Direct/Delayed Response Project: Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in the Northeast and Southern Blue Ridge Province

Volume II: Level I and Level II Analyses

by

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SECTION 7

WATERSHED SULFUR RETENTION

7.1 INTRODUCTION

The fate of sulfur deposited in a watershed is important in determining the response of the associated surface water because sulfate can act as a mobile anion in the soil matrix (see Section 3). In systems at steady state with regard to sulfur deposition (i.e., inputs = outputs or zero net retention), the leaching rate of either basic or acidic cations by the "carrier anion" sulfate has been maximized. Given no increase in sulfur deposition, future acidification (loss of ANC) of these systems would be determined principally by cation leaching and the possible depletion of the soil exchange complex. In systems below steady state (i.e., inputs > outputs), the acidifying effect of sulfate-driven cation leaching has not been maximized. As sulfate leaching increases in these systems, soil adsorption sites are filled on a net basis and acidification and the rate of acidification increases over time. A circumneutral surface water draining a watershed with positive net sulfur retention will continue to acidify and might become acidic (i.e., ANC < 0) as long as rates of sulfur deposition (inputs) exceed outputs. Thus, even if sulfur deposition decreases, some circumneutral systems will acidify and might become acidic. Knowing the patterns of watershed sulfur retention, therefore, is important with regard to understanding and forecasting the potential future effects of sulfur deposition on surface water chemistry. In this section we examine regional patterns of sulfur retention, as estimated using input/output budget analyses.

The purpose of the watershed sulfur retention component of the DDRP Level I Analyses is to estimate the current status of annual sulfur retention in watersheds of the eastern United States, with primary emphasis on the NE, Mid-Appalachian, and SBRP Regions. The Mid-Appalachian Region provides important information for the interpretation of sulfur retention patterns from the NE to the SBRP. Specific objectives of this section are to

- examine the influence of in-lake sulfur retention on watershed sulfur retention estimates;

- assess the contributions of internal sources of sulfur to (and the possible influences on) sulfur input/output budget calculations;

- characterize current average annual input/output budgets in the NE, Mid-Appalachians, and SBRP using (1) data from intensively studied sites and (2) estimates computed using regionally extensive datasets;

- compare annual sulfur retention patterns within and among regions to determine possible trends relative to water chemistry, soils, and atmospheric deposition; and

- conduct an uncertainty analysis of the sulfur retention estimates based on the associated uncertainties of the factors used in the input/output budget calculations.

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7.2 RETENTION IN LAKES AND WETLANDS

7.2.1 Introduction

Section 3.3 describes several processes that can cause sulfur to be retained within watersheds. One of the processes considered is retention by sulfate reduction in wetlands and/or lakes. Retention in these environments occurs principally by dissimilatory reduction, with sulfate used as an electron acceptor and with hydrogen sulfide, organic sulfur, or metal sulfides as end products (Rudd et al., 1986; Brezonik et al., 1987).

The occurrence of sulfate reduction in anaerobic hypolimnetic waters in lakes has long been recognized, but has been considered unimportant in long-term sulfur budgets because sulfides are reoxidized during lake overturn. Recent studies in several locations have shown, however, that sulfate reduction in (anaerobic) sediments overlaid by oxic lake waters can be a major sink for sulfur (e.g., Cook et al., 1986; Baker et al., 1986a). Reduction rates are approximately first order for sulfate concentration, and in-lake rates are apparently limited by diffusion rates into sediments (Baker et al., 1986b; Kelly et al., 1987). Sulfides produced in lake sediments are largely retained within the sediment profile on a permanent basis, with little reoxidation or volatilization (Rudd et al., 1986; Brezonik et al., 1987). Because sulfate reduction is rate limited (i.e., by diffusion of sulfate) rather than capacity limited (Rudd et al., 1986), reduction will likely continue roughly at current rates (expressed as percent retention) on a long-term basis.

Measured and computed mass transfer coefficients for sulfate vary over a relatively narrow range (Baker et al., 1986b; Kelly et al., 1987), but the importance of in-lake sulfur retention on lake/watershed sulfur budgets is highly variable and is greatly influenced by hydraulic residence times of lakes. Sulfur retention within lakes has been discussed and modelled by Baker et al. (1986b) and by Kelly et al. (1987), who developed identical equations to predict sulfate retention in lakes:

$$\% \ SO_4 \ Retention = \frac{k_{SO4} * 100}{(Z/t_w) + k_{SO4}} \qquad \text{(Equation 7-1)}$$

where:

$\quad k_{SO4}$ = sulfate mass transfer coefficient (m yr^{-1})
$\quad Z$ = lake depth (m)
$\quad t_w$ = hydraulic residence time (yr)

Baker et al. (1986b) and Kelly et al. (1987) computed mass transfer coefficients using sulfur input/output budgets from the literature and determined average constants of 0.54 and 0.46 m yr^{-1}, respectively.

Transfer of sulfate from the water-sediment interface to the anoxic zone of the sediments occurs principally by diffusion. Thus, absolute transfer rates are relatively low, with the result that reduction in sediments is a small component of lake sulfur fluxes except in lakes with long hydraulic residence times. High sulfur retention has been reported for a diverse group of seepage lakes and other lakes with long hydraulic residence (e.g., Baker et al., 1988; Schindler et al., 1986b; Lin and Schnoor, 1986). In contrast, Shaffer and Church (1989) evaluated in-lake alkalinity production [to which sulfate reduction is the largest

contributor (Schindler, 1986; Brezonik et al., 1987)] and sulfur retention for regional lake populations in subregions of the Eastern Lake Survey (ELS) (Linthurst et al., 1986a), and concluded that in-lake processes have only a minor effect on ANC and sulfur budgets for most drainage lakes in the northeastern United States, Upper Midwest (UMW), and Southern Blue Ridge (SBR). [For this section only, SBR refers to lakes in ELS subregion 3A, which includes portions of the Piedmont and Ridge and Valley provinces (Linthurst et al., 1986a), and encompasses a larger geographic area than the stream systems within the Pilot Stream survey region (Messer et al., 1986a) of the SBRP considered elsewhere in the DDRP.]

Dynamics of sulfur in freshwater wetlands have been studied in detail at only a few sites and probably cannot be described effectively at regional scales by relationships such as the in-lake retention expression (Equation 7-1). Rates of sulfur reduction in wetlands can be very high (Weider and Lang, 1988) and, even small wetland areas, depending on their location within a watershed, can retain a substantial fraction of watershed sulfur inputs (Calles, 1983; Weider and Lang, 1988). Generalization of wetland area - sulfur budget relationships is difficult, however, because the importance of wetland retention on watershed sulfur budgets depends on the location of the wetland in the watershed and the portion of watershed runoff flowing through it. Also, sulfur reactions in wetlands and wet soils can change seasonally or in wet/dry years. Wetlands and wet soils can act as sulfur sinks (reduction of sulfur) during wet periods when the system is anaerobic, but can become major sulfate sources due to reoxidation of sulfides upon drying (Bayley et al., 1986; Nyborg, 1978).

In this section, we use the sulfur retention model of Baker et al. (1986b) with hydrologic data from the ELS (Linthurst et al., 1986a; Kanciruk et al., 1986a) to estimate sulfur retention in drainage lakes (including reservoirs) in the northeastern United States and the Southern Blue Ridge. Because we lack models to make direct estimates of sulfur reduction in wetlands, regression analyses are used to describe relationships between watershed sulfur input/output budgets and wetlands for DDRP watersheds. Results of these analyses are described in Sections 7.4 and 8.5.

7.2.2 Approach

The ELS characterized lake depth and hydraulic residence time for a statistically representative set of lakes in selected areas of the eastern United States, including the Northeast (Linthurst et al., 1986a; Kanciruk et al., 1986a). For these analyses, we used a subset of the ELS population comprised of all drainage lakes and reservoirs with lake areas <2000 ha. Target populations are listed in Table 7-1. Using ELS data with Equation 7-1 and assuming a value of 0.5 m yr^{-1} for k_{SO4} (Baker et al., 1986b; Kelly et al., 1987), we estimated sulfur retention by in-lake reduction for drainage lakes in the northeastern United States and for DDRP watersheds. Due to major uncertainties in defining hydrologic boundaries for seepage and closed lakes and resulting uncertainties in hydrologic and chemical budgets, estimates of in-lake sulfur retention were made only for drainage lakes and reservoirs. Based on the sampling design described by Linthurst et al. (1986a), we extrapolated results from sampled lakes to obtain target population estimates for each region and for the five ELS subregions in the Northeast.

Table 7-1. Summary of Computed Sulfur Retention by In-lake Reduction for Lake Systems in the Eastern United States. Data for the Southern Blue Ridge and Upper Midwest are from Shaffer and Church (1989)

Region percent	Drainage Lakes[a] #	%	t_w [b] (yr)	Computed % S retention median	90 %ile	maximum	% of lakes with > 10 computed S retention
ELS Region 1	6288	(88)	.20	3.1	11.1	38.8	12.5
1A	1091	(87)	.23	2.8	9.0	25.6	7.7
1B	1421	(96)	.25	3.9	12.8	38.8	19.1
1C	1276	(86)	.17	2.5	7.9	19.4	7.9
1D	1071	(81)	.18	3.7	12.5	21.1	17.3
1E	1429	(94)	.23	3.0	11.1	26.6	14.4
NE DDRP lakes	137	(94)	.46	4.2	12.5	25.6	18.6
SBR (ELS 3A)	250	(97)	.10	1.2	4.0	5.4	<.11
UMW (ELS 2)	4404	(52)	.48	5.3	13.0	19.3	23.2

a "Drainage Lakes" indicates drainage lakes and reservoirs; # is target population, % is percentage of all lakes in the ELS target population in each region.

b Hydrologic retention time (yr).

7.2.3 Results

Estimates of sulfur retention for drainage lakes and reservoirs in ELS Region 1 (northeastern United States, Plate 5-1) are summarized in Table 7-1 and in Figure 7-1. Computed in-lake retention was generally low, with a median retention in the NE of 3.1 percent and more than 10 percent sulfur retention in only 12.5 percent of northeastern drainage systems. Maximum computed retention in northeastern lakes was 39 percent. Retention in individual ELS subregions was comparable to the region as a whole; retention in Subregions 1A (Adirondacks) and 1C (Central New England) was slightly lower than the regional distribution, and retention in Subregions 1B (Poconos/Catskills) and 1D (Southern New England) slightly higher. Because drainage lakes and reservoirs comprise 88 percent of lakes in the region and at least 81 percent of target lakes in individual subregions, retention data summarized here represent by far the majority of target lake systems in the region. Computed retention for DDRP lakes is generally comparable to, but is slightly higher than, that of the regional target lake population. The fraction of drainage systems in the DDRP lakes is higher than for the ELS population estimate, due principally to reclassification of several DDRP lakes (from closed or seepage to drainage) based on data from DDRP watershed mapping activities (Section 5.3).

For comparison, data from Shaffer and Church (1989) for two other ELS regions are also included in Table 7-1. Lakes in the SBR (ELS Subregion 3A) are dominated by drainage systems and reservoirs, which have very short hydraulic residence times and are consequently projected to have very low in-lake sulfur retention. Median computed retention in SBR lakes is only 1.2 percent, and maximum retention is 5.4 percent. Estimated retention in lakes of the UMW (ELS Region 2) is somewhat higher than in the NE, with median projected retention of 5.3 percent and more than 10 percent retention in almost one-fourth of drainage systems. An important difference between the NE and UMW lies in the relative abundance of lake hydrologic types; seepage and closed lakes account for almost half of all lakes in the UMW and in-lake processes are probably an important sulfur sink in most of these lake systems.

The estimates of low sulfur retention in northeastern lake systems are consistent with independent lines of evidence regarding watershed sulfur budgets and in-lake processes. Our estimates of low sulfur retention, consistent with sulfur input/output budgets developed by Rochelle and Church (1987) and discussed in Section 7.3, show lake/watershed systems in the region to be, on average, very close to steady state. Data presented here also are consistent with estimates of Shaffer et al. (1988) and Shaffer and Church (1989), based on watershed-to-lake area ratios for ELS watersheds, which suggest that in-lake processes (principally sulfate reduction) are a minor contributor to ANC budgets in most northeastern lake/watershed systems.

The relative importance of in-lake sulfate reduction to basin sulfur budgets in most systems is largely determined by two factors: (1) absolute rates of sulfate reduction and (2) lake hydrologic variables (more explicitly, the volume of water from which sulfate is removed or the annual discharge per unit lake area). Rates of sulfate reduction (as K_{SO4}) apparently vary among lakes over a fairly narrow range (Rudd et al., 1986; Kelly et al., 1987; Brezonik et al., 1987) and in typical drainage lakes of the eastern United States are probably comparable to rates measured in systems in which reduction is a major component of sulfur budgets (Brezonik et al., 1987; Kelly et al., 1987). Hydraulic residence times of lakes, however, vary greatly among regions. For example, at the Experimental Lakes Area in Ontario and in many seepage lakes (e.g., Schindler et al., 1986b; Lin and Schnoor, 1986; Baker et al., 1986a), residence
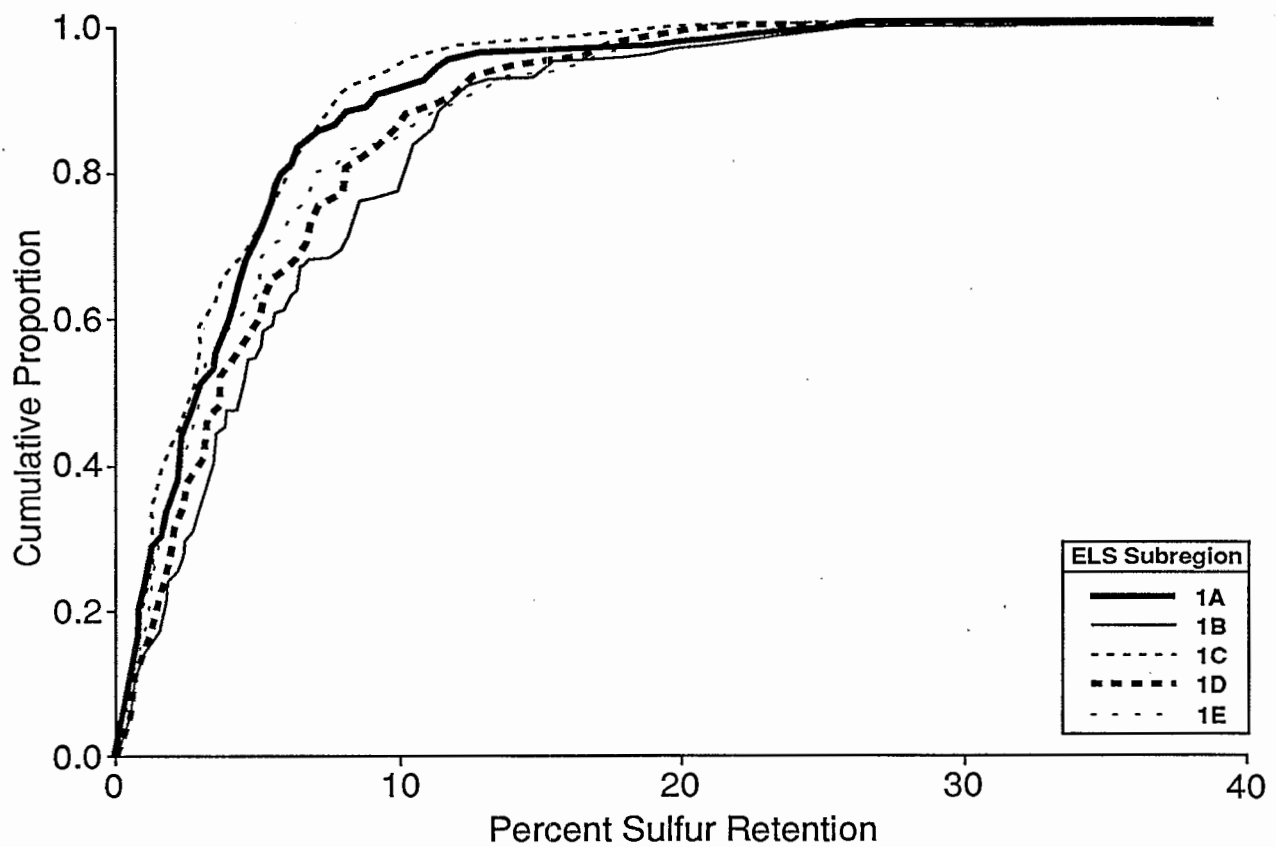
Figure 7-1. Estimated percent sulfur retention by in-lake processes in drainage lakes in ELS Region 1 (northeastern United States). Retention was computed using the model of Baker et al. (1986b).

times are long and sulfur budgets are greatly influenced by in-lake reduction. By contrast, residence times in most drainage lakes of the northeastern United States are short, averaging about two months (Linthurst et al., 1986a). The relatively minor role of in-lake reduction in drainage lakes of the northeastern United States is a consequence of short hydraulic residence times, rather than of low inherent sulfate reduction rates. The importance of residence time is explicit in the models of Baker et al. (1986b) and of Kelly et al. (1987). Those authors concluded that in lakes with short hydraulic residence times (one year or less), including most lakes in the northeastern United States, in-lake processes have little net effect on watershed sulfur budgets.

7.3 WATERSHED SULFUR RETENTION

Our first investigation of the regional patterns of sulfur retention consisted of a review of sulfur input/output budgets at intensively studied sites (Rochelle et al., 1987). Figure 7-2 summarizes the findings from this review. Definitive statements about sulfur retention on regional scales could not be made because of lack of spatial coverage by the intensively studied sites and inconsistencies in data used for budget calculations. There are trends, however, in sulfur retention from North to South in the eastern United States, especially relative to the extent of the Wisconsinan glaciation, with higher retention in the southern areas (Figure 7-2). The DDRP Level I sulfur retention analysis examines these apparent trends in more detail using regionally consistent sulfur input and output data (Section 5) for the surface water sites sampled by the Eastern Lake Survey (ELS) and National Stream Survey (NSS).

7.3.1 Methods

7.3.1.1 Input/Output Calculation

In the Level I sulfur retention analysis, we used an annual mass balance approach to estimate percent retention. The general equation used to calculate percent sulfur retention is:

$$\% \text{ Retention} = (((S_w + S_d) - (R * S_s))/(S_w + S_d))*100 \qquad \text{(Equation 7-2)}$$

where: Inputs

S_w = wet sulfur deposition (mass length^{-2} time^{-1})
S_d = dry sulfur deposition (mass length^{-2} time^{-1})

Outputs

R = runoff (length time^{-1})
S_s = surface water sulfur (mass length^{-3})

Equation 7-2 relates the total sulfur input (on a mass basis) to each watershed to the total sulfur output. We applied this equation to each of the study watersheds examined in the Level I sulfur retention analyses (ELS and NSS sites).

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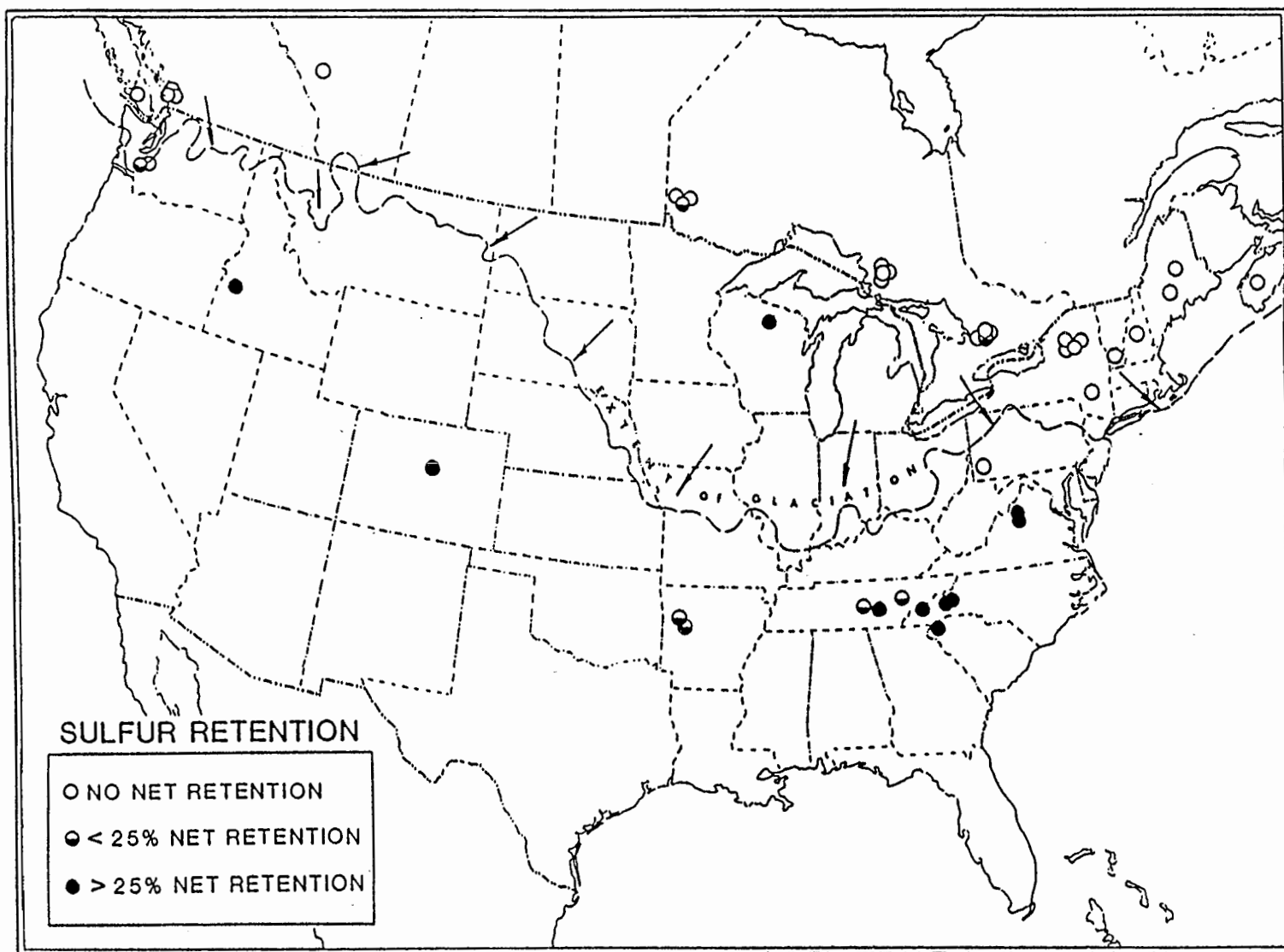
Figure 7-2. Percent sulfur retention for intensively studied sites in the United States and Canada relative to the southern extent of the Wisconsinan glaciation (adapted from Rochelle et al. (1987)).

7.3.1.2 Data Sources

7.3.1.2.1 Inputs -

Wet sulfur deposition was estimated for each site using chemistry data from the National Trends Network/National Acid Deposition Program (NTN/NADP) network and precipitation data from the NOAA National Climatic Data Center (NCDC) network (Section 5.6). Briefly, wet sulfate concentrations and precipitation were kriged to each site, and wet deposition was calculated (see Wampler and Olsen, 1987, for a detailed description of the calculation). Dry sulfur deposition was estimated based on output from the Regional Acid Deposition Model (RADM) (see Section 5.6).

7.3.1.2.2 Outputs -

We used estimates of annual runoff for the 30-year period of 1951-80 (see Section 5.7 for details). For the purpose of these analyses we assumed that the vast majority of sulfur leaves the watershed in the form of dissolved sulfate (David and Mitchell, 1985; Mitchell et al., 1986). Section 5.3 discusses the chemistry data used in these analyses. For additional information concerning the ELS and NSS surface water sulfate estimates, see Linthurst et al. (1986a), Messer et al. (1986a), and Kaufmann et al. (1988). Seepage lakes and closed lakes were excluded from the analyses.

7.3.2 Uncertainty Estimates

7.3.2.1 Introduction

We used a Monte Carlo approach to evaluate the uncertainty associated with estimates of annual average sulfur retention. (The specific Monte Carlo procedure used is very similar to that described in Section 6.3.) The critical step in applying the Monte Carlo routine is developing error rates on each of the input/output variables used in calculating percent sulfur retention (see Equation 7-2). We determined an uncertainty distribution for each of these variables. The uncertainty distributions were propagated through the retention equation to determine an estimate of the overall uncertainty of the percent sulfur retention calculations.

7.3.2.2 Individual Variable Uncertainties

7.3.2.2.1 Input variables -

Two variables are used to estimate the total sulfur input to each surface water system - wet and dry sulfur deposition. The determination of uncertainty estimates for these variables is discussed in Section 10.10. For the sulfur retention uncertainty analyses, we used relative standard deviation (RSD) estimates of 0.25 for S_w and 0.50 for S_d.

7.3.2.2.2 Output variables -

7.3.2.2.2.1 Runoff --

The sulfur output from each watershed is a product of the estimated annual average surface water sulfate concentration and the annual runoff. Rochelle et al. (in press) determined that runoff for individual watersheds could be estimated from the map of Krug et al. (in press) within ± 15 percent. Based on this determination, we used an RSD of 0.15 for runoff in the sulfur retention uncertainty analysis.

7.3.2.2.2.2 Surface water sulfate concentration --

We estimated the annual average surface water sulfate concentration from the single fall index value for the northeastern lakes (Section 5.3) or an average of 3 (Pilot Stream Survey) or 2 (NSS Phase I) spring baseflow samples for the SBRP and Mid-Appalachian streams, respectively (Section 5.3). As described below, we used extensive temporal data from intensively studied sites to estimate the variability arising from using an index to represent average annual sulfate concentrations. Table 7-2 lists the sites from which data were available and the frequency of data collection at each site.

First, we calculated flow-weighted annual averages for each year for each site and a spring and/or fall flow-weighted average concentration. The fall and spring flow-weighted averages were calculated using sulfate concentrations for samples collected during periods that corresponded to the sampling windows used in the ELS (mid-September to early November) (Linthurst et al., 1986a) and NSS (March 15 to May 15) (Messer et al., 1986a; Kaufmann et al., 1988). An additional criterion defining the NSS sampling window was to sample prior to spring leaf-out. The spring samples collected by the NSS were non-event samples (i.e., baseflow). To maintain consistency we checked the weekly data used from the intensively studied SBRP and Mid-Appalachian sites (Table 7-2) to ensure that no samples that were unduly influenced by events were included in the spring flow-weighted average calculations.

Sulfur budgets for SBRP watersheds might be biased to some extent by their reliance on streamwater sulfate concentration data collected during spring baseflow periods. Spring baseflow chemistry closely approximates weighted mean annual chemistry computed from weekly grab samples for many southeastern systems. However, data representing precipitation/snowmelt episodes were not collected as part of the Pilot Stream Survey. For the few watersheds in the Southeast for which at least some episodes have been characterized, there has been a consistent trend of increased sulfate concentration during storm episodes [Deep Run and White Oak Run, VA (Hendrey et al., 1980; P.W. Shaffer, unpublished data), Fernow, WV (D. Helvey, personal communication), Walker Branch, TN (Johnson and Henderson, 1979), Coweeta, NC (Swank and Waide, 1988), Panola Mountain, GA (N. Peters and R. Hooper, personal communication)]. Due to the highly variable extent of episodic sulfate increases and the extremely limited data available for the region, the episodic bias in sulfur budgets for the Southeast cannot be quantified. In one system in the SBRP for which detailed sulfate export budgets have been determined (Coweeta WS #2, three years of data), sulfate export calculated from flow-proportional sampling was 19 percent higher than export calculated from weekly grab sample data (Swank and Waide, 1988). The only other watershed in the region for which comparable analyses have been completed is Panola Mountain, GA. Panola, located in the Piedmont near Atlanta, is physiographically and climatically different from the DDRP watersheds in the SBRP, and is subject to extreme episodic

Table 7-2. Intensively Studied Sites Used in Surface Water Chemistry Uncertainty Analysis

Site Name	Years of Study	Sample Frequency for Chemistry	Reference
<u>Northeast</u>			
ILWAS			R. Goldstein,
Woods Lake	5	weekly	pers. comm.
Panther Lake	5	weekly	
Sagamore Lake	5	weekly	
RILWAS			C. Driscoll,
Arbutus Lake	3	monthly[a]	pers. comm.
Black Pond	4	monthly	
Bub/Sis Lakes	3	monthly	
Darts Lake	3	monthly	
Moss Lake	2	monthly	
Pancake Hall Creek	1	bimonthly	
Rondaxe Lake	4	monthly	
Townsend Lake	1	monthly	
West Lake	4	monthly	
Windfall Pond	3	monthly	
Clear Pond	4	monthly	
Heart Lake	2	monthly	
Otter Lake	2	monthly	
<u>SBRP and Mid-Appalachian Streams</u>			
Coweeta 34	6	weekly	J. Waide,
Coweeta 36	11	weekly	pers. comm.
Deep Run	6	weekly	J. Galloway,
White Oak Run	5	weekly	pers. comm.
Fernow	10	weekly	D. Helvey,
Biscuit Brook	4	variable[b]	pers. comm.
Shenandoah Nat. Park (52 streams)	1	bimonthly	Lynch and Dise, 1985

a   Samples were collected between 10 to 13 times per year.
b   Biscuit Brook is an episodic study site. Samples collected periodically through out each year, however, during selected events extensive water chemistry samples were taken; often on an hourly time basis.

increases in sulfate following prolonged dry periods. Estimation of annual sulfate export from spring baseflow samples at Panola appears to underestimate total annual sulfate export by as much as 50 percent (N. Peters and R. Hooper, unpublished data). The bias observed at Panola should be regarded as an upper bound that might be approached by a few SBRP systems. The climate and moisture regimes of SBRP watersheds are more similar to those at Coweeta than to the more xeric conditions at Panola and at Walker Branch, TN (which also experiences large episodic increases in sulfate but with uncertain effects on sulfate export budgets; Johnson and Henderson, 1979), suggesting that the 19 percent bias observed at Coweeta is probably not atypical of SBRP watersheds (J. Waide, personal communication).

