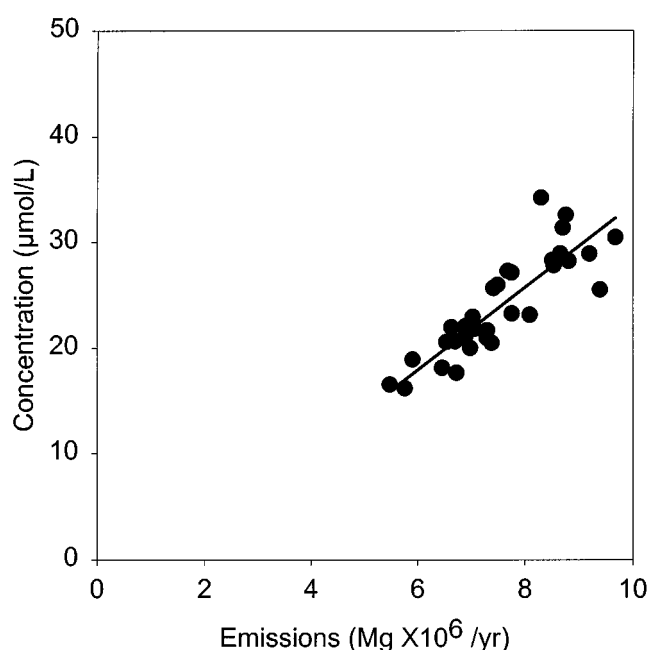
Figure 2. Linear relationship between annual SO_4^{2-} concentrations in bulk precipitation at HBEF and SO_2 emissions from the source area given in Figure 1 during 1965–1997. The linear regression has a slope of 3.90 and an r^2 of 0.74.

The HBEF data are useful because they give a longer-term perspective to these complicated processes.

Short-term records

Short-term data (even up to 5 yr) can be misleading regarding long-term trends (Likens & Bormann 1995), but it is interesting to note that SO_4^{2-} concentrations at HBEF increased from 1983 to 1994 (Table 1) corresponding to increases in SO_2 emissions, then dropped abruptly between 1994 and 1995, and more significantly, increased slightly from 1995 to 1998, while still being consistent with the long-term decline (Figure 1(a)). Although rates varied for different parts of the record, overall, the annual volume-weighted concentrations of SO_4^{2-} declined by -0.44 μmol/liter-yr ($r^2 = 0.80$) during 1965–1998 at HBEF (Table 1).

The pattern of decline in SO_4^{2-} concentrations seen at HBEF since about 1980 also is consistent with data from nearby sites in Maine and Vermont (Figure 1(b)). The National Atmospheric Deposition Program/National

Table 2. Atmospheric inputs of water and sulfate in bulk precipitation for Watershed 6 of the Hubbard Brook Experimental Forest, New Hampshire during 1965 to 1998.

Year	Precipitation (cm)	Precipitation deviation from long-term mean (% deviation)	Bulk precipitation concentration (μmol/liter)	Bulk precipitation deposition (mol/ha-yr)
1965	115.6	−18.9	34.2	395.5
1966	131.4	−7.8	32.6	427.7
1967	137.4	−3.6	31.4	430.9
1968	136.9	−3.9	28.9	395.7
1969	149.1	+4.6	25.5	380.5
1970	126.3	−11.4	30.4	384.6
1971	127.0	−10.9	28.2	358.3
1972	149.3	+4.8	28.9	431.6
1973	182.4	+28.0	28.3	516.2
1974	147.4	+3.4	27.8	409.7
1975	154.0	+8.1	23.1	356.5
1976	162.2	+13.8	27.1	439.8
1977	146.9	+3.1	26.0	381.2
1978	117.7	−17.4	27.3	320.9
1979	150.7	+5.8	23.3	350.7
1980	116.6	−18.2	25.7	299.3
1981	173.6	+21.8	23.0	398.5
1982	117.3	−17.7	22.0	258.0
1983	155.9	+9.4	18.1	282.8
1984	151.6	+6.4	17.7	267.8
1985	125.8	−11.7	20.6	259.1
1986	147.8	+3.7	20.7	305.3
1987	133.8	−6.1	17.7	236.5
1988	110.7	−22.3	22.1	244.5
1989	149.2	+4.7	20.0	298.7
1990	181.9	+27.6	21.0	381.6
1991	139.9	−1.8	20.5	287.0
1992	131.3	−7.9	21.7	285.0
1993	137.8	−3.3	21.8	300.6
1994	126.3	−11.4	21.1	266.0
1995	148.4	+4.1	16.6	245.8
1996	182.4	+28.0	16.2	295.8
1997	132.8	−6.8	18.9	251.4
1998	147.5	+3.5	16.8	248.0

Trends Network (NADP/NTN; NADP 1999) collects wet-only data at all three of these sites shown in Figure 1(b); the NADP collector at HBEF (NH O2) is located at lower elevation (252 m) than the HBEF bulk precipitation collector (550 m).