Data from 2 extensively studied sites, Biscuit Brook, NY, and Shenandoah National Park (SNP), VA, required special considerations. The Biscuit Brook data were collected as part of a program to monitor events. As a result, the dataset contained sections of very extensive temporal data (hourly) along with more infrequent sampling through the year. For this dataset, the flow-weighted annual average sulfate concentration was estimated by calculating the area under the hydrograph to properly weight the influence of any particular event flow value on the overall average (Figure 7-3). We were not able to perform a complete hydrograph separation analysis [such as described by Dunne and Leopold (1978)] due to the highly variable temporal sampling of the flow measurements. To determine the spring flow-weighted average we used a flow of 10 cfs as the maximum flow that could be regarded as equal to baseflow. The 10-cfs "limit" was determined after examination (simple hydrograph separation) of 4 years of available data.

The SNP dataset contains bimonthly flow and water chemistry data for 52 steams for one year. We calculated the flow-weighted annual average using the 6 flow and concentration measures. Two of the 6 values fell within or were close to the March 15 to May 15 time frame used to calculate estimates of spring baseflow sulfate concentration. The 2 samples were collected near the beginning and the end of the period (March 15-19 and May 17-20, respectively). Although the March sample was barely within the period, there was evidence that the flows were higher than the usual spring baseflow values for the SNP area (P. Shaffer, personal communication). The May sample was well after leaf-out and the concentration values were low compared to more extensive data available for Deep Run and White Oak Run. [These two watersheds, located in the SNP, are included in the 52-site SNP dataset. They also have been extensively monitored as part of the Shenandoah Watershed Acidification Survey (SWAS) (P. Shaffer, personal communication).] Although the March sample had very high flows, as noted above, we used it, rather than the sample from May 15, for the error analysis. The March sample sulfate concentration was closer than the May sample to the spring flow-weighted average sulfate concentrations for Deep Run and White Oak Run.

After we calculated the 2 flow-weighted averages (annual average and fall average for lakes or spring average for streams) for all years of data for the intensive study sites listed in Table 7-2, we then calculated an estimate of the percent difference (%Diff) between the two averages, as described in Equation 7-3.

$$\%Diff = ((Ind\_Avg - Ann\_Avg)/Ind\_Avg)*100 \qquad \text{(Equation 7-3)}$$

t = time
f = flow
c = sulfate concentration

$$\text{Avg. } c = \frac{\sum \left(\left(\left(\left(f_i * c_i\right)+\left(f_{i+1} * c_{i+1}\right)\right)/2\right)^*\left(t_{i+1}-t_i\right)\right)}{\sum \left(\left(\left(f_i + f_{i+1}\right)/2\right)^*\left(t_{i+1}-t_i\right)\right)}$$
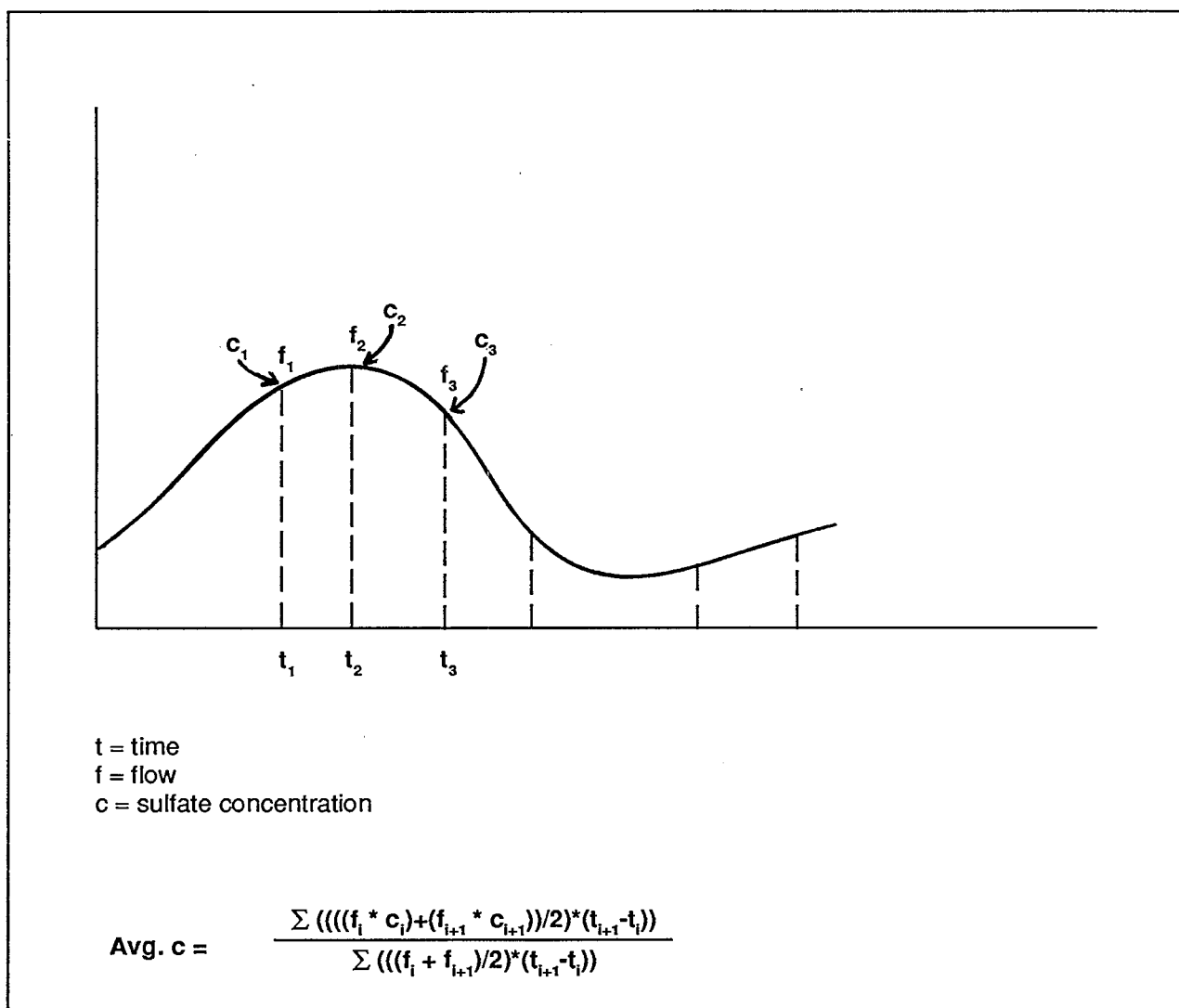
Figure 7-3. Model of flow-weighted average concentration calculations for Biscuit Brook.

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where:
    Ind_Avg   =   flow-weighted average sulfate concentration for the
                    index sample time frame (spring or fall)
    Ann_Avg   =   the flow-weighted annual average sulfate concentration

In the final step, we used the estimate of %Diff for each watershed and year to determine an estimate of the uncertainty associated with using the fall index value or the spring baseflow estimate to represent average annual chemistry for the sulfur retention analysis. First, we determined the distribution of %Diff for each set of data (e.g., ILWAS, RILWAS, Fernow). Next, we estimated an appropriate uncertainty estimate to be used in the uncertainty calculations for the sulfur retention analyses using the standard deviations around the mean %Diff for each of the intensively studied datasets (Table 7-3). The combined dataset had a mean value only slightly above zero and was slightly skewed to higher values. Both of these aspects can be attributed to the SNP data, which are probably somewhat high because March data were used. The overall distribution was approximately bell-shaped, with over 95 percent inside ±2 standard deviations of zero. Therefore, a lognormal distribution with an RSD of 9.4 percent was used to describe the uncertainty.

7.3.2.3 Uncertainty Calculation - Monte Carlo Analysis

Once uncertainty estimates were obtained for each of the input/output variables, the next step was to combine the information to obtain an overall estimate on uncertainty on the percent retention estimate. We did this using Monte Carlo analysis. The basic strategy employed in the Monte Carlo analysis was to randomly select for each iteration a value for each input/output variable (e.g., runoff) from the distribution of possible values as determined by the associated uncertainty for that variable. These randomly selected input/output variables were then used to calculate an estimate of percent sulfur retention for that particular iteration. We randomly selected 11 watersheds from the study regions and ran the Monte Carlo uncertainty using 10,000 iterations. (This number of iterations was chosen based on the simplicity of the sulfur retention equation and the computer CPU required. We performed several tests to evaluate the influence of the number of iterations on convergence of the mean and standard deviation and found that results were generally the same with significantly less than 10,000 iterations.) The overall uncertainty of the percent retention estimate was determined from the variance of the percent sulfur retention estimates calculated from the Monte Carlo iterations.

Based on the results of the Monte Carlo, we determined that a multiplicative normal distribution best described the percent sulfur retention uncertainty. Finally, we plotted the standard deviation of the Monte Carlo runs for each watershed against the average percent retention from the runs. Equation 7-4 presents the results of the linear regression that describes this relationship.

$$\text{Std. Dev.} = 30.1 - 0.30\,(\text{Avg.}) \qquad \text{(Equation 7-4)}$$
$$R^2 = 0.99$$
$$\text{Prob} > F = 0.0001$$
$$\text{MSE} = 0.15$$

This relationship, along with estimated variance, was used to calculate a 90 percent confidence interval about the percent sulfur retention population estimates presented in Section 7.3.4 (see Figures 7-7 and 7-10).

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Table 7-3. Summary Statistics on Percent Differences Between Flow-weighted Average Annual Sulfate Concentration and the Fall/Spring Flow-weighted Averages

Study Site	N[a]	Mean	Median	Std. Dev.	Min	Max
NE						
RILWAS	12	-1.1	-3.6	10.0	-9.7	15.6
ILWAS	32	-3.0	-3.0	8.4	-36.4	8.9
SBRP & Mid-Appalachian						
Fernow	10	-6.7	-5.7	7.5	-19.0	4.5
Coweeta-34	6	-8.5	-7.5	6.0	-15.9	0.0
Coweeta-36	11	-1.8	-1.2	10.5	-28.0	8.7
Biscuit	3	4.2	1.5	5.6	0.4	10.6
SNP	52	8.9	8.6	5.4	0.0	23.3
SWAS[b]	11	-3.3	-2.4	5.5	-14.7	5.0
	137	1.4	1.5	9.5	-36.4	23.3

[a] N is a combination of the number of years of data and the number sites.

[b] SWAS includes White Oak Run and Deep Run and stands for the Shenandoah Watershed Acidification Study.

7.3.3 Internal Sources of Sulfur

7.3.3.1 Introduction/Approach

Sources of sulfur within a watershed can be important factors affecting the interpretation of the annual percent sulfur retention estimates calculated using the input/output budget analyses. In the DDRP we are interested in percent sulfur retention relative to sulfur deposition. Sulfur from sources such as acid mine drainage, natural weathering of sulfide-bearing bedrock, or sulfate-containing sedimentary rocks can increase the surface water concentration of sulfate, thus biasing the results of the annual input/output budget calculations. We have used 2 approaches to identify watersheds with internal sources of sulfur. The first approach uses information on bedrock geology to identify watersheds associated with sulfur-bearing bedrock. In the second approach we determine an estimated surface water sulfate concentration for each site that, if exceeded, indicates (at a designated probability level) that at least some sulfate is derived from internal sources. This calculation is based on the determination of theoretical steady-state sulfate concentrations. This section describes the methods used for, and the results of, (1) the bedrock geology analyses and (2) the computation of an upper limit steady-state sulfate concentration.

7.3.3.2 Bedrock Geology

The first step in the bedrock analysis was to identify the types of bedrock within each of the DDRP watersheds. The DDRP subset of watersheds (NE=145, SBRP=35) within the ELS lake and NSS stream populations was selected to test whether the approach could be used to identify systems with potential internal sources of sulfur. Using the GIS, we overlaid watershed boundaries onto state geology maps (Section 5.4.1.7.3.1 and 5.4.2.7.2.1) and then identified the mapped bedrock units within the boundaries (Plate 5-13). State geology maps used in the analysis are listed in Table 7-4.

After we identified the mapped units associated with a watershed, we then assessed the potential for each unit to contribute sulfur to surface waters. We developed a 3-level stratification for classifying each bedrock type. Mapped units with high probabilities for contributing sulfur were assigned the value "Y". Primarily, these units consisted of calcareous rocks or of rocks identified in the state map legends as "sulfitic", "pyrite-bearing", or a similar description. Bedrock units containing potentially large amounts of sulfur, but with more limited contact with surface waters, were assigned a value of "P". These units, consisting of black and gray shales, sulfitic slates, fossiliferous sediments (potential carbonate sources), and "rusty weathering" metasediments, all probably contain substantial amounts of mineral sulfides. Because of limited permeabilities, however, the units in most cases will retain the native sulfur unless the bedrock has been disturbed (e.g., by quarrying or mining operations). All other bedrock types were assigned a classification of "N", indicating a low potential for supplying sulfur to local surface waters. Table 7-5 summarizes the classification scheme.

These are 2 caveats to the above classification system. First, we assigned the classifications independent of potential weathering rates. Although both the rapidly weathering bedrock (e.g., limestone) and the more resistant material (e.g., sulfitic schist) are assigned the same code, the more highly weatherable rock yields a higher flux of sulfur per unit time. Second, we assigned the classifications based on data compiled at a state map level. This latter fact causes 2 potential problems. First, because

Table 7-4. Bedrock Geology Maps Used in the DDRP Internal Sources of Sulfur Bedrock Geology Analyses

State	Scale	Reference
CT	1:250,000	Rodgers (1985)
GA	1:500,000	Pickering and Murray (1976)
MA	1:250,000	Zen (1983)
ME	1:500,000	Osberg et al. (1985)
NH	1:250,000	Billings (1980)
NY	1:250,000	Isachsen and Fisher (1970)
NC	1:500,000	Brown (1985)
PA	1:250,000	Miles (1980)
RI	1:250,000	Quinn (1971)
SC	1:250,000	Overstreet and Bell (1965)
TN	1:250,000	Hardeman (1966)
VT	1:250,000	Doll et al. (1961)
WV	1:250,000	Cardwell et al. (1968)

Table 7-5. Potential for Sulfur Contribution by Geologic Type

Sulfur Contribution Potential	Geologic Type
Y	Calcareous
	Limestones
	Dolostones
	Sulfitic
	Marbles
	Carbonaceous
	Pyrite-bearing
P	Black/gray shales
	Fossiliferous
	Rusty weathering (schists)
N	All other types (includes sandstones, conglomerates, most metamorphics, igneous, etc)

of the scales of the state geology maps, local concentrations of sulfide-bearing bodies are frequently not delineated; therefore, potential local sulfur sources in individual watersheds are not always identified. Second, as a result of correlation difficulties, the location of contacts between contiguous units might not be depicted accurately on the watersheds. This could result in the mis-identification of the presence (or absence) of sulfur-bearing units on a particular watershed.

Using the above classification scheme, we formulated and tested the hypothesis that watersheds having large areal percentages of bedrock falling into the "Y" and "P" groups would more likely have excess sulfur appearing in the input/output budgets (i.e., net negative retention of sulfur). Evaluation of this hypothesis, however, indicated no significant correlation between net sulfur retention and the group classification.

We attribute the lack of a correlation between these variables to several factors. First, DDRP watersheds were selected and stratified based on lake ANC (Section 5.2). No systems with ANC values greater than 400 μeq L^{-1} were included in the northeastern sample population, thereby effectively eliminating from the sample most watersheds with carbonate-bearing bedrock. In those watersheds with carbonate-bearing bedrock, the fraction of areal coverage is generally sufficiently small to mask any internal contributions to the sulfur budgets. As a result, because of the restrictions of our target population and, thus, sample, we do not get an evenly balanced sample of the different bedrock types. Second, DDRP watersheds acting as large net sources for sulfur (e.g., 1D1-093, 1E1-123) generally are associated with major disturbances (e.g., quarrying operations). This observation suggests local sources for the sulfur and, thus, information not identified on state geology maps. As noted above, the disturbances probably enhance the flux of sulfur from bedrock to the surface water, magnifying the internal contributions to the sulfur budgets. Finally, watersheds exhibiting modest excess sulfur fluxes, but associated with "N"-type bedrock, probably reflect unidentified local sources of sulfur. Again, the discrepancy could result from scale problems with the state maps, or could simply reflect local concentrations of sulfur-bearing minerals.

In summary, at the level of resolution currently available, bedrock geology does not explain a significant portion of the high sulfate outputs found in the sulfur input/output budgets. Although in many instances, local sources for sulfur are bedrock-related, it is not possible to isolate those sources using information compiled for state geology maps. More detailed investigations (outside of the scope of this Project) would be required to isolate and identify these sources and resolve the discrepancies.

7.3.3.3 Upper Limit Steady-State Sulfate Concentration

7.3.3.3.1 Introduction -

The second approach selected to determine an estimate of the number of systems with internal sources of sulfur was based on an estimated steady-state sulfate concentration. As discussed previously (Section 7.1), steady state is obtained when sulfur outputs from a watershed equals inputs. The sulfate concentration of the surface water at that point is the steady-state sulfate concentration, and an estimate can be computed from the inputs and the runoff, as noted in Equation 7-5 below:

$$[SO_4^{2-}]_{ss} = (S_w + S_d)/R \qquad \text{(Equation 7-5)}$$

where: $[SO_4^{2-}]_{ss}$ = steady-state sulfate -- [average annual concentration (mass length^{-3})]

S_w = wet sulfur deposition (mass length^{-2} yr^{-1})

S_d = dry sulfur deposition (mass length^{-2} yr^{-1})

R = runoff depth (length yr^{-1})

Steady-state sulfate concentration can be computed for any individual site for which we have estimated inputs and runoff. If the observed (i.e., by ELS or NSS) sulfate concentration at a site is greater than the computed steady-state concentration, a source of sulfur internal to the watershed is suspected.

As discussed previously (Section 7.3.2.3), each of the estimates of inputs and runoff has an associated uncertainty. The computed steady-state sulfate concentration has an uncertainty that is a function of these input uncertainties. Thus, we can compute for each surface water (i.e., lake or stream reach) an upper limit steady-state sulfate concentration that, if exceeded, serves to indicate the occurrence (with known probability) of an internal source of sulfur.

7.3.3.3.2 Objectives -

The objectives of the steady-state sulfate concentration analysis are

(1) to apply an uncertainty analysis (of the type presented in Section 7.3.2) to determine an estimate of the steady-state sulfate concentration and associated uncertainty, and

(2) to calculate an upper limit steady-state sulfate concentration that, if exceeded, indicates the presence of internal sources of sulfur.

7.3.3.3.3 Calculation of steady-state sulfate -

7.3.3.3.3.1 Data --

We used the long-term annual average estimates of wet and dry sulfur (Section 7.3.1.2.1) and the 30-year average annual runoff (Section 5.7) to calculate estimates of steady-state sulfate concentration for each watershed (Equation 7-5).

7.3.3.3.3.2 Monte Carlo analysis --

Figure 7-4 presents a flow chart of the steady-state sulfate analysis and subsequent use of the steady-state sulfate concentration to identify internal sources of sulfur. Briefly, the first step in developing the upper limit steady-state sulfate concentration is to determine an estimate of the uncertainty associated with the steady-state calculation. We conducted a Monte Carlo analysis similar to the one discussed in Section 7.3.2.3 using the parameter uncertainty estimates for S_w, S_d, and R. We performed Monte Carlo simulations (10,000 iterations) for 34 watersheds selected at random from the NE, SBRP, and Mid-Appalachian study sites (NSWS). The results of the Monte Carlo analysis provided an estimate of the
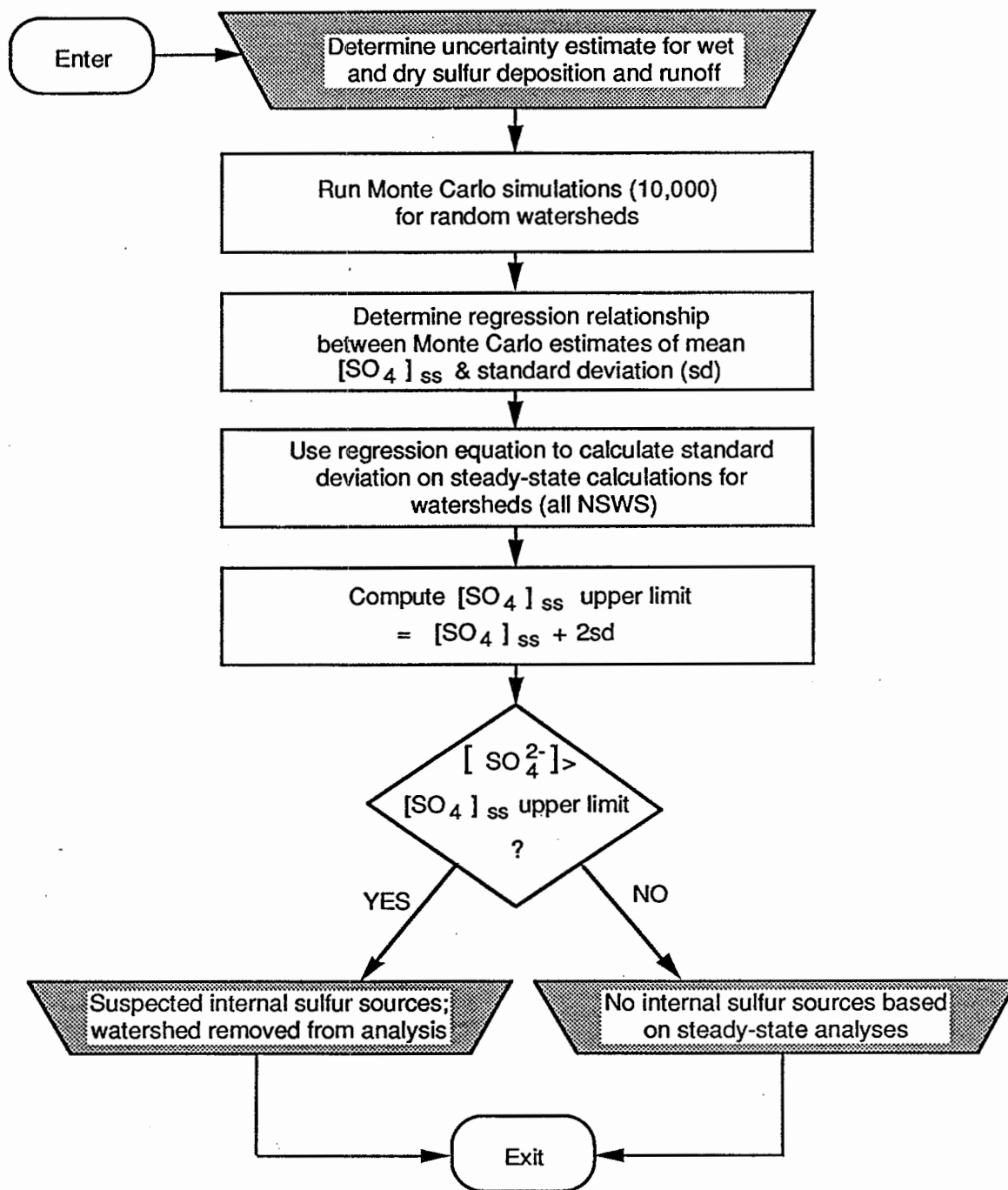
Figure 7-4. Flow chart for the determination of internal sources of sulfur using the steady-state sulfate concentration.

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standard deviation around the mean steady-state sulfate using the uncertainty estimates for each of the 34 watersheds.

7.3.3.3.3.3 Development and application of the regression equation --

We then plotted the standard deviation versus the calculated mean steady-state sulfate concentration (based on 10,000 runs) for the 34 watersheds (Figure 7-5) and determined the regression equation with the standard deviation as the independent variable.

$$\text{Est. Std. Dev.} = -4.9 + 0.339 \text{ mean } [SO_4^{2-}]_{ss} \qquad \text{(Equation 7-6)}$$
$$R^2 = 0.99, \ p = 0.0001$$

We then substituted the computed (or nominal) value of steady-state sulfate concentration for each watershed into Equation 7-6 to calculate an associated standard deviation applicable to each site (note that there is an individual estimate for each site). Analyses of the Monte Carlo runs for the 34 watersheds indicate that a log normal distribution best describes the uncertainty associated with steady-state sulfate concentration. In applying the regression equation to each watershed, we conducted a log transformation of the prediction procedure to reflect the observed distribution of the uncertainty in steady-state sulfate concentration.

The final step in the analysis of steady-state internal sources was to apply the calculated standard deviation on steady-state sulfate concentration to determine an upper limit. We added twice the estimated standard deviation (97.5 percent confidence interval) to the computed steady-state sulfate concentration and then compared the result to the measured sulfate concentration. If the computed upper limit steady state sulfate concentration was equal to, or greater than, the measured sulfate concentration, then we assumed no significant internal sources of sulfur. Conversely, if it was less than the measured sulfate concentration, we strongly suspected that some source of sulfur was contributing to the surface waters in addition to that estimated from atmospheric deposition.

This analysis does not work well for sites in regions that retain large amounts of deposited sulfur (e.g., the SBRP). In such regions, statistical outlier analyses (e.g., see Section 8) need to be performed to identify unusually disturbed or affected sites.

A summary by region of the number of ELS and NSS watersheds removed from the average annual percent sulfur retention analysis is given in Table 7-6. These sites were identified using the upper limit steady-state sulfate concentration estimates. The additional sulfur is probably from some internal weathering source (as discussed above) or possibly could be due to a very localized emissions source.

7.3.4 Results and Discussion

We calculated percent sulfur retention for sites located in the NE, Mid-Appalachians, SBRP, and several adjacent regions. Sites identified as having internal sulfur sources through the steady-state sulfate concentration analysis were eliminated (Table 7-6). Also, 3 SBRP sites sampled as part of the Pilot Stream Survey were dropped due to outlier surface water chemistry (i.e., ANC > 1000 μeq L^{-1}).
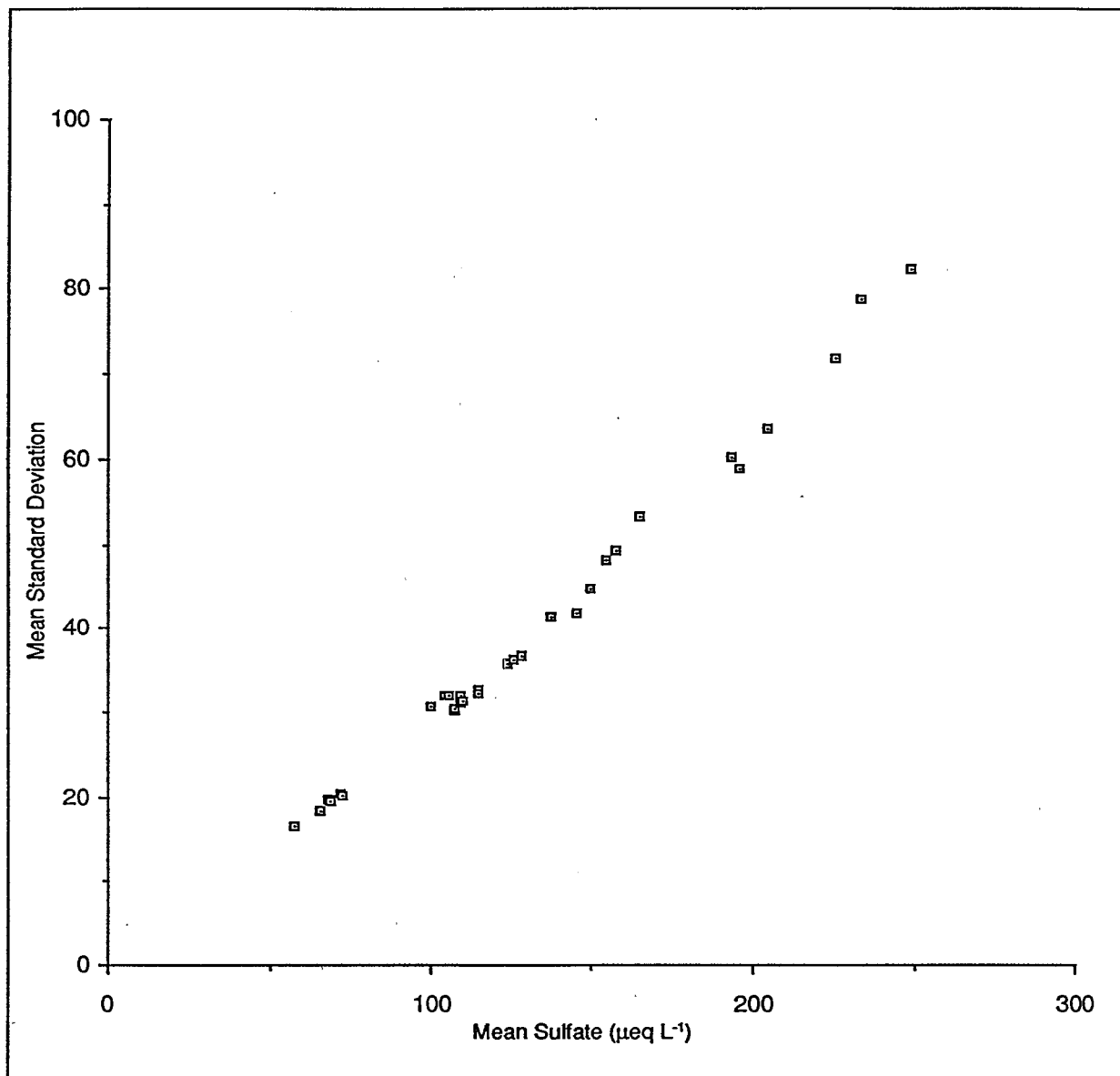
Figure 7-5. Scatter plot of the Monte Carlo calculated standard deviation versus the calculated mean $[SO_4^2]_{ss}$ (based on 10,000 runs per watershed) n=34.

Table 7-6. Summary of Watersheds (by ELS and NSS Subregion) Dropped Due to Suspected Internal Sources of Sulfur Identified by Steady-State Analysis

Region	# of Watersheds
Eastern Lake Survey	
1A	3
1B	5
1C	15
1D	12
1E	18
3A (SBRP)	2
Pilot Stream Survey	0
National Stream Survey	
1D	12
2BN	9
2CN	23
2X	7
3A	2
3B	7

We used a modified version of the long-term annual average (LTA) sulfur deposition in these analyses. This modified LTA sulfur deposition does not include the 20 percent increase in dry deposition discussed in Section 5.6 for the TY and standard LTA deposition data. The TY and standard LTA data were only available for the primary DDRP study sites (NE=145, SBRP=35). The sulfur retention analyses use surface water chemistry from approximately 1,000 sites (lakes and stream reaches) sampled as part of the ELS and NSS. The dry sulfur deposition data provided by AREAL-RTP (see Section 5.6) were the only internally consistent dry sulfur deposition data for all of the ELS and NSS sites. These dry sulfur deposition estimates were combined with the long-term wet sulfur deposition estimates to form the modified-LTA deposition dataset. To test the overall effects of not using the 20 percent increase in these analyses, we adjusted the modified-LTA data with a 20 percent increase in dry sulfur for the ELS Northeast sites. This adjustment created a dataset analogous to the TY and standard LTA data. We then calculated percent sulfur retention using the adjusted data and compared the results to the unadjustified modified-LTA sulfur retention results (Figure 7-6). An inspection of Figure 7-6 indicates that there is only a slight shift in the distribution of percent sulfur retention between the two datasets. This slight shift is unimportant relative to the principal conclusions drawn from these regional sulfur retention analyses. Similarly, analyses using the TY dataset yield results very close to those computed using the modified-LTA dataset. Thus, the latter dataset is used for the remainder of the analyses presented in this section.

7.3.4.1 Northeast

Results from analyses using the modified-LTA deposition data indicate that lake systems in the NE are generally at or near zero percent net sulfur retention (Table 7-7; Figure 7-7A; Plate 7-1). Rochelle and Church (1987) conducted a sulfur retention analysis using runoff and deposition data for the water year prior to ELS and NSS sampling and showed similar results. Also, we examined sulfur retention patterns in the NE for individual ELS subregions. Although lakes in Subregion 1B have the highest percent net retention, lakes in all subregions are, on average, very close to zero percent net retention (Table 7-7).

7.3.4.1.1 Evaluation of sulfur retention mechanisms in NE watersheds -

Although most NE watersheds are near sulfur steady state, a small number of watersheds are characterized by high apparent sulfur retention. During development of preliminary sulfur input/output budgets for lakes in the northeastern United States, we identified a subset of watersheds for which budget analyses indicated significant sulfur retention. Because analyses of sulfate adsorption at that time suggested that adsorption was likely to delay sulfur response in NE watersheds for a very limited time, it was unclear how sulfur was being retained in this subset of watersheds. In an effort to understand sulfur retention in these systems and in an effort to evaluate potential future sulfate increases at those sites, we identified for additional analysis a group of 45 NE watersheds having high computed sulfur retention. Soils, vegetation, land use, depth to bedrock, and bedrock geology were mapped on 44 of the watersheds (permission to map was denied for one) during the fall of 1987 and spring and summer of 1988 (Figure 7-8). Watersheds were mapped by the USDA SCS according to protocols developed for the original NE DDRP soil survey (Section 5.4), except that mapping criteria were modified to require discrete mapping of wetland areas 2 acres or larger, rather than the 6-acre map unit delineations used for other soils and for vegetation. After completion of mapping, soil map units were correlated to the soil sampling classes defined for the initial DDRP NE soil survey, except for soils on parts of two watersheds in Pennsylvania. Those soils were correlated to sample classes defined for Mid-Appalachian soils, and

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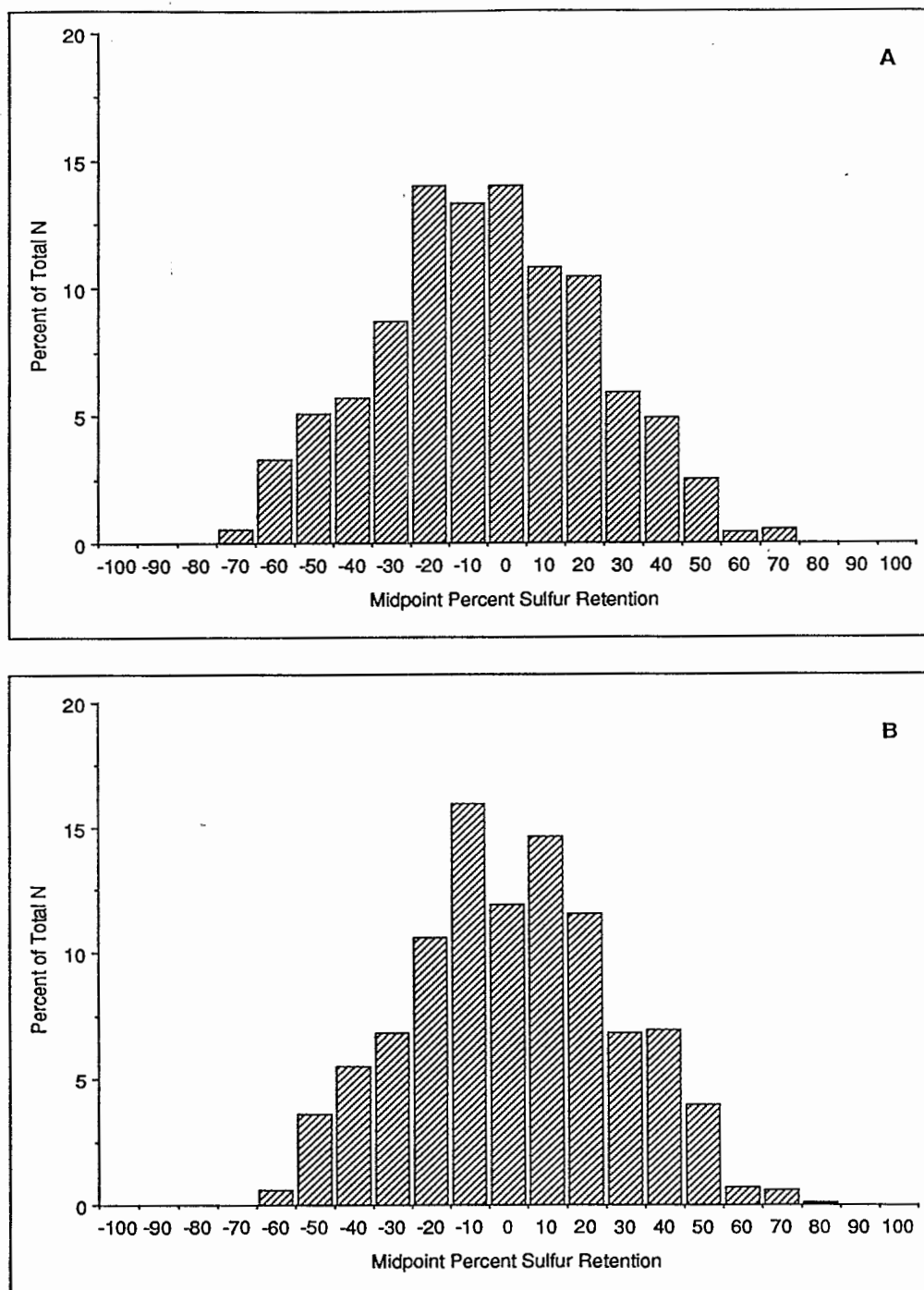
Figure 7-6. Comparison of percent sulfur retention calculated using (A) modified-LTA deposition and (B) modified-LTA deposition adjusted with a 20 percent increase in dry deposition.

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Table 7-7. Percent Sulfur Retention - Summary Statistics by Region

Region	N[a]	Mean	Median	Std. Dev.	Min.	Max.
NE						
ELS Rg1	5,828	-5.0	-5.2	27.6	-69.8	73.3
1A	1099	-11.9	-13.9	22.5	-63.5	60.6
1B	1285	8.9	7.6	25.9	-65.6	73.3
1C	1190	-3.8	-7.2	27.3	-65.7	63.3
1D	966	-11.5	-8.9	29.9	-69.8	53.9
1E	1288	-9.4	-11.7	26.5	-61.9	51.0
Mid-App						
NSS 2Bn	12,580	27.9	39.6	43.1	-82.6	90.6
NSS 2Cn	6,478	-4.0	3.1	31.8	-82.7	55.2
SBRP						
PSS	2,031	67.5	75.4	23.2	-54.3	88.0
ELS Rg. 3a	247	68.0	78.6	32.8	-64.4	92.9
Misc.[b]						
S. App. Pla.						
NSS 2X	4,329	43.4	50.3	37.5	-63.6	86.0
Piedmont						
NSS 3A	7,199	68.4	78.0	24.1	-9.8	91.9
Mid Atlantic Coastal Plain						
NSS 3B	9,535	30.5	34.2	38.4	-60.4	92.7
Poconos/Catskills						
NSS 1D	2,724	-21.5	-29.2	31.2	-71.2	67.1

[a] Estimated target population calculated using NSWS weights (see Linthurst et al., 1986a; Messer et al., 1986a; Kaufmann et al., 1988) for information on weights.

[b] Additional regions sampled as part of NSS Phase I (see Plate 7-1).
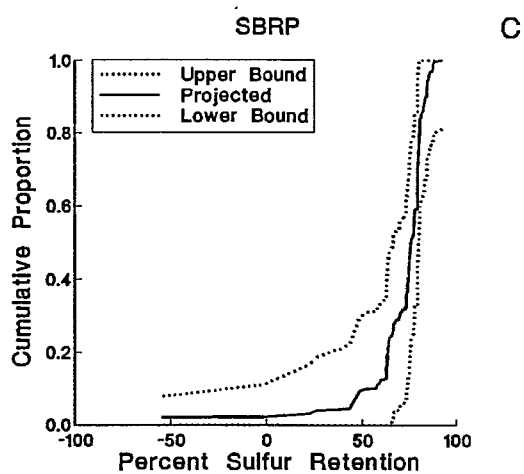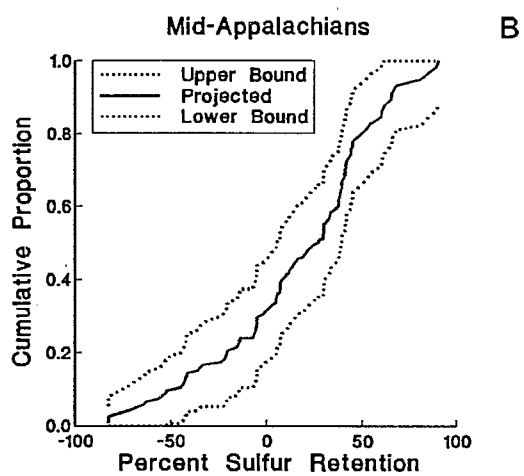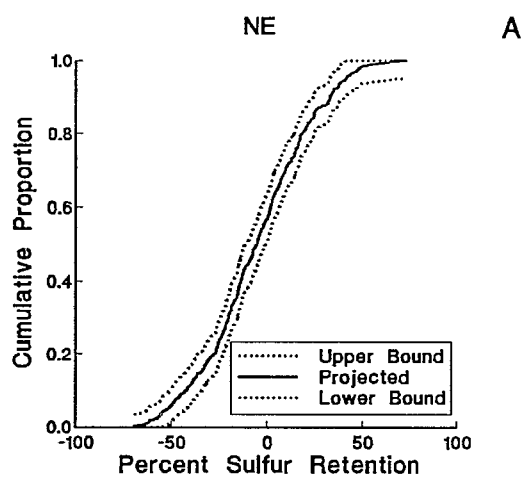
Figure 7-7. Population-weighted distribution of projected percent sulfur retention (upper and lower bounds for 90 percent confidence interval): (A) Northeast; (B) Mid-Appalachians, and (C) Southern Blue Ridge Province.

Plate 7-1. Sulfur retention and wet sulfate deposition for National Surface Water Survey subregions in the eastern United States.

NSWS SUBREGIONS
MEDIAN % SULFUR RETENTION
AND WET SULFATE DEPOSITION

**MEDIAN PERCENT
SULFUR RETENTION**

- < 0
- 0 - 20
- 20 - 40
- 40 - 60
- 60 - 80
- 80 - 100

Average Annual
Wet Sulfate
Deposition (g m^{-2} yr^{-1})*

2.25

2.25

2.25

2.50

2.75

3.00

2.25

3.25

3.50

3.50

3.25

3.00

2.50

2.25

2.50   2.75

2.25

2.00

2.00

2.00

1E
1C
1A
1D
1B
2Cn
2Bn
3B
2X
2As
2X
3A
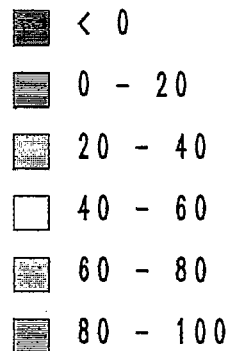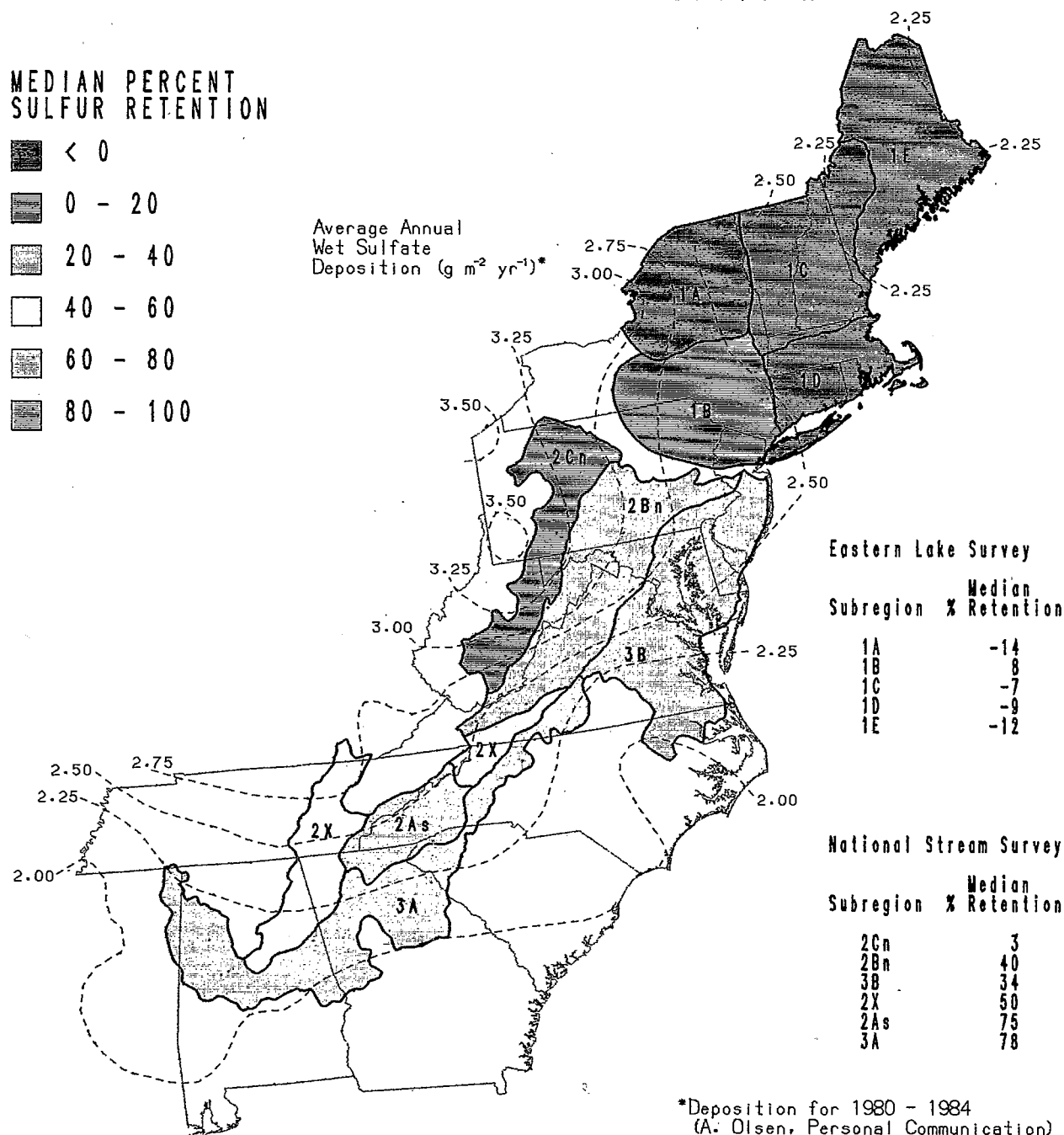
Eastern Lake Survey

Subregion	Median % Retention
1A	-14
1B	8
1C	-7
1D	-9
1E	-12

National Stream Survey

Subregion	Median % Retention
2Cn	3
2Bn	40
3B	34
2X	50
2As	75
3A	78

*Deposition for 1980 – 1984
  (A. Olsen, Personal Communication)

DDRP STUDY SITES
Supplemental Watershed Mapping

- Supplemental Mapping Sites
+ Study Sites
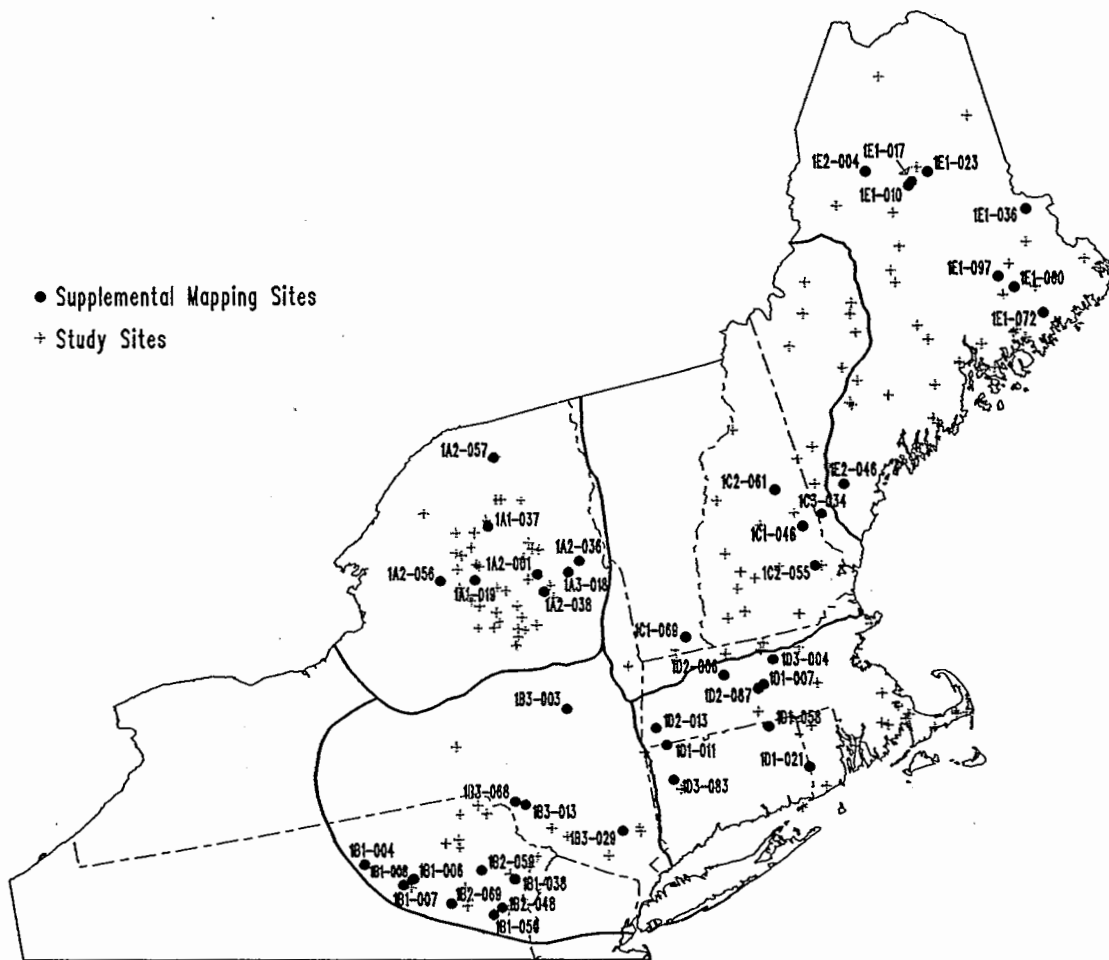
Figure 7-8. Supplemental watersheds mapped for special evaluation of sulfur retention.

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the watersheds were dropped from the analysis. We have used these mapping data to assist in an analysis of retention in these watersheds.

7.3.4.1.1.1 Approach --

Watersheds for this analysis were selected from the NE lakes sampled in Region 1 as part of the ELS, using preliminary watershed sulfur input/output budgets developed with 1984 Water Year data. Criteria for watershed inclusion were (1) lake type -- limited to drainage lakes and reservoirs; (2) watershed area -- less than 3000 ha; and (3) watershed sulfur budgets (1984 Water Year data) characterized by one or more of the following:

- at least 20 percent sulfur retention;

- a 20 μeq L^{-1} or greater difference between lake sulfate and steady-state sulfate concentration;

- lake sulfate concentrations at or below the tenth percentile of sulfate concentrations in the respective ELS Subregion.

The budget/concentration criteria were not intended as independent selection criteria; rather, multiple criteria were defined to ensure inclusion of lake systems with high apparent absolute and/or relative sulfur retention. With few exceptions, watersheds met at least 2 of the sulfur budget/concentration criteria, and most met all three.

We assessed watershed sulfur budgets using procedures and uncertainty estimates as described in Section 7.3. Based on uncertainty analyses presented in Section 7.3, we determined that retention should be regarded as significant if computed percent sulfur retention exceeds 37.5 percent.

7.3.4.1.1.2 Results and Discussion

Table 7-8 summarizes sulfur budget status for the 42 NE watersheds considered, and also lists computed in-lake sulfur retention and proportions of wet soils on each watershed. Using the criterion of 37.5 percent to define significant retention, 27 of the 42 watersheds had significant (positive) sulfur retention. If actual retention was not significant for any of the 535 lakes in the ELS sample (all regular ELS Region 1 drainage lakes and reservoirs, excluding DDRP lakes and lakes with watersheds > 3000 ha) from which the 42 watersheds of concern were identified, an expected 13 lakes would fall above the 95 percent confidence window of 37.5 percent. Assuming that retention estimates for each watershed are independent, if there were in fact no lakes with significant sulfur retention in the sample population, the probability of observing significant (computed) retention in $\geq$ 27 watersheds is 0.00057. From these results we can conclude that although sulfur retention in many of the 42 watersheds is not statistically significant, a small proportion of watersheds in the NE target population are characterized by significant positive sulfur retention.

Indirect evaluation of soils data for the NE virtually rules out the possibility that significant net sulfate adsorption is presently occurring in these watersheds. Response times for the 38 NE soil sample classes are comparable to NE watershed responses presented in Section 9.2; none of the sample classes is

Table 7-8. Summary of Sulfur Retention Status and of Watershed Variables Contributing to Sulfur Retention for 42 Watersheds in the Northeastern United States

LAKE ID	ws area (ha)	WA:LA	rtn. time (yr)	sulfate (μeq L⁻¹) lake	s-s	ws sulfur rtn (%)	In-lake rtn(%)[a]	adj. ws rtn (%)[b]	% of watershed area wetland	H02+H03	I25
1A1-019	94	11.4	0.24	80.6	98.7	18.3	4.7	13.6	8.1	19.3	0.0
1A1-037	105	14.2	0.94	61.1	105	41.9*[c]	4.9	37.0	15.9	10.3	0.0
1A2-001	225	15.2	0.08	64.8	95.9	32.4	4.3	28.1	2.3	3.9	0.0
1A2-036	574	20.8	0.11	84.3	126	33.2	4.5	28.6	4.4	8.0	0.0
1A2-038	91	4.3	0.34	78.3	106	25.9	12.0	13.5	4.5	4.1	0.0
1A2-056	78	7.1	1.17	42.5	108	60.6*	8.0	52.6*	10.7	15.4	0.0
1A2-057	232	4.3	1.31	84.0	104	19.0	13.0	6.5	0.0	0.7	0.0
1A3-018	153	9.6	0.55	54.0	119	54.7*	8.1	46.5*	0.0	4.1	0.0
1B1-004	106	11.8	0.32	91.7	179	48.8*	7.1	41.7*	0.0	0.0	38.6
1B1-006	124	5.0	0.59	104.5	183	43.0*	14.0	29.0	7.7	1.9	51.4
1B1-007	146	12.4	0.18	79.5	187	57.4*	6.9	50.5*	2.7	4.9	17.4
1B1-008	131	3.5	2.25	102.4	184	44.2*	18.0	26.4	9.9	3.6	34.8
1B1-038	501	78.2	0.02	62.6	143	56.2*	0.9	55.2*	0.6	17.2	9.8
1B2-059	57	4.0	0.59	72.3	179	59.6*	16.0	43.2*	7.0	7.0	46.1
1B2-069	168	15.5	0.20	121.8	216	43.5*	6.2	37.3	0.0	0.0	3.2
1B3-003	105	7.3	1.81	118.3	144	17.8	11.0	7.2	7.2	0.3	8.4
1B3-013	125	13.4	0.26	93.1	149	37.6*	5.4	32.2	3.3	0.3	15.3
1B3-029	37	6.6	0.62	67.4	199	66.2*	12.0	54.7*	0.0	0.9	0.0
1B3-068	120	10.2	0.22	73.9	147	49.7*	6.8	42.9*	4.3	1.5	11.1
1C1-046	422	17.5	0.43	61.2	100	39.0*	4.4	34.5	9.7	4.9	0.0
1C1-069	274	25.9	0.06	50.2	108	53.7*	2.5	51.2*	7.9	4.2	0.0
1C2-055	295	8.9	0.99	65.5	109	39.8*	8.3	31.5	14.2	4.8	0.0
1C2-061	368	11.7	0.25	59.1	75.6	21.8	4.5	17.3	13.3	9.1	0.0
1C3-034	136	12.3	0.25	52.4	92.2	43.2*	5.6	37.6*	13.6	5.8	0.0
1D1-007	165	18.2	0.13	93.7	124	24.3	4.1	20.2	14.7	8.0	0.0
1D1-011	641	14.3	0.32	74.3	128	42.0*	4.5	37.5	10.6	5.5	0.0
1D1-021	180	6.8	0.25	79.5	98.5	19.3	7.7	11.6	19.2	12.0	0.0
1D1-058	464	12.0	0.10	69.3	120	42.1*	5.5	36.7	21.6	4.8	0.0
1D2-006	138	20.2	0.12	58.8	128	53.9*	3.7	50.2*	17.2	12.8	0.0
1D2-013	192	8.6	0.30	93.5	130	28.2	7.6	20.6	8.8	0.6	0.0
1D2-087	148	10.4	0.14	67.7	130	47.8*	7.0	40.9*	17.6	8.9	0.0
1D3-004	185	15.0	0.16	81.6	124	~34.3	4.9	29.4	2.5	1.9	0.0
1D3-083	21	3.0	0.86	95.6	143	33.0	16.0	17.3	0.0	0.0	0.0
1E1-010	217	17.3	0.35	33.6	50.4	33.2	3.5	29.8	9.6	9.6	0.0
1E1-017	418	44.9	0.07	29.1	50.3	42.2*	1.4	40.8*	8.4	6.1	0.0
1E1-023	234	28.2	0.04	36.8	53.8	31.7	2.3	29.4	36.5	21.7	0.0
1E1-036	148	6.8	0.18	40.9	65.9	38.0*	8.9	29.1	46.7	26.0	0.0
1E1-060	84	8.3	1.31	35.1	64.3	45.3*	7.0	38.3*	24.4	16.6	0.0
1E1-072	197	1.2	6.60	38.2	65.6	41.7*	23.0	18.6	17.0	7.9	0.0
1E1-097	49	1.7	1.36	36.5	67.3	45.7*	22.0	23.7	5.4	4.2	0.0
1E2-004	198	11.0	0.08	38.4	60.8	37.0	6.4	30.6	90.4	12.7	0.0
1E2-046	634	12.8	0.25	44.2	90.1	51.0*	5.4	45.5*	20.0	16.2	0.0

[a] Computed using Equation 7-1.
[b] Percent retention minus percent in-lake retention.
[c] Asterisks indicate significant retention (α = 0.05).

projected to be retaining sulfate or to have solution sulfate concentrations less than steady state under current conditions (based on the historic deposition sequences used in Section 9). Therefore, it is highly unlikely that the observed retention on these watersheds can be explained by adsorption.