The bulk precipitation concentrations of SO_4^{2-} at HBEF follow the SO_2 emission pattern since 1994 much better (Figure 1(a) and (c)) than do the wet-only NADP/NTN data for HBEF (Figure 1(b) and (c)). In fact, during 1979–1997, the relation between annual volume-weighted concentrations of SO_4^{2-} in bulk precipitation and SO_2 emissions had an r^2 of 0.59, whereas the HBEF wet-only data (NH O2) vs. SO_2 emissions had an r^2 of 0.33. The abrupt decline in bulk precipitation concentrations between 1994 and 1995 (Figure 1(a)), however, was no larger than other declines in SO_4^{2-} documented during the previous 30 years at HBEF. Although concentrations are declining significantly at all of these sites, again, the decline is not unusual since 1990 and especially since 1995 (Figure 1(a)).

Discussion

Major declines in emissions of SO_2 have been occurring during recent decades in the eastern U.S. and have been correlated with significant decreases in SO_4^{2-} concentrations in precipitation (Figures 1 and 2; Lynch et al. 1995; Shannon 1999). Deposition, however, is the key variable ecologically as sensitive ecosystems respond primarily to deposition of acidifying substances, rather than to emissions directly (Likens et al. 1998). Unfortunately, many sensitive ecosystems in eastern North America have not yet shown improvement in response to decreased emissions of SO_2 (e.g. Driscoll et al. 1989; Likens et al. 1996a, b; Stoddard et al. 1999). Clearly, inputs of other chemicals, such as nitric acid and base cations, must be considered in addition to S in attempts to resolve the acid rain problem (e.g. Likens et al. 1996a, b, 1998).

Resource managers are suggesting that additional controls on emissions will be needed because present levels of acidic deposition are still high enough to prevent 'recovery' of many sensitive ecosystems (e.g. Stoddard et al. 1999; Jefferies et al. 2000). Deposition is clearly linked to emissions, but greater reductions must be realized before concentrations of SO_4^{2-} in precipitation can be forced below current levels and beyond the variability driven by short-term natural phenomena. Even so, because of the close relationship between emissions and concentrations, further reductions in emissions ultimately should be effective in reducing acid rain impacts on sensitive ecosystems.

Conclusions

- There has been a significant decline in annual SO_4^{2-} concentrations (-0.44 μmol/liter-yr) in bulk precipitation at HBEF during the past 34 years, and a similar decline in concentrations of wet-only precipitation at HBEF and at nearby sites in the northeastern U.S. during the past 18 years.
- Annual deposition of bulk SO_4^{2-} has declined significantly (-5.6 mol/ha-yr) at HBEF during the past 34 years. Annual variability in SO_4^{2-} deposition is correlated both with changes in SO_2 emissions and with amount of precipitation.
- The relationship between annual SO_4^{2-} concentrations in bulk precipitation at HBEF and regional SO_2 emissions is robust. Thus, further reductions in emissions of SO_2 in the source area should result in lower SO_4^{2-} concentrations and ultimately in lower atmospheric deposition.
- Meteorological variability may contribute to significant changes in the long-term record of precipitation S chemistry and may obscure (or exceed), at least on an annual basis, changes due to reductions in SO_2 emissions.
- The striking drop in SO_2 emissions in 1995 was reflected in the SO_4^{2-} concentrations measured in bulk precipitation at HBEF, but did not produce an unusual change within the perspective of the 34-yr record.
- Short-term records can be quite misleading; thus, it may be too early to assess critically the effectiveness of the 1990 CAAA. The full impact of Phase II of the 1990 CAAA, which was implemented in 2000, clearly remains to be determined. Nevertheless, available long-term data are important to the current debate about the reauthorization of the Clean Air Act.

Acknowledgments

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