Direct estimation of in-lake sulfur retention, using the model of Baker et al. (1986b) (Section 7.2), suggests that in-lake processes are a minor sulfur sink in most NE lake systems. For many of the 42 watersheds under consideration here, however, the relative importance of in-lake reduction is apparently much higher (Table 7-8). Computed retention for the 42 lakes ranged from 0.9 to 23.1 percent, exceeding 10 percent for 10 watersheds and 20 percent for 2 watersheds. If watershed sulfur budgets are adjusted by computed in-lake retention, retention in 12 of 27 watersheds drops below the 37.5 percent threshold that is used to define significant retention. In other words, for almost half of the 27 watersheds with significant computed sulfur retention, in-lake reduction has a significant influence on watershed sulfur retention status.

Wetlands and wet soils might also contribute significantly to sulfur retention in many of these watersheds. Table 7-8 lists percentages of watershed areas covered by wetlands (SCS land use classifications) and by soils in sample classes H02 and H03 (wetlands) and I25 (deep, very poorly to somewhat poorly drained aquepts). These data indicate that all but 3 of the 15 watersheds with significant sulfur retention (after adjusting for in-lake retention) have at least 10 percent coverage of wetlands or wet soils (these areal proportions are not additive on watersheds; much of the area designated as wetlands on SCS land use maps is also classified in soil sample classes H02 or H03); wetland area exceeds 10 percent on 19 of the 42 watersheds with maximum coverage exceeding 90 percent. Evidence of net sulfur retention in wetlands is inferential; actual sulfur retention in these soils depends not only on the extent but also the location of these areas within a watershed and the fraction of watershed runoff flowing through them.

Analyses to date suggest that there is significant sulfur retention in a small proportion of NE lake watersheds. Evaluation of Level II modelling data (Section 9) also indicates that adsorption is unlikely to play a significant role in that retention. The most likely processes contributing to retention in this group of watersheds are a combination of in-lake retention, which is important in those lakes having long hydrologic retention times (Section 7.2), and reduction in wetlands/wet soils. Unlike adsorption, reduction in lake sediments and wet soils is a rate-limited, rather than a capacity-limited process; retention by reduction mechanisms can therefore continue at current rates indefinitely because no capacity exists to be filled or exhausted. Reduction in lakes provides a permanent sink for sulfur, but the extent of retention in wetlands and wet soils can change on an annual or even seasonal basis. During dry periods, soils in wetlands and other anaerobic areas could reoxidize, resulting in oxidation of reduced sulfur and, potentially, its release as sulfate. The role of wetlands and wet soils can consequently shift from that of sulfate sink to source during dry periods; the potential for long-term retention in such systems is thus dependent on watershed hydrologic conditions.

7.3.4.2 Mid-Appalachians

The Mid-Appalachian Region does not present as clear a picture of percent sulfur retention as the NE (Table 7-7; Figure 7-7B). For this study we have defined the Mid-Appalachian Region as a combination of NSS Subregions 2Bn and 2Cn (Plate 7-1). Kaufmann et al. (1988) defined these regions as the Valley and Ridge and Northern Appalachians, respectively. We found that percent retention was

more evenly distributed with no strong patterns of low or high percent net retention. In general, for both subregions, percent net retention is low with average values less than 30 percent. Subregion 2Cn has significantly lower percent retention estimates on the average than Subregion 2Bn. Subregion 2Cn receives higher sulfur deposition than does Subregion 2Bn (Plate 7-1). Although Subregion 2Cn probably has a high incidence of potential acid mine drainage influence, systems identified by Kaufmann et al. (1988) as having potential internal sulfur sources were also subsequently identified in our steady-state analysis (Section 7.3.3.3) and dropped from this analysis and presentation of results.

The Southern Appalachian Plateau and the Mid-Atlantic Coastal Plain have percent retention on the average of 30 to 40 percent (Table 7-7; Figure 7-9). In these regions there is a pattern toward higher net retention, although a large amount of scatter in percent sulfur retention remains. The Catskills/Pocono Region has a median net sulfur retention of -21.5 percent. This region is a transitional area from the NE, where glaciated soils predominate, to the Mid-Appalachians, where older and more weathered soils predominate.

7.3.4.3 Southern Blue Ridge Province

Median net sulfur retention for the SBRP is approximately 75 percent (Table 7-7; Figure 7-7C). Rochelle and Church (1987), working with sulfur deposition data from Water Year 1984, found similar results. The average percent sulfur retention for the Piedmont Region (adjacent to the SBRP) is also high compared to the NE and Mid-Appalachians (median = 78.0, Table 7-7 and Figure 7-9).

7.3.4.4 Conclusions

When collectively examined, definite spatial trends in net sulfur retention are evident among the NE, the Mid-Appalachian Region, and the SBRP. Percent sulfur retention generally increases from North to South in the eastern United States (Figure 7-10; Plate 7-1). Plate 7-2 provides an additional view of the North to South regional patterns of percent sulfur retention. Using the broad major land use resource area (MLRA) classes (USDA, 1981) to stratify the NSWS study sites, Plate 7-2 indicates again that the SBRP and adjacent areas are retaining higher amounts of incoming sulfur deposition when compared to the Mid-Appalachian Region.

Also, indications are that net retention of sulfur in the NE on the average is zero or close to zero. Net sulfur retention in the Mid-Appalachian Region appears to be in transition between the NE and SBRP. A simple analysis of variance indicates that, on the average, percent net retention is significantly different among these 3 regions.

We attribute the spatial patterns in sulfur retention shown here to 2 key factors: (1) soil type, and (2) sulfur deposition. Whereas soils of the SBRP are predominately weathered Ultisols and Inceptisols that tend to have high sulfate adsorption capacities, the NE Region is dominated by Spodosols, which characteristically have low sulfate adsorption capacities [e.g., see discussion by Rochelle et al. (1987)]. Soils of the Mid-Appalachian Region are predominately Inceptisols and Ultisols. Given the current patterns of wet sulfur deposition (Plate 7-1) and assuming that the Mid-Appalachian region has received elevated levels of sulfur deposition for a considerable period of time, it is apparent that this region is in transition
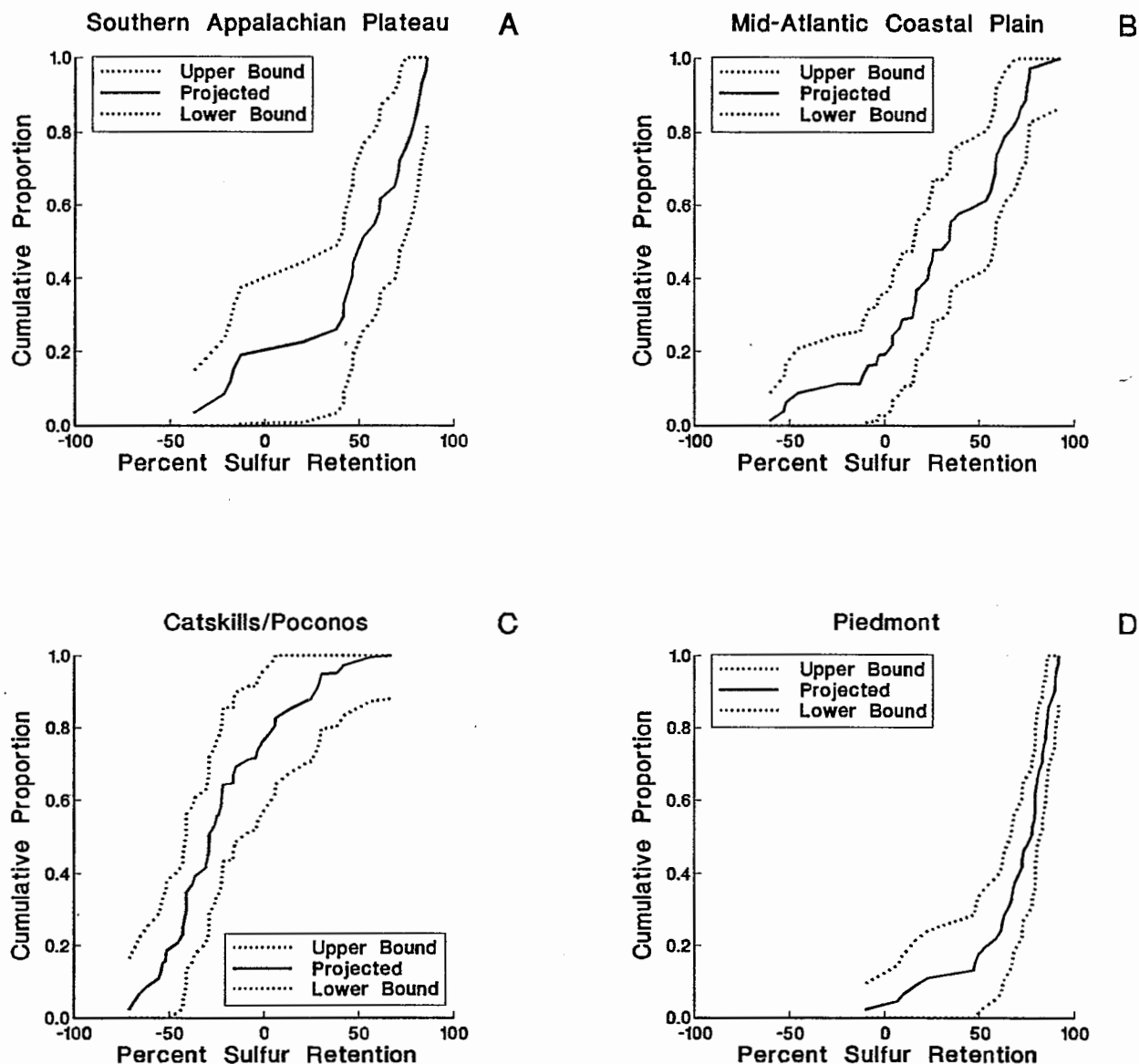
Figure 7-9. Population-weighted distributions of projected percent sulfur retention, with upper and lower bounds for 90 percent confidence intervals, for additional NSS subregions: (A) Southern Appalachian Plateau, (B) Mid-Atlantic Coastal Plain, (C) Catskills/Poconos, and (D) Piedmont.
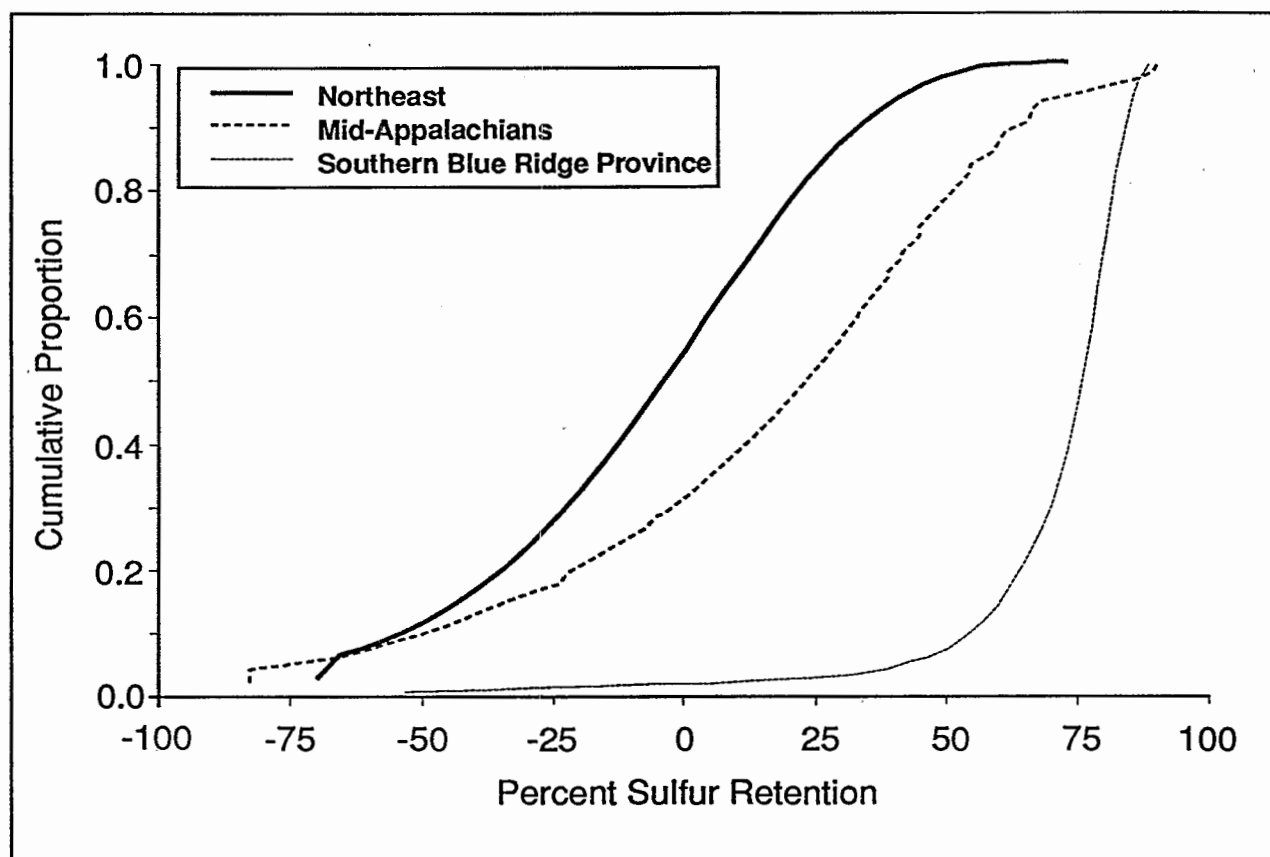
Figure 7-10. Combination regional population-weighted distributions of projected percent sulfur retention, with upper and lower bounds for 90 percent confidence intervals, for the Northeast, Mid-Appalachians, and Southern Blue Ridge Province (taken from Figure 7-7). See Plate 7-1 for delineation of the three regions.

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Plate 7-2. Regional percent sulfur retention by major land resource area (MLRA) based on target populations (ELS and NSS sites).

MAJOR LAND RESOURCE AREAS
MEDIAN % SULFUR RETENTION
AND WET SULFATE DEPOSITION

MEDIAN PERCENT SULFUR RETENTION

- < 0
- 0 - 20
- 20 - 40
- 40 - 60
- 60 - 80
- 80 - 100
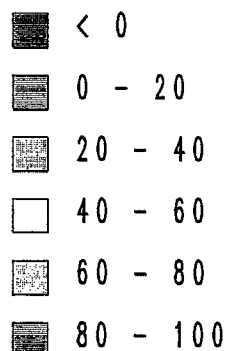
MAJOR LAND RESOURCE AREAS

R - Northeastern Forage and Forest Region

S - Northern Atlantic Slope Diversified Farming Region

N - East and Central Farming and Forest Region

P - South Atlantic and Gulf Slope Cash Crops, Forest, and Livestock Region

Average Annual Wet Sulfate Deposition (g m^{-2} yr^{-1})*
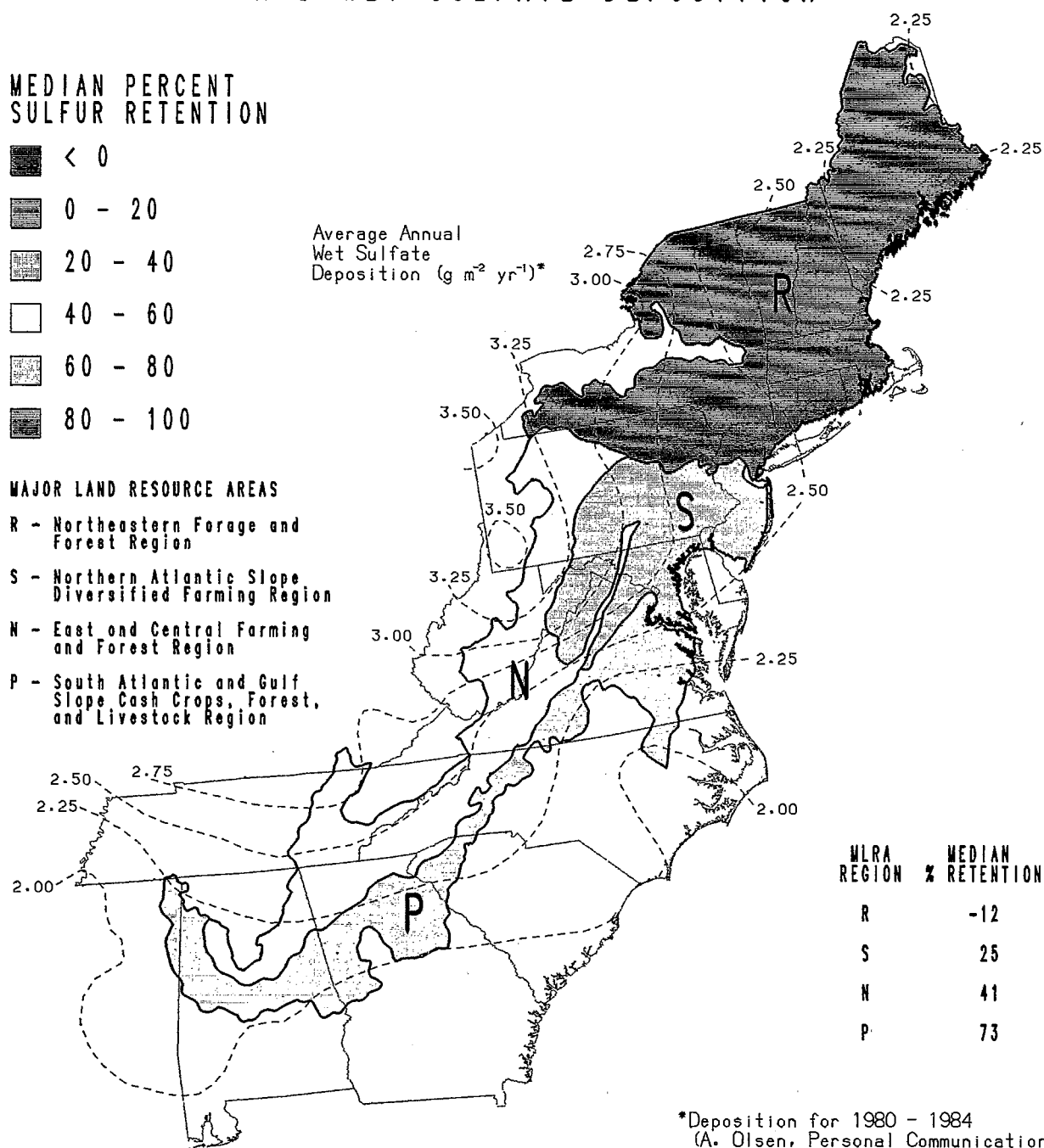
MLRA REGION	MEDIAN % RETENTION
R	-12
S	25
N	41
P	73

*Deposition for 1980 - 1984
(A. Olsen, Personal Communication)

toward a situation of lowered percent net sulfur retention and significantly elevated surface water sulfate concentrations. We feel that this change is a direct consequence of elevated atmospheric sulfur deposition. The SBRP is probably undergoing such a transition but with a lag, or "delay", in time. The dynamics of transitions in the NE and SBRP are the subject of DDRP analyses in Section 9 and 10 of this report. Analyses for the Mid-Appalachian Region will be examined in subsequent DDRP activities. Relationships among sulfur deposition, edaphic characteristics, and sulfur retention in the NE and SBRP are examined in Section 8.

SECTION 8

LEVEL I STATISTICAL ANALYSES

8.1 INTRODUCTION

The chemistry and quality of surface waters in natural settings are the result of inputs from deposition, terrestrial processes, and in-lake or in-stream processes. In this section we consider the relationships between subtending surface water chemistry and inputs from deposition and the physical and chemical attributes of the catchments. The scope of these analyses includes the DDRP sample of northeastern lakes and streams in the Southern Blue Ridge Province (SBRP). We will not, however, consider in-lake or in-stream processes explicitly in this analysis because data are not available for these processes on a regional basis.

Level I Analyses are designed primarily to address the first two DDRP objectives (see Section 2.2): (1) regional description of soil and watershed characteristics and (2) characterization of the relationships between watershed attributes and surface water chemistry. These Level I Analyses are of particular importance to the DDRP because they are designed to corroborate some of the fundamental assumptions of the DDRP on a regional basis. Previous research has generally been limited to observations from a small sample of sites. To make model-based regional projections of future surface water chemistry, it is important to determine whether or not the findings of previous studies on watershed and surface water chemistry relationships can also be observed on a regional basis. If they cannot, other approaches may need to be taken. At the same time, it is critical to know if we are overlooking important relationships that should be included in the Level II and Level III Analyses.

The principal objective of the analyses in this section is to determine which soil and watershed characteristics are most strongly related to surface water chemistry. Some of the questions we hope to answer are the following: Can surface water chemistry be linked to specific watershed and soil characteristics? Are there controls on surface water chemistry that are not yet identified? Which deposition and/or watershed factors explain most of the observed variability in surface water sulfate concentrations? Do the characteristics of the near-stream or near-lake areas have a greater influence on surface water chemistry than the watershed as a whole?

We realize that many of the results of these analyses may only provide further evidence to support relationships already known to exist. However, because of the quality, consistency, and extent of the data used in these analyses, new relationships between watershed characteristics and surface water chemistry are likely to be identified, and at the same time previously observed relationships will be reaffirmed.

8.1.1 Approach

The approach used in this section is an empirical, statistical evaluation of the relationships between selected watershed attributes gathered for the DDRP sample of watersheds and the chemistry of the surface water draining these watersheds. The principal dependent variables considered in this analysis include surface water sulfate concentrations, percent watershed sulfur retention (% S retention), surface water acid neutralizing capacity (ANC), the sum of surface water concentrations of calcium and

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magnesium (Ca plus Mg), and surface water pH. Although there are a number of other variables that could be considered, these are of primary interest to the DDRP. With the exception of % S retention, each of the dependent variables is a direct measure of surface water chemistry. Percent S retention is computed as the ratio of the difference between watershed sulfur inputs (from deposition) and surface water sulfur concentrations to sulfur inputs (see Section 7). Percent S retention is a measure of the amount of sulfur arriving via deposition that is retained by the watershed. A summary of the dependent variable data from the northeastern sample of 145 lakes and SBRP sample of 35 streams is presented in Tables 8-1 and 8-2, respectively.

The deposition data used in this section are the "long-term annual average" (LTA) deposition data. These data have annual resolution and represent atmospheric deposition as of the early to mid-1980s. The LTA deposition dataset is described more fully in Section 5.6.3.2 and summary statistics are given in Tables 8-3 and 8-4 for the 145 northeastern and 35 SBRP sample watersheds, respectively.

For this analysis we have grouped catchment attributes into six groups. The variables in these groups serve as the independent or explanatory variables. The groups are: (1) derived hydrologic variables (Section 8.3), (2) mapped bedrock geology (Section 8.4), (3) land use and vegetation (Section 8.5), (4) mapped soils (Section 8.6), (5) depth to bedrock (Section 8.7), and (6) measured chemical and physical soil properties (Section 8.9). Variables in each of the groups are thought to have significant influence on some aspect of surface water chemistry. We consider deposition with each of the attributes to identify the key relationships between the dependent variables and each attribute. We include deposition in each of these analyses because it is inextricably linked to surface water chemistry. Failure to include deposition would in all likelihood result in inclusion of surrogate deposition variables in the regression models. As a separate analysis we also consider the relationship between the deposition variables and surface water sulfate concentrations and ANC (Section 8.2).

Because none of these attribute groups alone can fully account for the observed variability in the dependent variables, we also consider them in combination. In Section 8.8 we combine the deposition and the mapped variables (groups 1-5), excluding the measured chemical and physical properties; and then in Section 8.10 we integrate deposition and all of the watershed attributes.

8.1.2 Statistical Methods

In Section 8 there are tables presenting descriptive statistics of the explanatory variables, as well as tables presenting results of regression analyses. In each case, the descriptive statistics are population-weighted, unless otherwise noted. Population weighting provides estimates of the parameters in the target population, rather than estimates for the DDRP sample only. None of the regression analyses in this section is weighted. Based on the discussion in DuMouchel and Duncan (1983) and on the similarity of the across-strata relationships among the variables, weighted regressions were deemed unnecessary.

Additionally, in the tables of regression results we have included a plus (+) or minus (-) sign to indicate the direction of significant relationships, rather than a numeric estimate of the regression parameter. These statistical analyses should be considered descriptive rather than predictive. Regression estimates have been excluded to discourage their use in predictive equations or naive computations of the relative importance of the explanatory variables.

Table 8-1. Surface Water Chemistry and Percent Sulfur Retention Summary Statistics for the Northeastern DDRP Sample of 145 Lake Watersheds

Variable[a]	Mean	Std. Dev.	Min.	Q1[b]	Median	Q3[b]	Max.
Sulfate	112.6	45.2	33.8	82.4	105.5	130.8	303.6
% S retent.	-9.7	41.3	307.7	-23.3	-6.5	14.9	61.1
ANC	126.3	113.6	-53.3	33.3	97.3	213.0	391.6
Ca+Mg	223.1	126.4	35.0	125.3	191.8	292.6	560.3
pH	6.9	0.8	4.5	6.7	7.2	7.5	8.0

[a] Units on sulfate, ANC, and Ca+Mg are μeq L^{-1}. Sulfur retention is expressed as a percent. pH is unitless.

[b] Q1 is the 25th percentile, and Q3 is the 75th percentile.

Table 8-2. Surface Water Chemistry and Percent Sulfur Retention Summary Statistics for the DDRP Sample of 35 SBRP Stream Watersheds

Variable[a]	Mean	Std. Dev.	Min.	Q1[b]	Median	Q3[b]	Max.
Sulfate	40.3	34.1	14.7	19.8	23.6	42.2	178.6
% S retent.	65.1	26.0	-60.5	60.1	74.9	79.1	88.6
ANC	286.8	447.9	16.2	98.8	126.5	171.1	1710.5
Ca+Mg	285.4	455.1	46.0	85.8	117.2	189.4	1841.6
SOBC[c]	371.0	466.2	92.8	156.0	223.4	244.7	1958.5
pH	7.1	0.41	6.4	6.9	7.0	7.2	8.4

[a] Units on sulfate, ANC, Ca+Mg, and SOBC are μeq L^{-1}. Sulfur retention is expressed as a percent. pH is unitless.

[b] Q1 is the 25th percentile, and Q3 is the 75th percentile.

[c] SOBC = Sum of base cations (Ca+Mg+Na+K)

Table 8-3. Summary Statistics for Wet and Dry Deposition on the DDRP Sample of 145 Northeastern Lake Watersheds (units are μeq m^{-2})

Variable	Mean	Std. Dev.	Min.	Q1[a]	Median	Q3[a]	Max.
SO4-WET	44900	10300	26700	35200	46100	53800	62300
SO4-DRY	22800	10100	9300	16000	20100	26100	60400
H-WET	46800	12000	24500	36000	47300	57800	67300
H-DRY	24600	16300	1600	11000	23900	32300	77400
CA+MG-WET	8200	3600	4800	5800	7300	9200	24100
CA+MG-DRY	10600	3300	3000	8500	10100	13300	19500

[a] Q1 is the 25th percentile, and Q3 is the 75th percentile.

Table 8-4. Summary Statistics for Wet and Dry Deposition on the DDRP Sample of 35 SBRP Stream Watersheds (units are μeq m^{-2})

Variable	Mean	Std. Dev.	Min.	Q1[a]	Median	Q3[a]	Max.
SO4-WET	52400	4600	40800	49800	52900	54900	69400
SO4-DRY	33000	4300	20400	30900	33400	34700	42400
H-WET	45700	3900	36300	42300	45200	48000	61100
H-DRY	23300	5400	11100	19800	22100	24800	36500
CA+MG-WET	10600	800	8500	10200	10700	11100	13200
CA+MG-DRY	18000	3900	6800	16500	19600	20200	22400

[a] Q1 is the 25th percentile, and Q3 is the 75th percentile.

The standard statistical approach used in this section begins with a stepwise regression of the explanatory variables on the surface water chemistry. This approach enables us to select explanatory variables in a way that avoids serious problems with collinearity. The stepwise regression was implemented in SAS (SAS Institute Inc., 1985, 1987), using a value of 0.15 for both the significance level for entry and the significance level for remaining in the model. Mallows' C_p statistic was used as a model selection criterion. Significance levels for the explanatory variables are given in tables in each section.

The selected model was then run as a standard linear regression to perform residual analyses, checking for outliers, leverage points, and problems with standard regression assumptions (Belsley et al., 1980). Cook's D statistic was used to identify leverage points (Madansky, 1988), i.e., observations that might exert an extreme influence on the estimates of the regression parameters. In addition, the effect on the regression parameters was assessed using the calculated DFBETAs (Belsley et al., 1980).

Plots of the studentized residuals were used to check for outliers, as well as homoscedasticity (constant variance of the residuals across the range of the dependent variable). Specific instances where log transformations of ANC or Ca plus Mg were necessary to produce homoscedasticity are discussed in Sections 8.3 and 8.7. If outliers or leverage points were found to be affecting the regression, the stepwise regression and subsequent residual analyses were performed again without the problematic observations.

Specific exceptions to this approach are discussed in the individual sections where the exceptions occur. In Section 8.5, the standard statistical approach is applied to rotations of principal components extracted from the original explanatory variables, rather than the variables themselves. In Section 8.8, Mallow's C_p statistic could not be used as the model selection criterion in the SBRP, and Akaike's information criterion was used instead.

8.2 RELATIONSHIPS BETWEEN ATMOSPHERIC DEPOSITION AND SURFACE WATER CHEMISTRY

8.2.1 Introduction

Atmospheric deposition and its effects on surface water chemistry have been extensively studied for several decades. Smith and Alexander (1986) found a strong positive correlation between sulfur emissions and surface water sulfate concentration on a regional basis. Neary and Dillon (1988) found that sulfur deposition had a positive relationship with lake sulfate and a negative relationship with ANC for a sample of 1168 Canadian lakes. Sullivan et al. (1988b) found significant correlations between median lake sulfate concentrations and wet sulfate deposition for the National Surface Water Survey (NSWS) sites. In this section we examine such relationships for the DDRP sample of watersheds using the wet and dry atmospheric deposition data for the Project (Section 5.6).

8.2.2 Approach

Surface water sulfate concentration and ANC are the two primary variables linked to the influence of sulfur deposition on surface water chemistry, and hence these two variables are the focus of this analysis. For explanatory variables, we used the LTA estimates of wet and dry deposition (discussed in Section 8.1.2). In addition to the individual wet and dry deposition estimates, we also used total sulfate

deposition and total. hydrogen deposition. In each case the total deposition value is the sum of the appropriate wet and dry deposition values. The statistical analyses are discussed in Section 8.1.2.

8.2.3 Results and Discussion

8.2.3.1 Northeast

The statistical analyses show a significant positive relationship between lake sulfate and total sulfate deposition (Table 8-5). Residual analysis of this regression revealed two strong outliers with lake sulfate levels much higher than predicted. These sites have quarry pits and will be discussed in Section 8.6.3.1. Removing these two sites with apparent internal sources of sulfur increases the amount of explained variability to 38 percent (Table 8-5).

There is a weaker relationship between ANC and deposition (Table 8-5). Wet and dry sulfate together explain only 18 percent of the variability in ANC in the northeastern lakes. Notice that the parameter estimates for wet and dry sulfate have opposite signs. In the stepwise regression used to select a model, wet sulfate deposition was selected in the first step, and then dry sulfate deposition was included as the deposition variable with the best relationship to the residuals from the first step. Residual analysis indicates that this is an adjustment in the model to correct for areas with high deposition and high ANC, such as Subregion 1B (the Poconos/Catskills, see Plate 5-1). The size of R^2 for ANC is not surprising, because ANC is strongly dependent upon mechanisms of ANC generation within watersheds (see Section 3).

8.2.3.2 Southern Blue Ridge Province

In the SBRP, sulfate deposition variables were not significantly related to stream sulfate concentration (Table 8-6). Because the stepwise regression used a 0.15 level of significance for entry into the model, this result indicates that the relationship between deposition and surface water sulfate is very weak.

The only deposition variable related to ANC was dry hydrogen deposition, but the parameter estimate is positive and is not significant at the 0.05 level (Table 8-6). The fact that the relationship is positive instead of negative suggests that dry hydrogen deposition may be acting as a surrogate for some other factor. Dry hydrogen deposition is significantly negatively correlated with runoff, so this result could represent a dilution effect due to increased runoff.

8.2.3.3 Summary

There is a significant relationship between surface water sulfate concentration and deposition in the NE, but not in the SBRP. Nonparametric statistical analysis shows that median sulfur retention is not significantly different from zero in the NE, but is significantly greater than zero in the SBRP. Rochelle and Church (1987) support this conclusion. Thus, watersheds are approximately at steady state with respect to sulfur deposition in the NE but not in the SBRP, as discussed in Section 7.3. Soils in the NE have little remaining sulfate adsorption capacity, so the lake sulfate concentrations reflect the deposition gradient (see Section 9.2). In the SBRP, the watersheds are still retaining sulfur to varying degrees.

Table 8-5. Results of Regressions Relating Surface Water Chemistry to Atmospheric Deposition in the Northeast Region (n = 145)

Water Chemistry Variable	R^2	Adjusted R^2	Deposition Variable in Model	Regression Sign	Signif.[a] Level
Sulfate	0.27	0.27	total sulfate	+	***
second model (omitting two outliers)					
	0.38	0.38	total sulfate	+	***
ANC	0.18	0.16	wet sulfate	+	***
			dry sulfate	−	***

[a] *** = significant at the 0.001 level

Table 8-6. Results of Regressions Relating Surface Water Chemistry to Atmospheric Deposition in the Southern Blue Ridge Province (n = 32)

Water Chemistry Variable	R^2	Adjusted R^2	Deposition Variable in Model	Regression Sign	Signif.[a] Level
Sulfate		none selected			
ANC	0.10	0.07	dry hydrogen deposition	+	S

[a] S = significant at 0.15 level, but not at 0.05 level

Watershed processes, e.g., adsorption by soils, are the primary controls on stream chemistry, so a clear relationship does not exist between deposition and stream concentration.

In neither region do the deposition estimates explain much of the variability in current ANC. This observation does not mean that sulfur deposition is unimportant in causing long-term surface water acidification (i.e., loss of ANC), but rather, highlights the important roles that watershed and soil factors play in determining current surface water ANC. These relationships are explored further in Section 9 and the remainder of Section 8.

8.3 DERIVED HYDROLOGIC PARAMETERS

Hydrologic processes are important factors affecting the response of surface waters to acidic deposition (Chen et al., 1984; Peters and Driscoll, 1987). The flowpaths followed by water moving through the terrestrial portion of a watershed have been hypothesized as important in controlling the chemistry of surface waters (Chen et al., 1984; Newton and April, 1982). Acidic deposition that rapidly moves through the watershed system will have limited contact with the soil, resulting in reduced potential for neutralization. In this part of the Level I Analyses, we test for relationships among mapped hydrologic, empirically modelled, and physically modelled data and selected surface water chemistry for the DDRP northeastern lake watersheds and SBRP stream watersheds. The objectives of these analyses are to identify watershed characteristics that are related to surface water chemistry and to infer the influence of potential flowpaths.

8.3.1 Soil Contact (Darcy's Law)

8.3.1.1 Introduction

An estimate of the annual flow rate of water moving through the soil and an index of soil contact time were calculated for each drainage lake watershed in the DDRP sample (n=136). Details of the calculation are presented in Section 5.7. Briefly, the estimate of soil-water flow rate and the index of soil contact are calculated using Darcy's Law.

$$Q = KAS$$

where: Q = lateral soil flow
K = estimate of saturated hydraulic conductivity
A = cross sectional area of flow
S = hydraulic gradient

The index of soil contact is calculated by dividing Q by the average annual runoff (R). Figure 5-27 outlines the steps involved in the Darcy's Law calculation. In this application, we have attempted to use the Darcy's Law approach to model flow and index of contact time at watershed scales. The resulting estimates of flow and index of contact are essentially estimates of the theoretical maximum potential for runoff to contact soil in a watershed.

Table 8-7 and Figures 8-1 and 8-2 summarize the results of the flow rate and index of soil contact calculations. The estimated flow rate and index of contact were less than 0.87 m yr^{-1} and 1.10 m yr^{-1}, respectively, for approximately 90 percent of the study watersheds. Of the remaining 14 watersheds (approximately 10 percent), 11 are located in Subregion 1D (see Plate 5-1). This region encompasses

Table 8-7. **Estimated Population-Weighted Summary Statistics on the Darcy's Law Estimates of Flow Rate and the Index of Flow Relative to Runoff**

Variable	Mean	Median	Std. Dev.	Min.	Max.
Rate (m yr^{-1})	0.45	0.09	2.34	0.002	18.2
Index (yr)	0.76	0.14	4.32	0.003	35.8
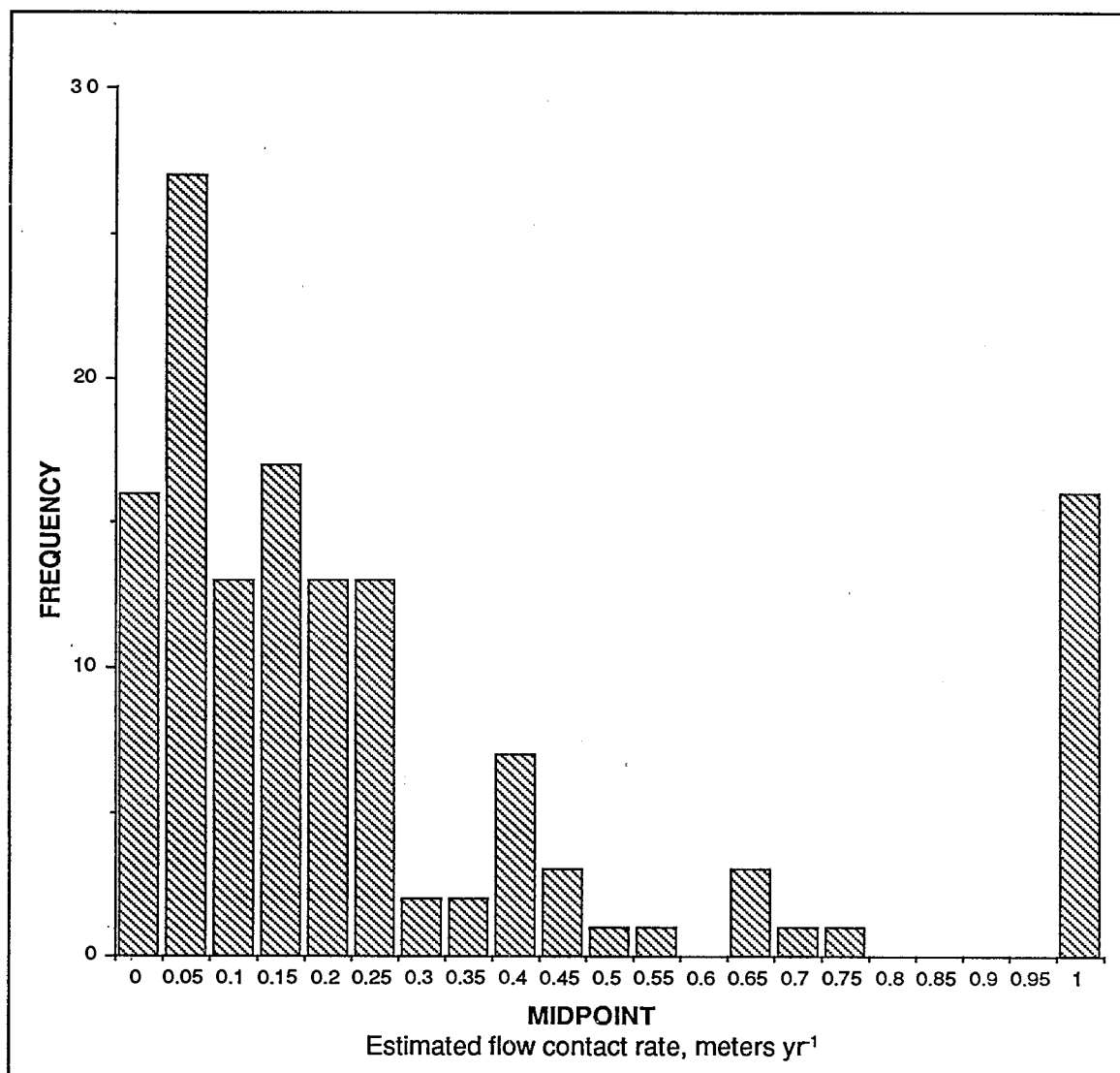
Figure 8-1. Distribution of estimated contact rate using Darcy's Law calculation.
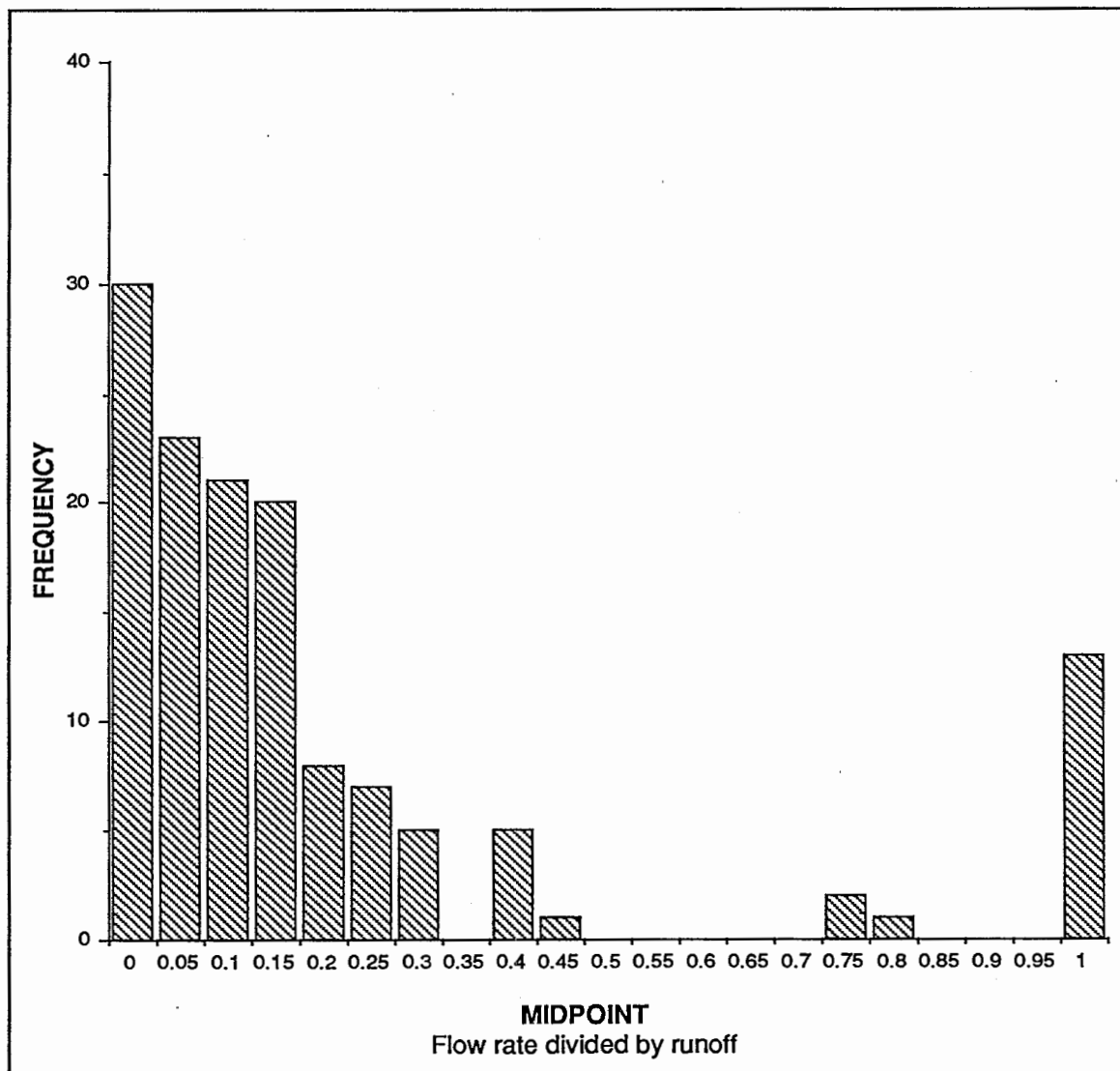
Figure 8-2. Distribution of index of contact (yr) using Darcy's Law calculation.

southern New England and is comprised mainly of Massachusetts, Connecticut, and Rhode Island. These watersheds have a high proportion of sandy soils that probably resulted in the high flow rate and index estimates. These sites also have low ANC concentrations, however, with 8 of the 11 1D watersheds having ANC values less than 50 μeq L^{-1}. The resulting chemistry is probably a function of the high deposition and the limited neutralizing capacity of the sandy soils found on many of the watersheds.

For the DDRP Level I Analyses, we have tested for correlations between the estimated flow rate and index of contact time and ANC, sulfate, sulfur retention, pH and Ca plus Mg on a regional and subregional level. We have excluded eight watersheds with large rate and index values (discussed above) from the general analysis because these sites represent a special situation in the NE and resulted in large outlier estimates.

8.3.1.2 Results and Discussion

Examining the DDRP northeastern region, we found very little correlation between the calculated estimates of the Darcy's Law flow rate and index of soil contact time and sulfate, percent sulfur retention, Ca plus Mg, ANC, or pH (R^2 ranging from 0.003 to 0.03). We also looked at correlations between the Darcy's Law calculations and the surface water chemistry variables on a subregional level. The subregions used were defined as part of the sampling strategy for the NSWS (see Section 5.7). We determined that there was very little correlation at the subregional level. Figures 8-3 and 8-4 show bivariate scatter plots of the rate versus ANC and the index versus ANC. Bivariate plots of the rate and index versus the other surface water chemistry parameters are similar. Figures 8-3 and 8-4 indicate a large amount of scatter in the chemistry relative to the rate and index values, particularly at the low values where most of the data tend to be concentrated.

Peters and Murdoch (1985) observed a strong relationship between the Darcy's Law index of hydrologic contact and surface water chemistry in the two systems (Woods and Panther Lakes) they studied as part of the Integrated Lake/Watershed Acidification Study (ILWAS). Our results differed significantly. One difference between the DDRP study and ILWAS is the heterogeneity of the systems studied. ILWAS involved two watersheds that had similar physical characteristics such as basin area, relief, lake area, percent forest cover, lake size, and lake volume (Murdoch et al., 1984). The major difference between the two watersheds was depth to bedrock with the acidic system having very shallow soils (low index contact; Woods Lake) and the circumneutral system (high index contact; Panther Lake) having very deep soils. As indicated in Section 5.7, soil depth is a key factor in the Darcy's Law calculation. These two watersheds probably represent the possible extremes in soil depth. There are significant variations in many of the above-mentioned characteristics among the regional DDRP watersheds. As an example, the DDRP lakes range in size from approximately 40 to 3000 ha. Another factor that has been identified as having significant effects on surface water chemistry is sulfur deposition (NAS, 1984). Wampler and Olsen (1984) found that wet sulfur deposition varied in the NE with a general southwestern to northeastern decreasing gradient. The DDRP study watersheds are located across the NE, and thus are subject to a high degree of variability in sulfur loading. The ILWAS watersheds, however, are only a few kilometers apart and receive very similar sulfur deposition (Murdoch et al., 1984).
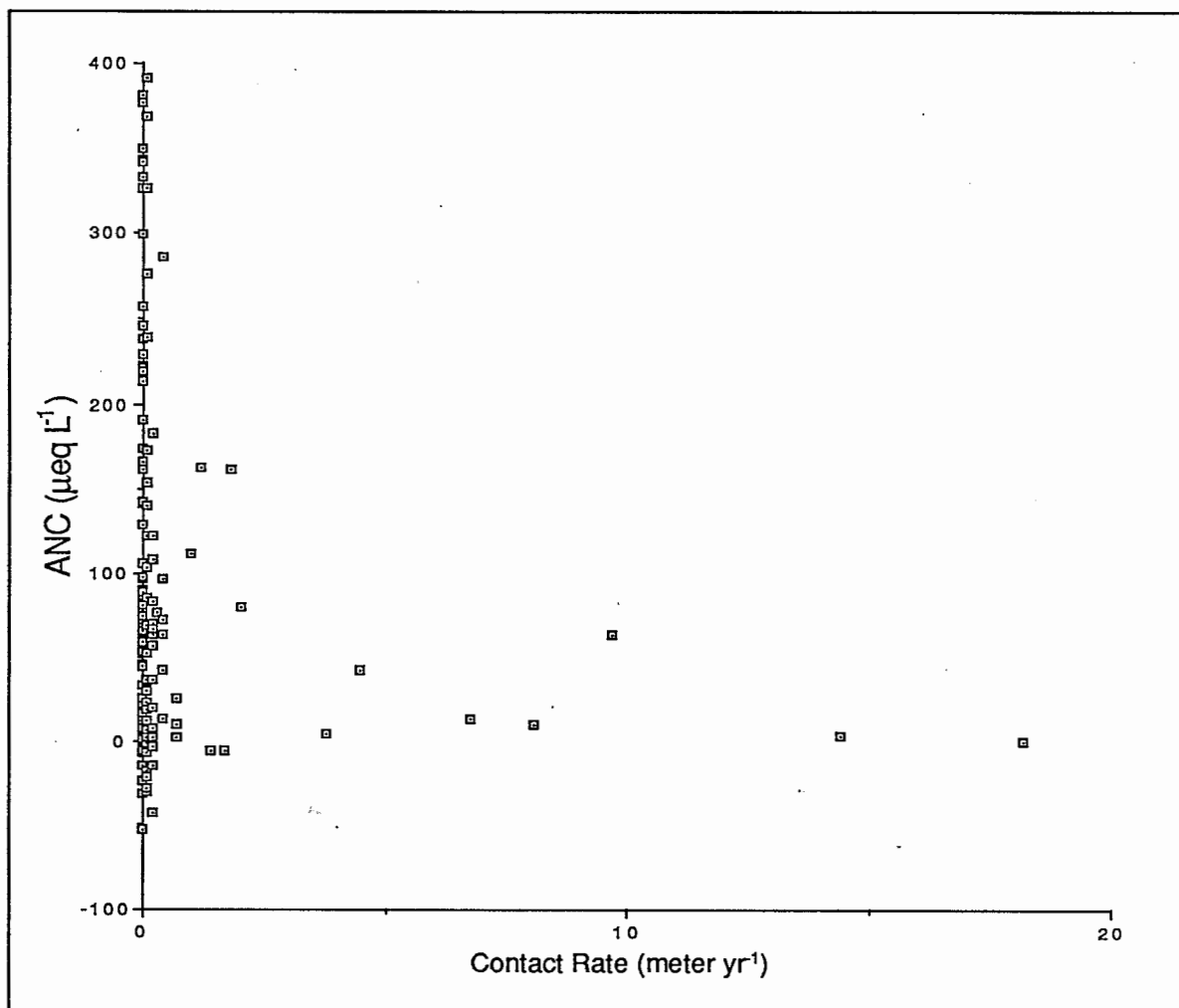
Figure 8-3. Scatter plot of ANC versus contact rate calculated using Darcy's Law.
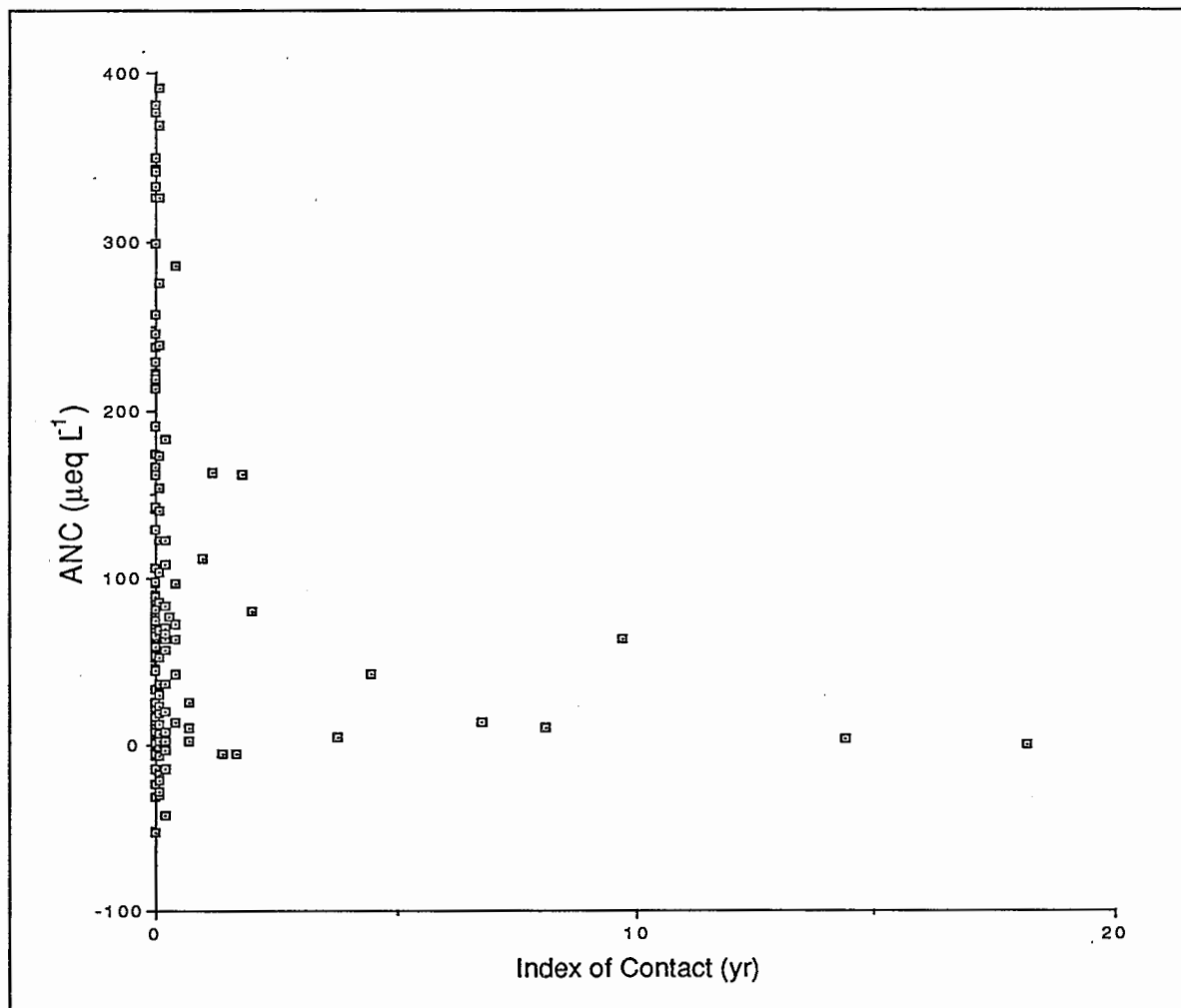
Figure 8-4. Scatter plot of ANC versus index of soil contact calculated using Darcy's Law.

A second factor affecting the Darcy's Law result is the precision of the data available for the DDRP study watersheds. The parameters used in calculating the lateral soil flow (Q) were estimated as watershed averages. For all three of the major parameters, hydraulic conductivity (K), soil depth (D, used in estimating cross-sectional area), and slope (S), an area-weighted average was calculated based on mapping data provided by the DDRP Soil Survey. By calculating areal averages some smoothing of the data occurred, which might not have accurately reflected the values of these variables where the main hydrologic activity in the watersheds occurs. Identifying which soils and depth-to-bedrock classes are most important in affecting the basin hydrology is difficult without extensive field measurements.

8.3.2 Geomorphic/Hydrologic Parameters

8.3.2.1 Introduction

A significant amount of work has attempted to relate hydrologic characteristics with mapped watershed geomorphic parameters for forested watersheds (Hewlett and Hibbert, 1967; Dingman, 1981; Carlston, 1963; Lull and Sopper, 1966; Vorst and Bell, 1977; Woodruff and Hewlett, 1970). In general, most previously reported research is at the event level or covers short time periods (i.e., days or weeks). In this study we are using the NSWS index chemistry value (see Section 5.3, Linthurst et al., 1986a; Messer et al., 1986a; Landers et al., 1988); therefore, hydrologic response should be viewed as an annual representation. We assume that if a system can be interpreted as a quick response system based on geomorphic/hydrologic information, then the system is, on the average annual basis, a quick response system. As discussed in Section 8.3, quick response systems should have less soil-runoff interaction, resulting in reduced potential for neutralization of acidic inputs.

In this part of Level I hydrologic analyses, we test for apparent relationships among mapped watershed hydrologic and geomorphic parameters that might affect (or be related to) hydrologic response and selected surface water chemistry variables for 144 lake watersheds in the NE and 32 stream watersheds in the SBRP. Three watersheds with ANC > 1000 μeq L^{-1} were not included in SBRP analyses. We are testing for correlations between chemistry and watershed factors on a large regional scale in the NE and SBRP (see Section 8.1.2 for discussion of statistics). Tables 8-8 (NE) and 8-9 (SBRP) contain summary statistics of the geomorphic/hydrologic parameters used for this analysis. Tables 8-10 (NE) and 8-11 (SBRP) contain variable names, descriptions, and units. Detailed information on database development is included in Section 5.7 (also, see Rochelle et al., in press-a).

Because we were specifically interested in the relationships between hydrologic/geomorphic factors and surface water chemistry, we chose not to include other independent variables (e.g., soils, deposition) that could influence or control surface water chemistry. In particular, for the NE, deposition explains a large proportion of variability in some of the surface water chemistry (see Section 8.2). In some cases the removal of deposition as a variable might have resulted in some variables acting as deposition surrogates. We will discuss those cases as appropriate.

We have, however, also performed analyses on northeastern watersheds stratified by sulfur deposition (wet plus dry). In these analyses, we used a simple stratification procedure based on the distribution of sulfur deposition for our study sites. We defined four classes based on the 25th and 75th

Table 8-8. Estimated Population-Weighted Summary Statistics for Northeastern Geomorphic/Hydrologic Parameters

Variable[a]	Mean	Median	Minimum Value	Maximum Value
MIN_EL	319.0	327.7	1.5	791.0
RT0	0.7	0.4	0.03	5.7
VOL	2.1	0.5	0.04	57.0
RUNOFF	64.0	64.0	49.1	77.6
WS_LA	19.8	11.5	2.6	110.1
A_W	5.4	3.4	0.15	30.2
A_L	0.4	0.2	0.02	4.6
A_H	0.5	0.3	0.02	6.4
H2O_WS	0.1	0.09	0.01	0.4
B_LEN	2.7	2.5	0.3	9.5
B_WIDTH	1.6	1.3	0.26	5.4
MAX_REL	134.3	103.7	10.7	604.7
REL_RAT	0.05	0.05	0.003	0.2
B_PERIM	10.2	9.0	1.7	31.4
PERIMRAT	3.6	2.9	0.76	9.9
TOTSTRM	3.1	0.9	0.0	32.8
PERIN	2.3	0.3	0.0	29.3
INT	0.8	0.0	0.0	11.8
STRMORDER	2.9	3.0	0.0	4.0
DDENSITY	0.6	0.4	0.0	3.2
PER_DD	0.4	0.1	0.0	1.9
B_SHAPE	1.9	1.8	0.2	5.1
ELONG	0.9	0.9	0.5	2.4
ROTUND	0.5	0.4	0.06	1.3
COMPACT	1.4	1.3	1.1	3.3
M_PATH7	765.2	489.1	48.3	3618.6
WM_PATH	1701.6	1433.6	59.5	8125.4

[a] See Table 5-37 for variable names, variable descriptions, and units.

Table 8-9. Estimated Population-Weighted Summary Statistics for Southern Blue Ridge Province Hydrologic/Geomorphic Parameters

Variable[a]	Mean	Median	Minimum Value	Maximum Value
B_LEN	4.8	4.5	1.8	10.8
B_PERIM	13.9	12.5	4.9	31.5
B_SHAPE	3.0	2.9	1.9	5.2
B_WIDTH	1.7	1.4	0.8	3.5
COMPACT	1.4	1.4	1.1	1.9
TOT_DD	2.6	2.3	0.8	5.3
ELONG	0.7	0.7	0.5	0.8
AUG_EL	831.5	716.3	448.8	1409.7
M_PATH	2398.3	1951.4	888.4	5611.4
MAX_REL	539.1	538.0	132.9	1368.6
REL_RAT	0.1	0.1	0.02	0.2
ROTUND	0.7	0.7	0.5	1.3
RUNOFF	82.0	86.3	38.1	114.3
TOTSTRM	11.3	7.7	0.0	41.4
STRMORDER	2.04	2.0	0.0	4.0
WM_PATH	2548.0	2091.8	888.4	5862.7
WS_AREA	9.6	7.3	1.5	30.0

[a] See Table 5-38 for variable names, variable descriptions, and units.

Table 8-10. Mapped and Calculated Geomorphic Parameters Collected for the Northeastern Study Sites (Same as Table 5-37)

Parameter	Description	Units
Measured		
B_CENT	Drainage basin centroid expressed as an X,Y coordinate	
B_LEN	Length of drainage basin; air-line distance from basin outlet to farthest upper point in basin	km
B_PERIM	The length of the line which defines the surface divide of the drainage basin	km
A_H	Area of all open water bodies in drainage basin	km^2
INT	Total length of intermittent streams as defined from USGS topographic maps of aerial photos	km
A_L	Area of the primary lake	km^2
L_CENT	Primary lake centroid expressed as X,Y coordinates	
L_PERIM	Perimeter of primary basin lake	km
MAX_EL	Elevation at approx. highest point	m
MIN_EL	Elevation of primary lake	m
PERIN	Total perennial stream length as defined from USGS topographic maps and aerial photographs	km
SUB_BAS(n)	Area of each subcatchment in the drainage basin	km^2
STRMORDER	Maximum stream order (Horton) of streams in the watershed (aerial photos used to aid in reducing coding problems between 7.5- and 15-minute maps)	

Table 8-10. (Continued)

Parameter	Description	Units
TOTSTRM	Total stream length; combination of perennial and intermittent	km
A_W	Total watershed area	km^2
Calculated		
B_SHAPE	Basin shape ratio; B_LEN^2/WS_AREA	
B_WIDTH	Average basin width; WS_AREA/B_LEN	km
COMPACT	Compactness ratio; ratio of perimeter of basin to the perimeter of a circle with equal area; (PERIM)/(2 × (π × A_W)$^{.5}$)	
DDENSITY	Drainage density; TOTSTRM/WS_AREA	
ELONG	Elongation ratio; (4 × WS_AREA)/L_BEN	
H20_WS	Ratio of open water bodies area to total watershed area H2O_AREA/WS_AREA	
MAX_REL	Maximum relief; MAX_ELEV - MIN_ELEV	m
M_PATH	Estimate of mean flow path	m
PER_DD	Drainage density calculated from perennial streams only; PERIN/WS_AREA	
PERIMRAT	Ratio of the lake perimeter to the watershed perimeter; Lake Perimeter/B_PERIM	
REL_RAT	Relief ratio; (MAX_ELEV-MIN_ELEV)/B_LEN	

Table 8-10. (Continued)

Parameter	Description	Units
ROTUND	Rotundity ratio; $(B\_LEN)^2/(4 \times WS\_AREA)$	
WM_PATH	Estimate of weighted mean flow path	m
WS_LA	Ratio of the total watershed area to the area of the primary lake	
Additional		
RT_a	Lake retention time	yr
V_a	Volume of the primary lake	$10^6 m^3$
R	Average annual runoff; interpolated to each site from Krug et al. (in press) runoff map	cm

Table 8-11. Mapped and Calculated Geomorphic Parameters Collected for the SBRP Study Sites.

Parameter	Description	Units
Measured		
B_CENT	Drainage basin centroid expressed as an X,Y coordinate	
B_LEN	Length of drainage basin; air-line distance from basin outlet to farthest upper point in basin	km
B_PERIM	The length of the line which defines the surface divide of the drainage basin	km
MAX_EL	Elevation at approx. highest point	m
MIN_EL	Elevation at watershed outlet	m
SUB_BAS(n)	Area of each subcatchment in the drainage basin	km^2
STRMORDER	Maximum stream order (Horton) of streams in the watershed (aerial photos used to aid in reducing coding problems between 7.5- and 15-minute maps)	
TOTSTRM	Total stream length; perennial	km
WS_AREA	Total watershed area	km^2
Calculated		
AVG_EL	Average elevation; (MAX_ELEV + MIN_ELEV)/2	m
B_SHAPE	Basin shape ratio; B_LEN ^{2}/WS_AREA	
B_WIDTH	Average basin width; WS_AREA/B_LEN	km

Table 8-11 (Continued)

Parameter	Description	Units
COMPACT	Compactness ratio; ratio of perimeter of basin to the perimeter of a circle with equal area; $(PERIM)/(2 \times (\pi \times A_W)^{.5})$	
DDENSITY	Drainage density; TOTSTRM/WS_AREA	
ELONG	Elongation ratio; $(4 \times WS\_AREA)/B\_LEN$	
MAX_REL	Maximum relief; MAX_ELEV - MIN_ELEV	m
M_PATH	Estimate of mean flow path	m
REL_RAT	Relief ratio; $(MAX\_ELEV-MIN\_ELEV)/B\_LEN$	
ROTUND	Rotundity ratio; $(B\_LEN)^2/(4 \times WS\_AREA)$	
TOT_DD	Estimated drainage density based on crenulations identified on topographic map	
WM_PATH	Estimate of weighted mean flow path	m
Additional		
R	Average annual runoff; interpolated to each site from Krug et al. (in press) runoff map	cm

percentiles and the median value of the deposition data (Table 8-12). We did not analyze sulfur retention based on the stratified watersheds because deposition is a component of retention.

8.3.2.2 Results and Discussion

8.3.2.2.1 Sulfate and Sulfur Retention -

8.3.2.2.1.1 Northeast --

We found negative relationships between surface water sulfate concentration and stream order, runoff, and maximum relief for the NE (Table 8-13). Northeastern watersheds that had low order streams (first and second order) were associated with high sulfate concentrations. Watersheds dominated by lower order streams tend to be headwater systems that are more likely to be dominated by quickflow runoff. Quickflow results in less potential for soil-runoff interaction and subsequent neutralization of acidic inputs. Also, we found that the watersheds with lower order streams tended to be located at the higher elevations. These systems typically receive higher sulfur deposition due to depositional patterns in the NE, particularly Adirondack watersheds. The combination of high sulfur deposition and reduced potential for soil interaction due to increased percent quick runoff leads to higher surface water sulfate concentrations. We found no significant relationships for the entire NE between sulfur retention and the geomorphic/hydrologic parameters.

8.3.2.2.1.2 Northeast - stratified by sulfur retention --

The results of statistical analyses between the hydrologic/geomorphic parameters and in-lake sulfate are presented in Table 8-14. Although some individual parameters were significantly related to sulfate for deposition classes 1 and 4, these were not consistent. None of the parameters appeared as a significant predictor in more than one of the deposition classes.

8.3.2.2.1.3 Southern Blue Ridge Province --

We identified no significant correlations between sulfate or sulfur retention and the hydrologic/geomorphic parameters for the SBRP (Table 8-15). A probable explanation for the lack of significant correlations is the relative homogeneity of the SBRP watersheds in terms of both sulfur chemistry data and the hydrologic/geomorphic parameter values.

8.3.2.2.1.4 Regional comparison --

In the NE, we identified stream order, runoff, and maximum relief as significant predictors for surface water sulfate concentration. These findings suggest that headwater streams are associated with high surface water sulfate concentrations due to a higher percentage of quick runoff. A higher percentage of quickflow would result in less soil interaction and, consequently, higher surface water sulfate. We found no significant relationships between the hydrologic/geomorphic parameters and sulfate concentration or sulfur retention in the SBRP.

Table 8-12. Stratification Based on Sulfur Deposition (Wet and Dry)

Class	Deposition ($g\ m^{-2}$)
1	<2.46
2	$2.46 \leq 3.33$
3	$3.33 \leq 3.74$
4	>3.74

Table 8-13. Results of Stepwise Regression Relating Surface Water Chemistry versus Geomorphic/Hydrologic Parameters for the Entire NE[a]

	ANC	Ca + Mg	SO_4^{2-}	pH
B_LEN				
COMPACT				
DDENSITY	+			+
ELEV				
H20_WS				
MAXREL		−	+	
PERIN	−			
RT				
RUNOFF	−	−	−	
STRMORDER	+		−	+
Adjusted R^2	0.15[b]	0.11	0.29	0.20

[a] ANC, Ca + Mg, and pH: n = 141
     SO_4^{2-}: n = 142

[b] Significant at the 0.15 level

Table 8-14. Stepwise Regression Equations for Surface Water Chemistry and Hydrologic/Geomorphic Parameters Based on Sulfur Deposition Stratification

Class = 1	ANC	pH	Ca + Mg	SO_4^{2-}
CQMPACT		+		
DDENSITY	+	+	+	
H2O WS				+
MAXREL				+
PER DD	-		-	
PERIMRAT	+			
RT			-	-
RUNOFF	-	-	-	-
Adjusted R^2	0.49	0.36	0.54	0.31

Class = 2	ANC	pH	Ca + Mg	SO_4^{2-}
B PERIM	+			
B WIDTH	+			
COMPACT			+	
MAXREL	+		+	
STRORDER			-	
WSAREA	-			
Adjusted R^2	0.39		0.27	

Class = 3	ANC	pH	Ca + Mg	SO_4^{2-}
ELEV		-	-	
DDENSITY	+			
H20 WS	-		-	
MEANPATH		-		
PER DD	-			
VOL⁻	+		+	
WSAREA		+	+	
Adjusted R^2	0.68	0.31	0.73	

Class = 4	ANC	pH	Ca + Mg	SO_4^{2-}
COMPACT	-			
ELEV	-			-
ELONG	-			
REL RAT				-
RUNOFF	-			-
Adjusted R^2	0.36			0.36

Table 8-15. Results of Stepwise Regression Relating Surface Water Chemistry and Geomorphic/Hydrologic Parameters for the SBRP[a]

	ANC Log	(Ca + Mg)	SO_4^{2-}	pH	Sulfur Retention
TOT_DD	+				
REL_RAT	-				
RUNOFF	-	-		-	
Adjusted R^2	0.39	0.15	b	0.16	b

[a] ANC, Ca + Mg, and pH: n = 32
SO_4^{2-} and sulfur retention: n = 31

[b] No variables met the 0.15 significance level for entry into the model.

8.3.2.2.2 pH, ANC, and (Ca plus Mg) -

8.3.2.2.2.1 Northeast --

Runoff was the only geomorphic/hydrologic parameter that was related to Ca plus Mg. The relationship is negative with an increase in runoff resulting in a decrease in Ca plus Mg (R^2 = 0.11). This relationship is probably due to a dilution effect.

As was the case with Ca plus Mg, we found significant relationships between ANC and the geomorphic/hydrologic parameters (Table 8-13, R^2 = 0.15). We found that drainage density and stream order were positively related with ANC and runoff was negatively related to ANC. As discussed above, stream order is probably reflective of the relative position of the watershed (i.e., headwater), with higher stream order systems tending to have smaller percentage contributions of quick runoff to total runoff. The negative relationship with runoff might be due to dilution effects.

Drainage density, maximum relief, and stream order were positively related to pH (R^2 = 0.20). The positive relationships between pH and stream order and pH and drainage density are probably functions of relative proportion of quickflow runoff associated with the high stream order systems. As discussed above, the low stream order systems tended to be located at high elevations and have a greater potential for quickflow runoff and high sulfur deposition. The high stream order systems we studied in the northeastern typically are low elevation systems with gentler slopes and larger watershed areas. These systems probably have a greater potential for soil interaction and subsequent neutralization of acidic inputs. Drainage density was relatively low for most of the northeastern watersheds since these watersheds are primarily lake watersheds. The higher drainage densities are generally found in the lower elevation areas where stream development is more advanced.

8.3.2.2.2.2 - Northeast - stratified by sulfate deposition class --

The results of statistical analyses between the hydrologic/geomorphic parameters, stratified by sulfate deposition class, and pH, ANC, and Ca plus Mg were presented in Table 8-14. No consistent relationships were found between the hydrologic/geomorphic parameters and pH or Ca plus Mg. None of the parameters appeared as a significant predictor in more than one of the deposition classes.

We found a significant positive correlation between ANC and drainage density in deposition classes 1 and 3. A significant negative correlation between ANC and runoff was found in deposition classes 1 and 4. No other consistent relationships were found. These findings are consistent with those for the entire NE and were discussed more fully in Section 8.3.2.2.2.1.

8.3.2.2.2.3 Southern Blue Ridge Province --

The results of statistical analyses between the hydrologic/geomorphic parameters and pH, ANC, and Ca plus Mg were presented in Table 8-15. A log-transformation of Ca plus Mg was used in this analysis to make the variance of the residuals constant. We found no significant relationships between pH and the hydrologic/geomorphic parameters in the SBRP.

We found relationships between ANC and the hydrologic/geomorphic parameters in the SBRP. ANC was negatively correlated with runoff and relief ratio and positively correlated with drainage density. Drainage density was based on crenulations identified on a topographic map. The negative correlation between ANC and runoff suggests that higher runoff results in lower ANC streams. This relationship probably reflects a dilution effect. Relief ratio was negatively correlated with ANC. High relief ratio watersheds tend to be headwater streams with a higher percentage of quick runoff, which would lead to less interaction of water with the soil matrix and, hence, lower ANC. The positive relationship between ANC and drainage density may also be a function of relative position of the watershed within the region.

We also found limited relationships between Ca plus Mg and the hydrologic/geomorphic parameters. As with ANC, Ca plus Mg was negatively correlated with runoff. As discussed previously, the negative correlation between Ca plus Mg and runoff is probably due to a dilution effect.

8.3.2.2.2.4 Regional comparisons --

We found similar hydrologic/geomorphic predictors for ANC and Ca plus Mg in the NE and SBRP. Although we found significant predictors for pH in the NE, no significant correlations were found in the SBRP. In the NE, stream order and drainage density were positively related to ANC. Lower stream order watersheds are primarily headwater systems that have a high percentage of quickflow and, therefore, would tend to have lower ANC. Similarly, drainage density is a measure of position within the watershed. Streams with lower drainage densities tended to be headwater streams while lower elevation watersheds tended to have a more developed drainage network. In the SBRP, ANC was also positively correlated with drainage density. Additionally, relief ratio was negatively correlated with ANC. Similar to drainage density and stream order in the NE, relief ratio is probably a function of the relative position of the watershed. Watersheds with high relief ratios tend to be headwater systems and, therefore, have lower ANC due to increased quickflow.

Runoff is a second factor that appeared to influence ANC and Ca plus Mg in both the NE and SBRP. Significant negative relationships were found for both ANC and Ca plus Mg in both regions. These relationships are probably due to the increased dilution of stream and lake chemistry in areas where runoff is high.

Other significant predictors were found in the NE but not in the SBRP. These predictors included basin perimeter for ANC, and drainage density, maximum relief, and stream order for pH. The identification of a larger number of predictors in the NE may be a function of either the larger sample size (141 in the NE vs. 32 in the SBRP) or the relative homogeneity of the SBRP.

8.3.3 TOPMODEL Parameters

The hydrologic model TOPMODEL, which is based on the variable source area concept, was used to characterize flow path partitioning of the DDRP watersheds. TOPMODEL was chosen because the model uses readily available topographic and soils information, and it predicts internal states that can be used to partition streamflow. A more complete description of TOPMODEL is given in Section 5.7.2.1.

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8.3.3.1 Introduction

TOPMODEL characterizes flowpath partitioning for each watershed by characterizing the spatially aggregated distribution function of ln(a/KbTanB) in the NE and ln(a/TanB) in the SBRP where "a" is the area drained per unit contour, "TanB" is the local slope, "K" is the hydraulic conductivity, and "b" is depth to bedrock (Beven and Kirkby, 1979; Beven, 1986; Wolock et al., 1989). Details of the calculations are presented in Section 5.7.2.1.1.3. Values of ln(a/KbTanB) and ln(a/TanB) have been correlated with the likelihood of producing surface runoff. Surface runoff is defined as saturation-excess ("return") flow rather than infiltration-excess ("Hortonian") flow. High values of ln(a/KbTanB) or ln(a/TanB) suggest areas within a watershed that are likely to produce surface runoff. These areas would typically be characterized as topographically convergent, low transmissivity areas. Conversely, low ln(a/KbTanB) or ln(a/TanB) values represent areas that have low potential for surface runoff generation (e.g., well-drained soils draining little upslope area). The mean of ln(a/KbTanB) or ln(a/TanB) is the critical parameter for characterizing an individual watershed (Wolock et al., 1989). In the NE, four watersheds were deleted from the analysis due to a lack of relief as portrayed in the 1:250,000-scale digital elevation models (DEM), resulting in a total of 141 study watersheds. In the SBRP, we eliminated three watersheds with ANC > 1000 μeq L^{-1} from the analyses resulting in a total of 32 watersheds.

For the NE, values of ln(a/KbTanB) are summarized in Table 8-16. Mean ln(a/KbTanB) values ranged from -3.38 to 3.40 with a regional mean of 1.03. Subregional means were highest in subregion 1B (2.40), followed by Subregions 1E (1.48), 1A (0.91), 1C (0.77), and 1D (-0.67). For the SBRP, values of ln(a/TanB) are summarized in Table 8-17. Mean ln(a/TanB) values ranged from 7.34 to 8.89 with a regional mean of 7.81. Within Level I Analyses, we have tested for correlations between mean ln(a/KbTanB) or ln(a/TanB) values and ANC, sulfate, sulfur retention, pH, and Ca plus Mg on a regional scale in the NE and in the SBRP. We used Spearman's correlation coefficient rather than Pearson's, as the scatter plots did not suggest a bivariate normal distribution. Spearman's correlation coefficient does not require normality.

8.3.3.2 Results and Discussion

8.3.3.2.1 Northeast

Statistical correlations between ln(a/KbTanB) and surface water chemistry are given in Table 8-18. We found no significant correlations between ln(a/KbTanB) and sulfur retention or sulfate concentration. Noisy but significant positive relationships were found between values of ln(a/KbTanB) and ANC (r = 0.28), Ca plus Mg (r = 0.31), and pH (r = 0.27). Scatter plots for these relationships are shown in Figures 8-5, 8-6, and 8-7, respectively. The relationship between ln(a/KbTanB) and pH is particularly noisy (Figure 8-7).

The positive correlations between values of ln(a/KbTanB) and ANC and Ca plus Mg are difficult to explain. High watershed mean values of ln(a/KbTanB) suggest that a larger percentage of storm flow originates from quickflow mechanisms (e.g., return flow), whereas watersheds with low values of ln(a/KbTanB) are dominated by subsurface storm flow. A larger proportion of quickflow should result in less overall contact of water with the soil matrix and, hence, lower ANC and Ca plus Mg.

Table 8-16. Population-Weighted Summary Statistics for ln(a/KbTanB) for the Northeast

Region	Mean	Std. Dev.	Min.	Max.
Northeast	1.03	1.08	-3.38	3.40
1A	0.91	0.86	-0.73	3.04
1B	2.40	2.42	1.34	3.40
1C	0.77	0.75	-1.20	1.71
1D	-0.67	-0.20	-3.38	1.33
1E	1.48	1.63	-0.59	3.18

Table 8-17. Population-Weighted Summary Statistics for ln(a/TanB) for the Southern Blue Ridge Province

Region	Mean	Median	Min.	Max.
SBRP	7.81	7.74	7.34	8.89

Table 8-18.   Spearman's Correlation Coefficients Between In(a/KbTanB) and Surface Water Chemistry

Region	n	ANC	SO_4	S Ret.	pH	Ca plus Mg
NE	141	0.28^a	0.05	0.28	0.27^a	0.31^a

[a] Significant at $p = 0.10$

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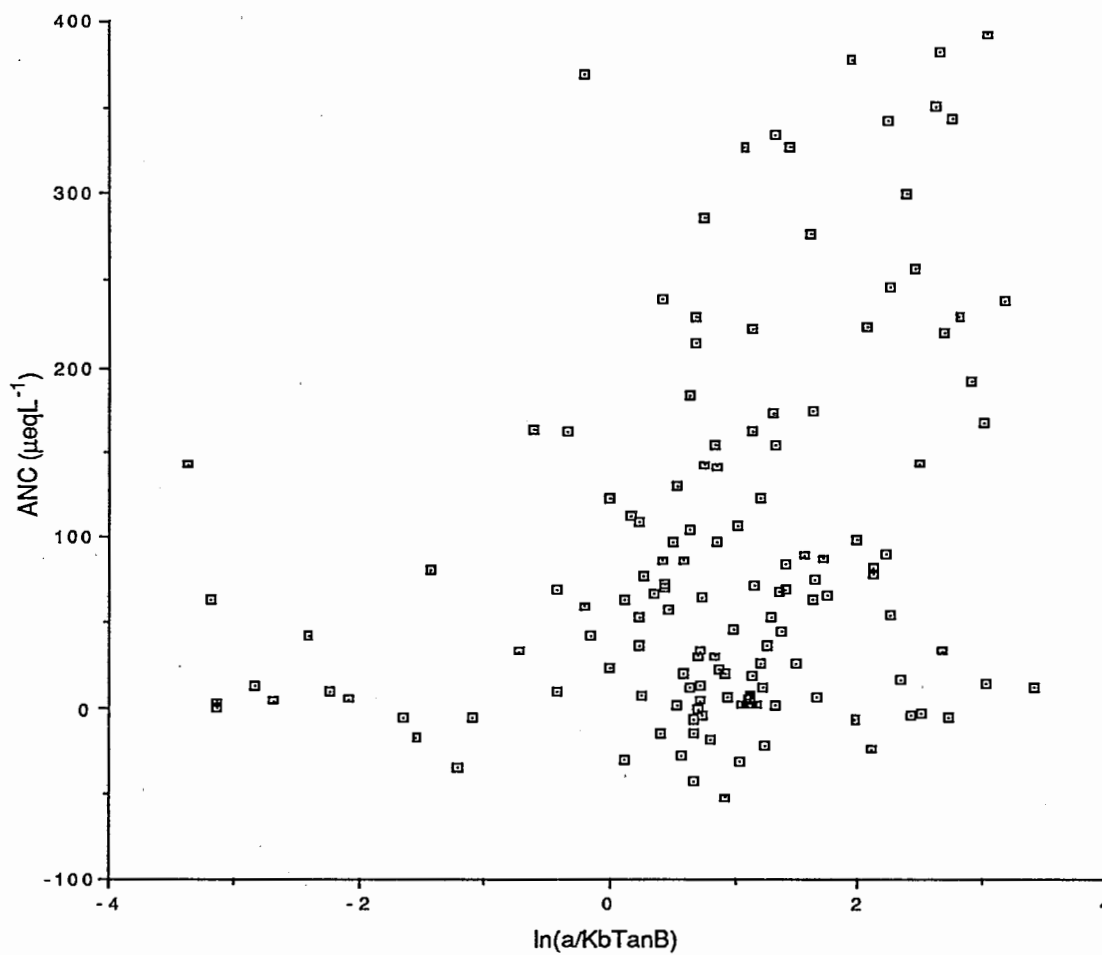
Figure 8-5. Scatter plot of ANC versus ln(a/KbTanB). TOPMODEL was used to calculate values of ln(a/KbTanB).
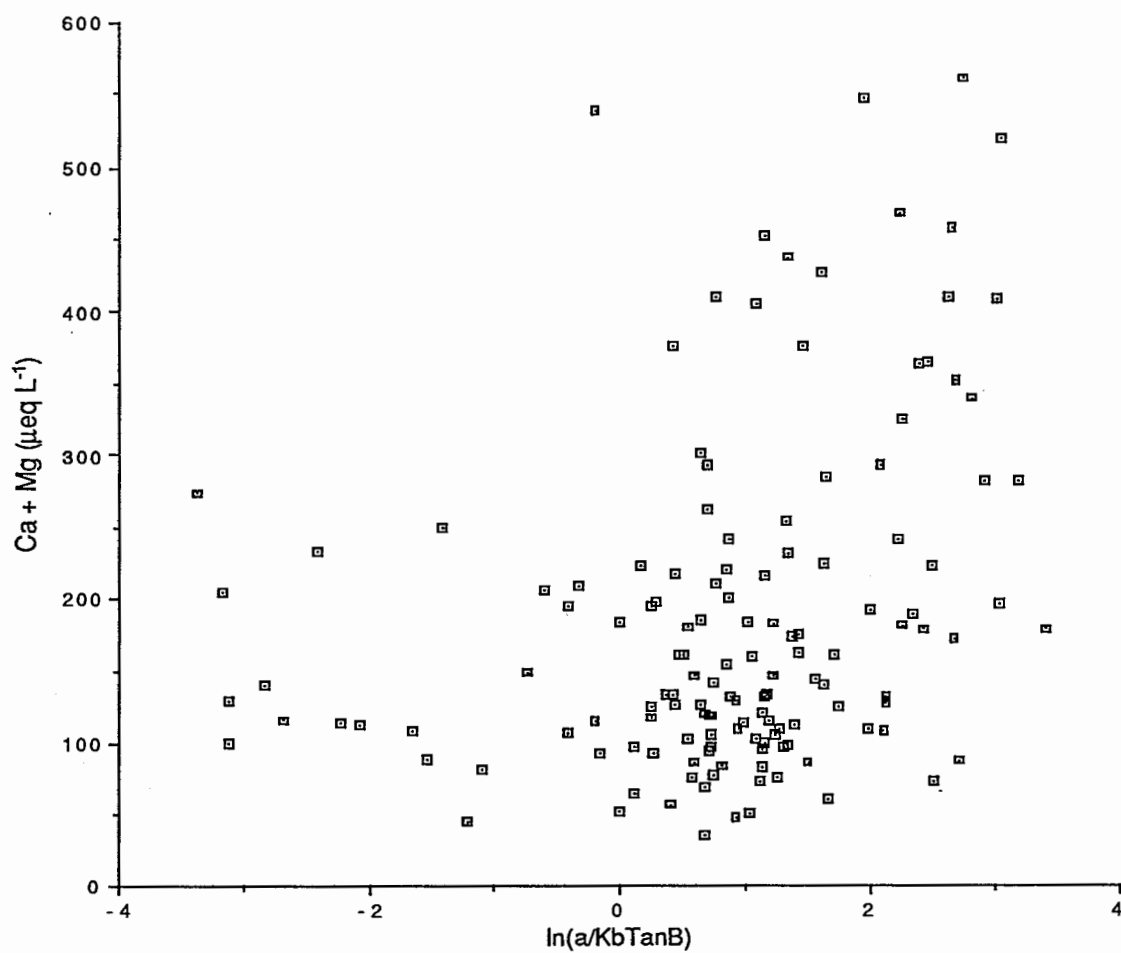
Figure 8-6. Scatter plot of Ca plus Mg versus ln(a/KbTanB). TOPMODEL was used to calculate values of ln(a/KbTanB).
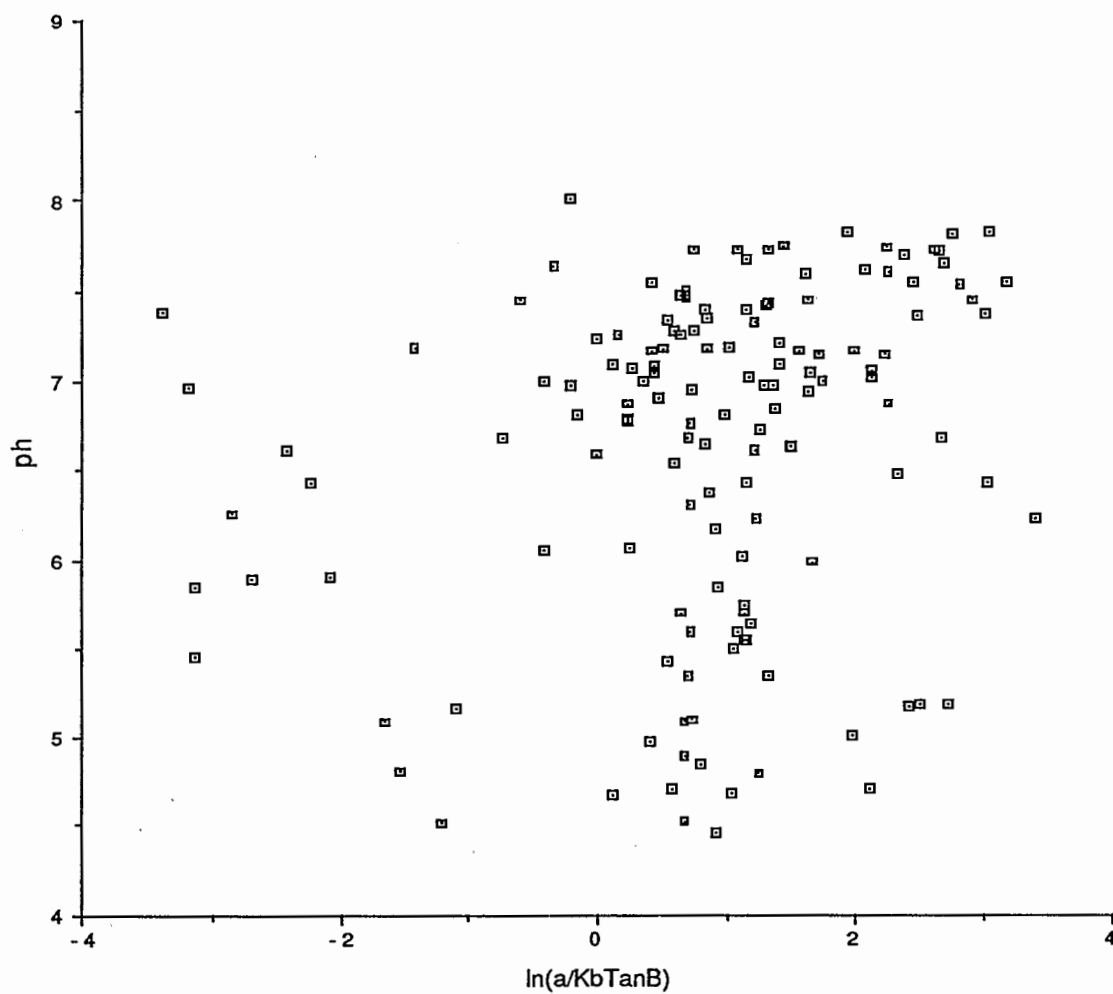
Figure 8-7. Scatter plot of pH versus ln(a/KbTanB). TOPMODEL was used to calculate values of ln(a/KbTanB).

Positive correlations between ln(a/KbTanB) and ANC and Ca plus Mg would seem to contradict the findings reported earlier (e.g., see Section 8.3.2). As discussed in Section 8.3.2, we found stream order to be consistent predictor variable for ANC. The relationship between stream order and ANC was positive, thus lower ANC tended to be associated with lower order streams. These lower order streams are generally high elevation with small drainage areas and, therefore, have a higher potential for quickflow runoff, resulting in low ANC. The positive correlation between values of ln(a/KbTanB) and ANC suggests, however, that more quickly responding systems result in higher ANC.

One possible explanation for the positive correlations between values of ln(a/KbTanB) with ANC and Ca plus Mg is given in Wolock et al. (1989). In watersheds with high mean values of ln(a/KbTanB) watersheds, less water passes through the soil matrix during high flows, as compared to low mean ln(a/KbTanB) watersheds, which are dominated by subsurface storm flow. Throughout the hydrochemical history of the catchments, more water has passed through those with the low mean ln(a/KbTanB) values than through those with high mean ln(a/KbTanB) values, thereby consuming more of the buffering capacity of the low mean catchments. If the buffering capacity of all catchments were initially the same and finite, then the low mean catchments should be more depleted of buffering capacity. Low mean catchments should, therefore, have lower ANC. Given this hydrochemical scenario, and assuming that ANC represents subsurface flow chemistry, then catchments with high ln(a/KbTanB) values should have high ANC.

Other factors may explain why ln(a/KbTanB) was not significantly related to surface water chemistry. First, there are numerous sources of uncertainty in the calculations of ln(a/KbTanB). Digital elevation models at 1:250,000 scale were used to compute values of "a" and "TanB". The DEMs are generalized to a large degree when compared to a watershed mapped at a scale of 1:24,000, which tends to become particularly critical on smaller watersheds. Additional uncertainties are functions of the errors associated with the DDRP Soil Survey information (e.g., error in map unit description, aggregation, depth-to-bedrock estimates). Second, there are many controls on surface water chemistry that were not considered within this analysis (e.g., watershed processes, sulfur deposition). For example, the physical and chemical characteristics of soils within "low" versus "high" ln(a/KbTanB) areas are undoubtedly different. The spatial variability of soils within a catchment, however, were not considered within these analyses. Finally, because TOPMODEL characterizes the partitioning of storm flow through the concept of variable source areas, it may be more suitable as an event model. Variable source areas tend to be active only during storm events and would not be expected to contribute a significant amount of runoff during baseflow conditions. Because NSWS surface water chemistry more accurately represents baseflow, it may be unrealistic to expect an index of variable source areas to be correlated with surface water chemistry.

8.3.3.2.3 Southern Blue Ridge Province --

Statistical correlations between ln(a/TanB) and surface water chemistry are shown in Table 8-19. We found no significant correlations between ln(a/TanB) and sulfate, sulfur retention, pH, ANC, or Ca plus Mg. The possible factors responsible for lack of a significant correlation between ln(a/TanB) and surface water chemistry are discussed more fully in Section 8.3.3.2.1.

Table 8-19. Pearson's Correlation Coefficients Between ln(a/TanB) and NSS Pilot Chemistry

Region	n	ANC	SO4	S Ret.	pH	Ca plus Mg
SBRP	32	0.28	-0.15	0.08	-0.07	0.18

8.3.3.3 Summary

In the Level I hydrologic analyses we attempted to relate empirically physically modelled parameters and mapped geomorphic/hydrologic parameters to surface water chemistry. The objective of these analyses was to use indirect measurements of hydrology, which can be obtained relatively easily, to describe surface water chemistry. These measurements include estimates of soil contact based on Darcy's Law, output parameters from the hydrologic model TOPMODEL, and mapped measurements of geomorphology and hydrology.

- We did not determine any significant relationships between the Darcy's Law estimates and surface water chemistry. The major factor determining this lack of relationship is the probable large error associated with watershed soil depth, hydraulic conductivity, and slope estimates.

- Although a limited significant relationship was identified between TOPMODEL output and surface water chemistry, this result was not necessarily explainable nor consistent with theory. One probable explanation for the lack of correlation is that TOPMODEL is based on the variable source area concept and is more appropriately an event level model.

- Relationships between the mapped geomorphic/hydrologic parameters and surface water chemistry were identified. The major variables that were significantly related were runoff, stream order, and an estimate of basin shape.

These findings suggest that hydrologic/geomorphic characteristics are related to surface water chemistry, although specific processes cannot be identified. Although we found little correlation between Darcy's Law and TOPMODEL with surface water chemistry, we chose to include these analyses within this report for documentation purposes. Our conclusions neither confirm nor repudiate the findings of April and Newton (1985) and Chen et al. (1984).

8.4 MAPPED BEDROCK GEOLOGY

A parameter hypothesized to be important in controlling the composition of surface waters is bedrock geology. Different lithologies exhibit different reactivities. Some, such as limestones or dolostones, are highly reactive. Waters in contact with these rock types quickly attain equilibrium with the carbonate regardless of the acidity of the incident deposition. Other lithologies are, effectively, unreactive. For example, quartzites will modify the composition of incident deposition only slightly. As a result, waters evolving from quartzite systems tend to strongly reflect the composition of the incident deposition.

In addition to lithology, a number of other factors contribute to the extent of interaction between bedrock and soil and ground waters. Porosity and permeability of the bedrock, in conjunction with other parameters (e.g., hydraulic head), control water contact times and the rates of infiltration through ground water. Longer contact times provide greater opportunity for the water to react with the bedrock, thereby increasing cation concentrations and ANC. Structural considerations, such as the strike of a bedrock unit relative to the aspect of the watershed could influence water infiltration and contact times as well. Unfortunately, quantifying these non-lithological characteristics of bedrock was not possible from the

sources used for this study. As a result, the analyses here focus on bedrock lithology as the variable of interest for evaluating statistical relationships between bedrock and surface water chemistry.

The first step in the bedrock analysis was to identify the types of bedrock within each of the DDRP watersheds. Using an ARC/INFO Geographic Information System (GIS) (see Section 5.4.1.7), watershed boundaries were overlaid onto state geology maps and the bedrock units mapped within the boundaries identified.

For the 145 watersheds located in the NE region, a total of 136 different mapped bedrock units were identified. The large number of bedrock types relative to the number of watersheds results in insufficient degrees of freedom for a reasonable statistical evaluation of the relationship between individual bedrock types and surface water chemistry. Therefore, it was necessary to group the different units into more generic classes in order to perform the analyses. This classification was accomplished in a two-step process. The first step was to assign each mapped unit to a generic bedrock type. Then, we assigned a relative reactivity to each of these generic rock types.

8.4.1 DDRP Bedrock Sensitivity Scale

A number of studies have been undertaken to evaluate the relationship between bedrock geology and surface water composition (Hendrey et al., 1980; Rapp et al., 1985; Shilts, 1981). These studies have been used on regional scales to help identify areas that are potentially sensitive to the effects of acidic deposition.

Hendrey et al. (1980) used a 4-point scale to delineate rocks of different reactivities. Highly reactive rocks, such as limestones, dolostones, or highly fossiliferous rocks, were assigned scores of (4). As the reactivity of the rocks decreased, the reactivity score was decreased. The reactivity scale of Shilts (1981) was developed along similar lines, except that he used a value of (1) to designate the most reactive lithologies. Some structural considerations were implicitly included in these rankings. For example, marine shales are cation-rich, but because of limited permeability and the presence of pyrite, these units were assigned reactivities of (2) on the Hendrey et al. scale and (3) on Shilts' scale. These ranking systems have proven useful for identifying regions potentially sensitive to acidification.

Rapp et al. (1984) developed a 10-point scale to evaluate the relationships between bedrock geology and surface water chemistry for lakes located in the Upper Midwest. On their scale, (1) represents the most reactive bedrock types (limestones, marbles, calcareous tills), while (10) represents the least reactive units (e.g., quartzites, organic deposits). Significant correlations were found between the amounts of nonreactive bedrock and surface water chemistry in their study area.

In attempting to use the above scales in the DDRP Level I analyses, several difficulties were encountered. The Rapp et al. scale was developed for the Upper Midwest. As such, it does not contain the range of lithologies encountered in the DDRP and is not appropriate for use here. In working with the other scales, a major problem has been the lack of resolving power for distinguishing the different contributions of weathering to the range of compositions observed among lakes. The watershed sample used in the DDRP was selected based on lake water ANC. Watersheds with surface water ANC > 400 μeq L^{-1} were excluded from the study, and the majority of systems have surface waters with ANC < 200

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μeq L^{-1}. Using the Hendrey et al. scale, the majority of systems included in DDRP have bedrock sensitivity scores of (2). Similar limitations have been encountered using the other scales in this evaluation. For this reason, we wanted to develop a sensitivity or reactivity scale that would allow us to distinguish the relative ANC generating capacities of a group of lithologically different but, otherwise, moderately unreactive rock types.

With this goal in mind, a 6-point scale was developed with the intent of separating rocks with slightly different reactivities into different categories. The top two categories, (5) and (6), are reserved for the reactive and highly reactive lithologies of Hendrey et al. (1980), corresponding to their classes (3) and (4). Within our classes (1) through (4), we attempted, then, to distinguish rock types that have only slightly different reactivities with surface or ground waters.

Classification of individual mapped bedrock units was accomplished in a two-step process. First, each mapped unit was classified according to a generic rock type. Table 8-20 lists the rock types considered. Once this step was completed, a reactivity score was assigned to each of the generic rock types. Table 8-21 summarizes the reactivities assigned. These assignments were reviewed by both project participants and a limited number of individuals external to the project. Consensus was usually, but not universally, attained for each of the scores. In all cases, project participants made final decisions concerning the selection of the relative reactivity score. The decisions regarding final reactivity assignments were made independent of any knowledge of the ANC of the surface waters associated with the specific bedrock units.

8.4.2 Results

For the DDRP samples in the NE and SBRP, multiple estimates of the aggregated bedrock reactivity were synthesized. In the following analyses, the variable <u>Mean</u> is the weighted average of the sensitivity codes for a watershed, where the weights are the areal proportions of the watershed covered by the bedrock type. The variable <u>Max</u> is the maximum sensitivity code observed on a watershed. The variable <u>H5up</u> is the percent of the watershed covered by bedrock with sensitivity codes that are at least 5.0. The statistical analyses on the DDRP data used standard regression procedures discussed in Section 8.1.2.

As can be seen in Table 8-22, the variables <u>Mean</u> and <u>Max</u> do not differ much between subregions in the NE, or between the NE and the SBRP. The average and maximum sensitivity codes for watersheds are highest in Subregion 1A and lowest in Subregion 1B, but it is unlikely that these differences are significant. <u>H5up</u>, the percent of the watershed with sensitivity codes of 5 or 6, has the highest average in Subregion 1E. This result means that more watersheds in this subregion are classified as having significant percentages of reactive to highly reactive bedrock types. The data for the SBRP indicate that the estimated sensitivity codes are similar to those for the northeastern subregions with lower proportions of the highly reactive bedrock types.

The measurement error analyses show that there are highly significant relationships between bedrock geology and surface water chemistry, particularly ANC and sum of base cations. These relationships may be masked in analyses performed on the DDRP watersheds, since measurement error models cannot be used with the more detailed geological information available on these watersheds. The possible masking of existing relationships should be kept in mind when reviewing these results.

Table 8-20. Tabulation of the Generic Bedrock Types Used to Classify the Mapped Units Identified on State Map Legends

Symbol	Description	Symbol	Description
I01	alkali feldspar granite	M01	mixed metamorphics
I02	granite	M02	quartzite
I03	quartz porphyry	M03	schist
I04	granite porphyry	M04	phyllite
I05	granophyre	M05	slate
I06	pegmatite	M06	gneiss
I07	aplite	M07	granitic gneiss/granofel
I08	syenite	M08	greenstones
I09	quartz syenite	M09	amphibolites
I10	alkali feldspar syenite	M10	serpentinites
I11	granodiorite	M11	chlor/amphib/epid schist
I12	tonalite	M12	marble
I13	monzonite	M13	sulfidic schist
I14	quartz monzonite	M14	calc-silicates
I15	diorite	M15	leucocratic gneisses
I16	quartz diorite	M16	migmatites
I17	alkali feldspar rhyolite	M17	mixed metaclastics
I18	rhyolite	M18	mixed types
I19	dacite		
I20	obsidian/pumice		
I21	diorite porphyry	C01	quartz sandstone
I22	andesite	C02	sulfidic pelite/shale
I23	latite	C03	chert
I24	trachyte	C04	iron formations
I25	phonolite	C05	pelite/mudstone
I26	gabbro	C06	shale
I27	anorthosite	C07	argillite
I28	norite	C08	conglomerate
I29	diabase	C09	sandstone
I30	basalt	C10	arenite/arkose
I31	charnockite	C11	graywacke
I32	ultramafic(s)	C12	siltstone
		C13	mixed clastics
C23	Organic deposits/peat	C14	calcareous shale
C22	mixed limestone/dolostone	C15	calcareous siltstone
C21	dolomites/dolostones	C16	calcareous sandstone
C20	limestones	C17	calcareous arenite
C19	interfingering ls/clastics	C18	calcareous conglomerate

Table 8-21. Tabulation of the Generic Bedrock Types Used to Classify the Mapped Units Identified on State Map Legends

Reactivity Score	Explanation	Generic bedrock types (from Table 8-22)
1	minimally reactive	C01 C02 C03 C04 C23 M02 M13 I06 I07 I09
2	slightly reactive	C05 C06 C07 C08 C09 C13 M03 M04 M05 M07 M16 M17 I01 I02 I03 I04 I05 I08
3	modestly reactive	C10 C11 C12 C14 M01 M06 M11 I11 I12 I17 I18 I19 I24 I31
4	moderately reactive	C15 M08 M09 M14 M15 I13 I14 I15 I16 I20 I21 I22 I23 I27 I28 I29 I30
5	reactive	C19 I25 I26 I32
6	highly reactive	C16 C17 C18 C20 C21 C22 M12

Table 8-22. Regional and Subregional Statistics for the Bedrock Sensitivity Code Variables

	Average	Median	Min.	Max.
Entire Region 1				
Mean	2.6	2.5	1.0	6.0
Max	3.3	3.0	1.0	6.0
H5up	3.6	0.0	0.0	100.0
Subregion 1A				
Mean	3.1	3.0	2.35	4.0
Max	3.7	3.5	2.5	6.0
H5up	0.8	0.0	0.0	18.8
Subregion 1B				
Mean	2.1	2.0	1.0	3.0
Max	2.4	2.0	1.0	5.0
H5up	0.02	0.0	0.0	0.4
Subregion 1C				
Mean	2.7	2.8	1.0	3.6
Max	3.8	3.5	1.0	6.0
H5up	3.4	0.0	0.0	43.8
Subregion 1D				
Mean	2.3	2.3	1.8	3.0
Max	2.9	2.3	2.0	5.0
H5up	1.3	0.0	0.0	18.6
Subregion 1E				
Mean	2.7	2.0	1.0	6.0
Max	3.5	2.5	1.0	6.0
H5up	14.5	0.0	0.0	100.0
Entire Region 2 (SBRP)				
Mean	2.2	2.0	1.0	3.4
Max	2.7	2.0	1.0	6.0
H5up	0.3	0.0	0.0	8.2

8.4.2.1 Sulfate and Percent Retention

8.4.2.1.1 Northeast -

As discussed in Section 8.2, sulfate deposition appears to be the dominant source of sulfate in northeastern surface waters. After sulfate deposition is taken into account, no bedrock geology variable appears in the model (Table 8-23). This observation is not surprising, because the reactivity of a rock type is not necessarily related to its sulfur-bearing potential. We would not expect most of the DDRP bedrock types to act as internal sources for sulfur. Some of the more reactive rock types, especially limestones and dolostones, will release sulfate by the dissolution of gypsum. However, we anticipate that "disturbed" systems, e.g., mining operations for coal or base metals, would serve as the primary internal sources of sulfur for surface waters. These operations expose fresh, unweathered sulfide minerals that can be oxidized and therefore have a high potential for contributing to the sulfur and hydrogen ion budgets in these systems.

The stepwise regressions suggest both the <u>Mean</u> and <u>Max</u> variables exhibit negative correlations with percent sulfur retention. That is, watersheds with the least reactive bedrock types tend to retain higher percentages of sulfate than do the watersheds containing more reactive bedrock types. The reasons for this correlation are not immediately obvious. One possible explanation might be that since the more reactive bedrock types may act as minor internal sources for sulfur, watersheds containing highly reactive lithologies may have soils that carry higher ambient loads of sulfur. As a result, these soils may allow a greater percentage of sulfur delivered to the watersheds via deposition to pass on to surface waters. If this were a small effect in watersheds containing bedrock with sensitivity codes of 5 or 6, then it is possible that these internal sources might not have been large enough to identify in the sulfate regression analysis, and yet be of sufficient magnitude to have a measurable effect on the sulfur budgets. An alternative explanation could be that the more acidic rock types provide conditions conducive to the generation of oxides in soils, hence increasing the sulfate adsorption capacities of the soils. Details of this hypothesis will be addressed in the section on soil chemical properties and their relationship to surface water chemistry (see Section 8.8.4.)

8.4.2.1.2 Southern Blue Ridge Province -

When we performed the regressions on the 32 SBRP watersheds, the only explanatory variable that appeared was <u>H5up</u>, i.e., the percentage of the watershed covered by bedrock with sensitivity codes of 5 or 6 (Table 8-24). <u>H5up</u> was positively correlated with surface water sulfate and negatively correlated with percent sulfur retention. On analysis of the residuals, however, these effects could be attributed primarily to one watershed (2A08808), which has high stream sulfate and very low % S retention. When this site and watershed 2A07827 (Table 8-24) were excluded from the regression, no regressor variables were identified as significant.

8.4.2.1.3 Comparison of Regions -

In both regions, the more reactive bedrock types are associated both with higher surface water sulfate and with lower percent sulfur retention. In this regard, the effect of bedrock on sulfur dynamics within the watershed appears to be similar across both regions. Although there is no *a priori* reason to

Table 8-23. Results of Regressions of Surface Water Chemistry on Bedrock Sensitivity Code Statistics and Deposition Estimates for Northeast

Water Chemistry Variable	R^2	Adjusted R^2	Variable in Model	Regression Sign	Signif.[a] Level
Sulfate	0.3618	0.3573	total sulfate	+	***
Percent Sulfur Retention	0.1370	0.1169	total sulfate	+	***
			Mean	-	**
			Max	+	S
ANC	0.0558	0.0491	H5up	+	**
Ca+Mg	0.0566	0.0432	H5up	+	*
			total H	+	*
pH	0.0878	0.0683	Max	+	**
			Mean	-	*
			H5up	+	S

[a] S = Not significant at 0.05 level
   * = Significant at 0.05 level
   ** = Significant at 0.01 level
   *** = Significant at 0.001 level

Table 8-24. Results for SBRP of Regressions of Surface Water Chemistry on Bedrock Sensitivity Code Statistics and Deposition Estimates

Water Chemistry Variable	R^2	Adjusted R^2	Variable in Model	Regress. Sign	Signif.[a] Level	Watershed[b] Removed
Sulfate	0.2526	0.2277	H5up	+	**	2A08808(B) 2A07827(B)
Model 2	none significant					
Percent Sulfur Retention	0.2790	0.2550	H5up	-	**	2A08808(B) 2A07827(B)
Model 2	none significant					
ANC	0.0859	0.0554	H5up	+	S	
Ca + Mg	0.2546	0.2297	H5up	+	**	2A07827(L) 2A07813(O) 2A08808(L)
Model 2	0.0791	0.0450	H5up	+	S	2A07826(O) 2A07833(L)
Model 3	none significant					
pH	none significant					

[a] S = not significant at 0.05 level
* = significant at 0.05 level
** = significant at 0.01 level

[b] (L) = site removed is a leverage point
(O) = site removed is an outlier
(B) = site removed is both a leverage point and an outlier

expect a relationship between the sensitivity scale and sulfur dynamics, our results do suggest that the most reactive bedrock types also act as (minor) internal sources for sulfate, which influences the way in which a watershed will respond to the effects of elevated sulfur deposition.

8.4.2.2 Sum of Base Cations, ANC, and pH

As discussed in Section 8.1, the sum of calcium and magnesium is used to represent base cations in these analyses. This representation was necessary because of the non-local sources for sodium (e.g., sea salt and road salt) to the surface waters in many of the study watersheds.

8.4.2.2.1 Northeast -

The stepwise regression analyses indicate positive relationships between surface water ANC and the regressor variable H5up. The positive relationship with the percent of watershed covered by high bedrock sensitivity codes indicates that the bedrock is contributing significant amounts of ANC through weathering.

In conjunction with these analyses, the regressions show that surface water pH has statistical relationships with the variables Max, Mean and H5up. The positive relationship with Max suggests that watersheds with higher bedrock sensitivity codes have higher pH values. The relationships with Mean and H5up may indicate correction factors for particular watersheds with high or low bedrock sensitivity codes.

We find a strong positive relationship between Ca plus Mg and the sensitivity code for the watershed. This finding suggests that there is a relationship between the presumed reactivities assigned to the bedrock types and the rate of cation supply to surface waters. The higher reactivity rankings are associated with higher weathering rates and, hence, stronger internal sources for base cations.

The stepwise regressions indicate that other variables contribute to the regulation of base cation concentrations in surface waters. In particular, there is a positive relationship between surface water calcium plus magnesium and the total hydrogen ion deposition. If this correlation has any significance in terms of ecological processes, then two explanations can be offered. First, the relationship may indicate possible leaching of base cations from the soil exchange complex in excess of the mass contributed by primary mineral weathering. The alternative explanation, especially for those watersheds containing some carbonate bedrock (e.g., limestones), would be that the higher incident acidic deposition allows for additional dissolution of the carbonate and hence contributes to the base cation budget.

8.4.2.2.2 Southern Blue Ridge Province -

The stepwise regression for the sum of calcium and magnesium concentration showed a positive correlation with H5up, as shown in Table 8-24. Residual analysis indicated that watershed 2A08808 was a strong leverage point. This site has already been discussed as an internal source of sulfur. Upon removing this site, as well as two other watersheds, from the analysis, the stepwise regression procedure still selected H5up. This correlation, however, was no longer significant at the 0.05 level.

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The stepwise regression for ANC showed a positive relationship between this variable and H5up. As in the calcium and magnesium model, the stepwise procedure selected H5up, but it was not significant at the 0.05 level. This regression and the previous one suggest that the higher bedrock sensitivity numbers are somewhat associated with increased base cation concentrations and ANC.

In the SBRP, the analyses do not show any consistent relationship between the bedrock sensitivity numbers and the pH of the surface waters across the region. The stepwise regression for pH selected none of the deposition or bedrock geology variables, presumably due to the lack of variability in the deposition gradient across the region.

8.4.2.2.3 Comparison of regions -

Hydrogen ion deposition appeared to be strongly related to base cation concentration in the NE, but not in the SBRP. This is probably due to the much smaller deposition gradient in the SBRP. In the NE, we observe an increase in base cation export from watersheds with increasing hydrogen ion deposition, but in the SBRP, the change in deposition is smaller, so that the change in base cations is not significant.

In both the NE and SBRP, positive relationships were observed between bedrock sensitivity codes, and ANC and base cation concentrations. In both regions, the regressions explained between 5 and 9 percent of the variability in the surface water variables, but due to a larger sample size, the regressors for the NE were highly significant.

The smaller sample size in the SBRP may also explain why no significant correlations between bedrock lithology and pH were observed there, while such relationships are observed in the NE.

8.4.3 Summary

Results of the studies of the relationships between the relative reactivities of the different bedrock types found within the DDRP watershed population and the associated surface water properties indicate several pertinent factors. About two-thirds of the variability associated with the assignment of the sensitivity numbers is attributable to measurement error. This means that our data are somewhat "noisy," and so relationships may be obscured or minimized. Nonetheless, there are significant relationships between the relative reactivities assigned to watersheds and associated surface water characteristics, in particular, base cation concentrations and surface water ANC values. These relationships do not appear to be as strong as we expected. In addition to measurement error the absence of strong relationships might be related to the population of systems being studied. In essence, most of the watersheds included in the study are underlain by nonreactive bedrock types, so many of the differences observed in the surface water chemistry might be more strongly controlled at this level by factors such as depth to bedrock or selected soil properties. The multiple regression studies will address these issues (see Section 8.8).

8.5 MAPPED LAND USE/VEGETATION

8.5.1 Introduction

The effects of vegetation and land use on surface water chemistry are both general and site specific. For example, species differences in root density, depth, and morphology affect how nutrients cycle from the soil to forest vegetation as well as the physical and biological processes that influence soil water infiltration and percolation. Both evergreen and deciduous vegetation strip or scavenge acidic deposition materials from the atmosphere before they reach ground waters and surface waters. Long-term effects of acidic deposition can be either beneficial or adverse to the nutrient status of forest soils and to forest health; the deciding factors are local site nutrient status, ongoing silvicultural practices, present forest species mix, and both the amount and type of atmospheric inputs received at specific localities (Johnson et al., 1982a, and Johnson et al., 1988).

Usually, surface waters within forested watersheds have lower turbidity and temperature and have lower nutrient loadings than water from agricultural or urban watersheds (Simmons, 1976; Chang et al., 1983; Comeau and Bellamy, 1986; Morgan and Good, 1988). One exception is forest land subjected to clear-cut harvesting and/or extensive site preparation (Pritchett and Fisher, 1987). The magnitude of water chemistry changes within or outside harvested watersheds is dependent upon clear-cut intensity (Tiedmann et al., 1988) and ionic species (Lawrence and Driscoll, 1988).

Within these broad generalizations substantial site-to-site variation occurs because of inherent natural spatial and temporal variability across the landscape. For example, in upland headwater forested watersheds receiving acidic deposition, surface water sulfate can predominate in areas having minimal vegetation and soil development; however, surface water concentrations of bases generally increase downstream where interactions of forest species composition, soil depth, and geochemical weathering are greater (Jeffries et al., 1988; Driscoll et al., 1987). In other situations, riparian zone vegetation reduces chemical concentrations in soil water (Schnabel, 1985) and lowers suspended sediment loads leaving agricultural watersheds (Cooper et al., 1986). Spatially, wetland position is also important: wetland fringes bordering water bodies seem to be more effective in modifying water quality than are upland wetlands remote from major downstream lakes (Johnston et al., 1988). Finally, significant temporal alterations in stream water chemistry have been attributed to both beaver activity (Driscoll et al., 1987b; Naiman et al., 1986) and changing historical or recent land use patterns (Buso et al., 1985; Hunsaker et al., 1986b).

Although northeastern lake and SBRP stream watersheds were primarily undisturbed and forested, significant amounts of other land uses were present. It was also known that many northeastern lakes had varying amounts of beaver activity and wetlands. The main DDRP objective in mapping land use and forest vegetation cover types was to determine whether any land uses were consistently associated with specific surface water chemistry variables. Section 8.5 examines those relationships that were found.

8.5.2 Data Sources

Land use and land cover data for northeastern lakes were obtained by interpretation of recent 1:12,000 color infrared (CIR) photography specifically acquired for DDRP (Section 5.4.1.6). For SBRP

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watersheds, SCS personnel determined land use from older (late 1970s) alternate black and white and CIR, quad-sized National High Altitude Photography (NHAP) photos (see Section 5.4.2.7). Forest cover types were determined during soil mapping activities (see Sections 5.4.1.3, 5.4.2.3). All land use, forest cover, and wetland data were entered into GIS (see Sections 5.4.1.7, 5.4.2.8) so that information could be analyzed by percent watershed area or actual hectare area in desired land use classes. Select data on acidic deposition, precipitation, and runoff were also included.

8.5.3 Statistical Methods

Relationships between water chemistry variables and many environmental variables have been examined via normal regression techniques for small (Osborne and Wiley, 1988) and very large (Hunsaker et al., 1986a) data sets. Some of the problems with regression approaches are: selection of an appropriate and parsimonious subset of regressors for the model; multicollinearity of the regressor variables; peculiar distributions of some of the regressors, particularly when some variables have many zero entries; and practical interpretability of results when many regressors appear in any one model.

For these reasons, we used principal component analysis or PCA (Johnson and Wichern, 1982; SAS Institute Inc., 1985, 1987) to analyze mapped land use and vegetation data. For land use data in the NE, the correlation matrix of the 42 regressor variables in Table 8-25 was used to generate the principal components. Thirteen principal components had eigenvalues greater than one. These factors (Table 8-26) were retained for further analysis. Together these principal components explained 81 percent of the variability in the correlation matrix. We used a varimax rotation of the original factors to improve the interpretability of the factors (Table 8-27). Then we performed stepwise regressions of the surface water chemistry variables on the rotated factors and examined the residuals for leverage points and outliers after verifying the standard assumptions of regression analyses (see Section 8.1.2).

For SBRP watersheds, initial analysis showed three watersheds with ANC $\geq$ 1000 μeq L^{-1}, due to local carbonate bedrock rich in calcium and magnesium. We excluded these three watersheds from all subsequent analyses. A correlation matrix of 39 regressor variables (Table 8-28) was used to generate the principal components. Eleven principal components had eigenvalues greater than one. These factors (Table 8-29) were retained for further analyses, because the correlation matrix was used to generate the components. Together, these principal components explained 93 percent of the variability in the correlation matrix. We used a varimax rotation of the original factors to improve factor interpretability (Table 8-30). Finally, we performed regressions of the surface water chemistry variables on the rotated factors for the SBRP watersheds, after examining residuals for leverage points and outliers (see Section 8.1.2).

8.5.4 Sulfate and Percent Sulfur Retention

8.5.4.1 Northeast

Lake sulfate was positively correlated with deposition (Section 8.2) and watershed development but negatively correlated with beaver activity, wetland percent, and precipitation and runoff factors (Table 8-31). The adjusted R^2 of 0.50 was the highest for all five water chemistry variables investigated. Because NE watersheds have low sulfate adsorption capacity and are assumed to be at sulfur steady

Table 8-25. Land Use and Other Environmental Variables Related to Surface Water Chemistry of Northeastern Lakes

Variable Kind	Variable Name	Explanation of Variable Name
Photointerpretation	B_DAM	total number of breached beaver dams
	B_LODGE	total number of beaver lodges
	C⁻	percent area in cropland
	C_H	area (ha) in cropland
	CABIN	total number of cabins counted
	E	percent area in forest
	E_H	area (ha) in forest
	G⁻	percent area in pasture
	G_H	area (ha) in pasture
	H⁻	percent area in horticulture
	H_H	area (ha) in horticulture
	IM_H2O	percent impounded water
	L_H	area (ha) in waste disposal land
	L⁻	percent area in waste disposal land
	M	percent area in cemeteries
	M_H	area (ha) in cemeteries
	N⁻	percent area in barren land
	N_H	area (ha) in barren land
	O_DAM	total number of old beaver dams
	OW_H	area (ha) in open water
	P	percent area in pits or quarries
	P_H	area (ha) in pits and quarries
	UC	percent area in urban commercial land
	UC_H	area (ha) in urban commercial land
	U_DAM	total number of unbreached beaver dams
	UI	percent area in urban industrial
	UI_H	area (ha) in urban industrial
	UV	percent area in urban residential
	UV_H	area (ha) in urban residential
	W	percent area in wetlands
	W_H	area (ha) in wetlands
SCS land and forest cover type	CON	percent area in conifers
	HWD	percent area in hardwood forest
	MIX	percent area in mixed forest
	LV_WET	percent open-wet area
	SCS_OPN	percent area in open (non-forest) land
Other data	H_D	dry H deposition, g m^{-2}
	H_W	wet H deposition, g m^{-2}
	ELEV	elevation in m from USGS topo maps
	PRECIP	precipitation in cm from National Climatic Data Center, Asheville, NC
	RUNOFF	mean annual runoff, in inches from Krug et al. (1985) (see Section 5.7.1)
	SO4_W	wet sulfate deposition, g m^{-2}
	SO4_D	dry sulfate deposition, g m^{-2}

Table 8-26. Factor Loadings for First 13 Principal Components after Varimax Rotation of the Correlation Matrix of Land Use and other Environmental Variables for Northeastern Lakes

Environmental Variables	Principal Components[a]						
	1	2	3	4	5	6	7
L-H	98*	-3	-1	0	3	1	-1
L	98*	-3	-1	0	3	1	-1
P H	94*	0	0	-1	-4	-4	-9
UV̄ H	92*	9	-2	4	3	-1	13
UC̄ H	81*	6	4	14	-2	46*	7
CAB̄IN	75*	10	-2	4	6	-3	37*
H H	41*	-31*	24	20	-1	0	25*
P̄	38*	4	1	-3	-13	-8	-18
H D	-5	88*	-1	17	4	4	0
H̄W	6	88*	-3	1	6	6	-10
SŌ4 W	5	86*	-8	-2	10	8	-20
S04 D̄	5	81*	-9	23	11	6	-2
ELEV̄	-3	61*	-7	-8	-17	-5	-16
CON	-7	-67*	-5	0	15	-2	-4
U DAM	-4	-1	89*	-4	2	8	16
O DAM	-1	-5	88*	2	-3	9	-8
IM̄ H20	-1	-8	87*	9	7	-1	12
B LODGE	-2	-8	78*	3	3	4	37*
B DAM	-1	6	75*	-2	-5	-8	-9
SC̄S OPN	10	5	-7	89*	4	9	3
G	-4	13	-9	86*	5	1	4
C H	6	-6	41*	73*	-8	-3	-3
C̄	-1	5	4	73*	-6	-1	-18
G H	3	2	5	71*	1	-4	39*
LV̄ WET	2	4	2	0	96*	-4	-1
W̄	2	3	2	1	96*	-4	-1
N	0	7	0	0	-5	97*	-2
UC	12	9	-6	9	-6	93*	-4
N H	-3	1	37*	-9	5	61*	10
OW̄ H	4	-14	10	0	-7	1	80*
E H̄	14	-10	63*	2	-1	-1	68*
W̄ H	20	-14	46*	8	34*	1	61*
M̄H	0	4	-1	0	-2	-1	0
M̄	-1	4	-1	0	-4	-1	-1
UV	17	8	-8	0	-9	-3	-4
E	-17	-10	9	-58*	-28*	-10	3
UI H	0	-4	-2	-1	6	3	19
UĪ	0	11	-3	0	-4	0	-6
ELS WET	-2	-4	-2	-6	37*	-1	9
H	23	-29*	2	15	-9	0	3
SCS WET	-2	10	5	4	37*	-5	6
PREC̄IP	5	27*	5	-18	11	9	-1
RUNOFF	-4	-14	-1	-15	-12	-5	13
MIX	2	-22	17	-8	-9	-1	5
HWD	0	61*	-7	-27	-10	0	-2

Table 8-26. (Continued)

Environmental Variables	Principal Components[a]					
	8	9	10	11	12	13
L-H	0	-5	-3	-2	1	1
L	0	-5	-3	-2	1	1
P_H	-1	12	11	-2	8	1
UV̄_H	-1	23	-2	7	-7	2
UC⁻H	1	-10	-4	3	0	-5
CAB̄IN	1	27*	-5	18	-14	1
H_H	3	4	14	38*	21	-20
P⁻	-2	35*	27*	0	16	1
H_D	4	-2	3	-4	-13	-16
H⁻W	7	-1	4	-9	35*	-5
SŌ4_W	1	16	11	-6	27*	-7
S04⁻D	3	9	9	-5	-13	-11
ELEV̄	-11	-39*	-15	-13	23	-3
CON	-4	-13	5	-25*	34*	-14
U_DAM	0	-1	-7	-12	5	15
O⁻DAM	-1	3	-1	6	-7	0
IM̄_H2	1	0	-2	-1	6	-3
B_LODGE	-2	-1	0	-4	-1	15
B⁻DAM	-2	-11	0	14	-2	-2
SC̄S_OPN	2	16	12	6	-6	5
G	3	11	-6	-18	-10	10
C_H	-4	-8	-1	20	3	-21
C⁻	-6	-9	-1	11	-6	-6
G_H	8	-1	-8	-8	-10	6
LV̄_WET	-4	-1	1	14	-1	-3
W⁻	-4	-1	1	14	-1	-3
N	-1	-2	1	0	2	-3
UC	-1	-5	0	6	2	-8
N_H	0	14	4	-19	-3	20
OW̄_H	-5	-3	4	8	5	2
E_H⁻	7	-10	7	2	3	2
W⁻H	1	-2	15	14	8	4
M⁻H	99*	-2	-2	3	-2	2
M⁻	99*	-1	-1	3	-2	3
UV	-4	87*	-6	5	-5	-6
E	2	-67*	-2	-15	5	-1
UI_H	-1	2	86*	0	8	3
UI⁻	-2	-3	86*	-2	-8	1
ELS_WET	13	-10	-6	63*	-1	-5
H	3	27*	5	62*	19	10
SCS_WET	-7	9	-2	59*	10	13
PREC̄IP	0	19	12	12	74*	-2
RUNOFF	-6	-27*	-13	12	72*	0
MIX	4	-4	2	10	-8	89*
HWD	-1	5	-9	0	-17	-62*

[a] Printed values are multiplied by 100 and rounded to the nearest integer. Values greater than 0.29 have been flagged by an asterisk.

Table 8-27. Interpretation of the First 13 Principal Components After Varimax Rotation of the Correlation Matrix of Land Use and Other Environmental Variables for Northeastern Lakes

Principal Component Rank	General Interpretation of Principal Component
PC1	developed land: waste disposal, pits and quarries, cabins, urban residential, and urban commercial
PC2	overall wet and dry deposition
PC3	beaver activity, wetlands, and cropland
PC4	pasture land and cropland; less forest
PC5	wetlands
PC6	barren and urban commercial land
PC7	open water, forest, and wetlands
PC8	cemeteries
PC9	cabins, urban residential, and pits and quarries; less forest
PC10	urban industrial land and pits and quarries
PC11	wetlands and horticulture
PC12	precipitation and runoff
PC13	more mixed and less hardwood forest

Table 8-28. Land Use and Other Environmental Variables Related to Surface Water Chemistry of Southern Blue Ridge Province Streams

Variable Kind	Variable Name	Explanation of Variable Name
SCS interpretations	C	percent area in cropland
	C_H	area (ha) in cropland
	E	percent area in grazed forest land
	E_H	area (ha) in grazed forest land
	F	percent ungrazed forest land
	F-H	area (ha) in ungrazed forest land
	G	percent area in managed or native pasture
	G_H	area (ha) in managed or native pasture
	H	percent area in horticulture
	H_H	area (ha) in horticulture
	L	percent area in waste disposal
	L_H	area (ha) in waste disposal
	K	percent area in rock outcrop
	K_H	area (ha) in rock outcrop
	M	percent area in cemeteries
	M_H	area (ha) in cemeteries
	N	percent area in pits and quarries
	N_H	area (ha) in pits and quarries
	O	percent area in miscellaneous land use
	O_H	area (ha) in miscellaneous use
	R	percent area in wetlands
	R_H	area (ha) in wetlands
	U	percent area in urban land
	U_H	area (ha) in urban land
	W_H	area (ha) in open water
	Z	percent area in ridge top barren land
	Z_H	area (ha) in ridge top barren land
Forest cover type	CON	percent area in conifers
	HWD	percent area in hardwood forest
	MIX	percent area in mixed forest
	OPEN	percent (dry) areas without forest or wetlands
Other data	CAMG_D	dry CA + Mg deposition, $g\ m^{-2}$
	CAMG_W	wet Ca + Mg deposition, $g\ m^{-2}$
	H_D	dry H deposition, $g\ m^{-2}$
	H_W	wet H deposition, $g\ m^{-2}$
	PRECIP	precipitation in cm from National Climatic Data Center, Asheville, NC
	RUNOFF	mean annual runoff, in inches from Krug et al. (1985) (See Section 5.7.1)
	SO4_W	wet sulfate deposition, $g\ m^{-2}$
	SO4_D	dry sulfate deposition, $g\ m^{-2}$

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Table 8-29. Composition of First 11 Principal Component Analysis (PCA) Factors After Varimax Rotation of the Correlation Matrix of Land Use and Other Environmental Variables Related to Surface Water Chemistry of Southern Blue Ridge Province Streams

Environmental Variables	PCA Factors										
	1	2	3	4	5	6	7	8	9	10	11
HWET	89*	22	6	-10	13	9	-12	-21	6	5	-4
SO4WET	88*	21	5	-10	18	9	-17	-22	3	8	-4
K	88*	-14	-4	0	-28	-15	14	5	-1	-5	-6
K_H	87*	-14	-4	0	-27	-13	15	7	-1	-5	-5
CAMGWET	85*	18	1	-2	17	17	-19	-26	-4	11	-3
W_H	72*	31*	-2	5	-14	39*	4	18	-5	-9	-4
PPT	69*	10	-5	-17	4	44*	-28	-31*	-4	2	-10
L	9	99*	4	-2	0	0	-1	5	-1	-1	-2
M_H	9	99*	4	-2	0	0	-1	5	-1	-1	-2
L_H	9	99*	4	-2	0	0	-1	5	-1	-1	-2
M	9	99*	4	-2	0	0	-1	5	-1	-1	-2
H	-2	-7	98*	-3	5	-7	0	-4	0	-1	-2
H_H	-1	-8	98*	-4	3	-8	0	0	0	-1	-4
OPEN	-3	18	80*	33*	8	-14	-8	38*	-9	-4	1
C	7	64*	74*	-2	2	12	-4	-4	-3	-3	1
C_H	7	66*	70*	-2	-1	19	-5	-4	-3	-4	2
F	4	-17	-81*	-33*	-7	10	7	-39*	8	3	-8
U_H	1	-4	9	98*	-9	-1	0	11	-1	-2	-4
R	-8	-1	-1	98*	-6	-7	-1	12	0	0	-3
R_H	-8	-1	-1	98*	-6	-7	-1	12	0	0	-3
U	-6	-4	16	95*	-11	-1	-2	5	-3	-3	-6
MIX	-9	-9	-5	-18	89*	3	20	-8	4	3	12
CAMGDRY	31*	9	-7	-28	60*	51*	3	-14	12	13	-9
HWD	6	-1	-31*	2	-88*	-19	-14	-8	4	-2	11
CON	13	2	-8	-4	9	84*	-3	-8	-13	3	1
SO4DRY	-8	2	-1	-17	58*	-59*	-2	5	7	9	20
HDRY	-5	0	6	14	-17	-83*	-15	13	-14	-3	27
O	-12	-1	-4	-2	15	3	95*	-9	-4	-3	-4
O_H	-10	0	-3	-2	14	2	94*	-8	-4	-2	-2
G_H	-21	8	10	19	-23	-5	-7	87*	-4	-3	-2
G	-12	17	14	15	14	-14	-23	81*	-13	-9	9
RUNOFF	41*	9	-18	-23	-11	25	-23	-50*	4	-7	-8
Z_H	-3	-1	-4	-2	4	-3	-4	-7	98*	-2	-3
Z	-3	-1	-4	-2	4	-3	-4	-7	98*	-2	-3
F_H	26	-11	-17	-4	-44*	16	49*	7	49*	-8	-9
N	2	-2	-3	-2	6	2	-3	-4	-2	99*	-3
N_H	2	-2	-3	-2	6	2	-3	-4	-2	99*	-3
E	-7	-4	-1	-6	0	-11	-5	2	-4	-4	96*
E_H	-13	-4	0	-8	-14	-15	-1	6	-4	-2	94*

[a] Printed values are multiplied by 100 and rounded to the nearest integer. Values greater than 0.29 have been flagged by an asterisk.

Table 8-30. Interpretation of the First 11 Principal Components after Varimax Rotation of the Correlation Matrix of Land Use and Other Environmental Variables for Southern Blue Ridge Province Streams

Principal Component Rank	General Interpretation of Principal Component
PC1	overall wet and dry deposition and precipitation
PC2	cemeteries, cropland, and waste disposal land
PC3	cropland, horticulture, and open land
PC4	open land, urban lands, and wetlands
PC5	mixed forest and dry Ca plus Mg and SO_4 deposition
PC6	open water and dry Ca plus Mg deposition
PC7	miscellaneous and ungrazed forest land
PC8	open land and pasture; less precipitation
PC9	ridge top barren land and ungrazed forest
PC10	pits and quarries
PC11	grazed forest land

Table 8-31. Results of Regressions Relating Surface Water Chemistry of Northeastern Lakes to Land Use and Other Environmental Data[a]

Water Chemistry Variable	R^2	Factor No.	Regr. Sign	Signif.[b] Level	Factor Explanation
ANC	0.37	4	+	***	agriculture: SCS open dry, G, C
		12	-	***	precipitation and runoff
Ca + Mg	0.42	4	+	***	agriculture: see above
		12	-	***	precipitation/runoff
pH	0.32	2	-	**	deposition
		4	+	***	agriculture: see above
		7	+	*	open water and wetlands
		11	+	*	wetlands and horticulture: H, ELS_wet, SCS_wet
		12	-	***	precipitation and runoff
Sulfate	0.50	2	+	***	deposition
		3	-	*	beaver activity, water, wetlands
		4	+	***	agriculture: see above
		5	-	**	wetlands: SCS, LV, ELS
		7	-	*	open water and wetlands
		9	+	***	development: cabins, P, Uv, H; less forest
		12	-	S	precipitation/runoff
Percent Sulfur Retention	0.19	5	+	***	wetlands (see above)

[a] n = 143
[b] S = Significant at 0.15 level
   * = Significant at 0.05 level
  ** = Significant at 0.01 level
 *** = Significant at 0.001 level

state (Section 8.2), a positive correlation between surface water sulfate and sulfate deposition is expected. Increased sewage and animal or chemical waste loadings to streams from agricultural and residential development also lead to greater overall surface water sulfate levels. Although sulfate deposition was associated with surface water sulfate levels, amounts in surface waters were less in small watersheds when beaver activity and wetland percentage were high. Low downstream sulfate concentrations, caused by increased anaerobic conditions and sulfate retention behind beaver impoundments has been documented by others (Driscoll et al., 1987; Goldstein et al., 1987), especially during low-flow summer months.

Percent sulfur retention was positively related to wetland percent (Table 8-31). Anaerobic wetland conditions favor sulfate reduction processes that in turn foster increased sulfur retention.

8.5.4.2 Southern Blue Ridge Province

Singular land uses acted as either leverage points or outliers and influenced regressions relating land use to both sulfate and percent sulfur retention. For sulfate, important land uses were pits and quarries, open land, and pasture. Eliminating watersheds with these land uses left no significant land use factors in regression models (Table 8-32). Evidently, the watershed with pits and quarries land use had an internal source of sulfur. Agricultural practices on open land and pasture, including soil amendments and animal husbandry, may result in increased sulfate loadings.

8.5.4.3 Regional Comparisons

In the NE, sulfate is strongly and positively correlated with deposition and agricultural and urban development. Since soils in the region have little remaining sulfate adsorption capacity (Section 7, Rochelle et al., 1989), incoming sulfur deposition or within-watershed generated sulfur quickly circulates to surface waters after storm events. Exceptions are small watersheds with beaver activity or wetlands. In these watersheds, sulfate reduction processes are the probable cause of decreased surface water sulfate concentrations and increased percent sulfur retention.

In the SBRP region, surface water sulfate and percent sulfur retention are both influenced by local internal sulfur sources from pits and quarries and pasture land. However, when such watersheds are eliminated from regression models, the homogeneous nature of the region stands out: upland forested watersheds with little agricultural or urban development. Under such conditions, land use is unrelated to either surface water sulfate or percent sulfur retention. Instead, both variables are more controlled by high sulfate adsorption capacity of soils in the region (Section 7).

8.5.5 ANC, Ca plus Mg, and pH

8.5.5.1 Northeast

Lake ANC was positively correlated with agricultural land use and negatively correlated with precipitation/runoff (Table 8-31); both factors in the regression were highly significant ($p \leq 0.001$). In watersheds having a greater percentage of agricultural, urban, or other disturbed land (Buso et al., 1985), ANC values of surface waters are generally higher than those found in mostly-forested, small-headwater

Table 8-32. Results of Regressions Relating Sulfate and Percent Sulfur Retention of Southern Blue Ridge Province Streams to Land Use Data

Dependent Variable	R^2	n	Regress. Sign	Significant Factor/ Land Uses Included	Significance Level[a]	Watersheds Removed[b]
Sulfate	0.78	32	+	10/pits & quarries	***	
			+	8/open land & pasture	S	2A07813(L)
	0.80	31	+	10/pits & quarries	***	2A08808(L)
		30		no significant factors	---	---
Percent Sulfur Retention	0.76	32	-	10/pits & quarries	***	2A08808(L) 2A07823(O)
		30		no significant factors	---	---

[a] S = Significant at 0.15 level
*** = Significant at 0.001 level

[b] (L) = Leverage point removed from regression
(O) = Outlier point removed from regression

watershed systems (Hunsaker et al., 1986a; Jeffries et al., 1988). Where precipitation and runoff are high, ANC in surface waters is reduced because of dilution effects.

Lake Ca plus Mg was positively correlated with agricultural land use but negatively related to precipitation and runoff (Table 8-31); both factors in the regression were highly significant ($p \leq 0.001$). Successful farming and related activities are generally located on deeper and higher base status soils unless low soil pH and poor fertility are offset by applying lime and fertilizers (Tisdale and Nelson, 1975). Where acidic deposition is high, soil bases can be leached from the soil and replaced by hydrogen and aluminum ions (Section 3); bases leached from the soil are flushed rather quickly from lakes associated with high runoff. The positive correlation of Ca plus Mg with agriculture (Comeau and Bellamy, 1986) but negative correlation with greater precipitation and runoff is indicative of these relationships.

Surface water pH was positively correlated with agriculture, wetlands, and horticulture but negatively correlated with precipitation and runoff (Table 8-31); all factors were significant ($p \leq 0.05$) in the regression. Agricultural and lowland (cranberry) horticultural land uses could be associated with higher pH in surface waters via fertilizer inputs. Wetlands and water impounding via beaver activity also contribute to sulfate reduction (Driscoll et al., 1987a) and an increase in pH (Section 7.2). Where precipitation and runoff are high, lake pH will be reduced because of dilution effects.

8.5.5.2 Southern Blue Ridge Province

All regression models relating ANC, Ca plus Mg, and pH of SBRP streams to land use factors were strongly influenced by leverage points (Table 8-33). Since Ca plus Mg and ANC are chemically related surface water variables, those land uses that had potential and significant impact on one also influenced the other variable. In all instances, the significant land uses were those which allowed within-watershed inputs of base elements to SBRP streams. Deleting all the leverage points removed all significant land uses from the ANC and Ca plus Mg models. For pH, removing only one leverage point with open land and pasture left no significant land use in the regression.

As stated in Section 8.5.4.2, the SBRP region is very homogeneous in terms of forest and land cover; overall, there is little agricultural or urban development. Where anthropogenic development or disturbance is present, it has very marked and significant impacts on ANC, Ca plus Mg, and pH of local ·streams.

8.5.5.3 Regional Comparisons

Agricultural land uses, particularly cultivated land and pasture were positively correlated with ANC, Ca plus Mg, and pH in both the NE and SBRP. In the small SBRP region, single land uses were usually leverage points or outliers in the overall analysis. Removing SBRP watersheds with leverage points and outliers from the analysis produced a more homogeneous data set comprised mostly of forested watersheds with little urban or other development. Under these conditions, land use was not readily correlated with ANC, Ca plus Mg, or pH.

For northeastern lakes, sulfur deposition was negatively correlated with pH. Via sulfate reduction processes under anaerobic conditions, northeastern wetlands mitigate the effects of high sulfur deposition

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Table 8-33. Results of Regressions Relating ANC, Ca plus Mg, and pH of Southern Blue Ridge Province Streams to Land Use Data

Dependent Variable	n	R^2	Regr. Sign	Significant Factors/ Land Uses Included	Significance Level[a]	Watersheds Removed[b]
ANC	32	0.11	+	8/ open land and pasture	S	2A07827(L) 2A07813(L)
	30	0.50	+	2/cemeteries, wasteland	*	---
			+	3/cropland, horticulture, open land	***	2A07802(L)&
			+	4/open land, urban areas, wetland	S	2A07826(L)& 2A07830(L)
	27	0.21	+	4/open land, urban areas, wetland	S	---
			+	10/pits and quarries	*	2A08808(L)
	26			no significant factors	---	---
Ca+Mg	31	0.28	+	10/pits and quarries	*	2A08808(L)
	30	0.21	+	10/pits and quarries	**	2A07813(L)
	28	0.18	+	3/cropland, horticulture, open land	S	2A07826(L)
			+	10/pits and quarries		2A07827(L)
	26	0.35	+	2/cemeteries, waste land	**	2A07802(L)
			+	4/open land, urban areas, wetlands	*	2A07830(L)
	25			no significant factors	---	---
pH	31	0.12	+	8/open land and pasture	S	2A07813(L)
	30			no significant factors	---	---

[a] S = Significant at 0.15 level
* = Significant at 0.05 level
** = Significant at 0.01 level
*** = Significant at 0.001 level

[b] (L) = Leverage point removed from regression
(O) = Outlier point removed from regression

and are associated with higher lake pH. In SBRP upland forested watersheds, there are few wetland or riparian zones to mitigate deposition effects on stream pH. Presently, however, high sulfate adsorption capacity of SBRP soils does help minimize deposition effects on stream water chemistry.

8.5.6 Summary and Conclusions

The major findings of this section are:

- In the NE, surface water sulfate is positively correlated with deposition and extent of agricultural and urban development.

- In small northeastern watersheds with beaver activity and wetlands, sulfate reduction processes decrease surface water sulfate concentrations and increase percent sulfur retention and pH.

- In the SBRP region, surface water sulfate and sulfur retention are influenced by local internal sulfur sources from pits and quarries.

- Agricultural land uses, particularly cultivated land and pasture were correlated with ANC, Ca plus Mg, and pH in both the NE and SBRP. However, in the SBRP region, removing outlying or influential sites produced a homogeneous dataset in which land use was not readily correlated with ANC, Ca plus Mg, and pH.

- In both the NE and SBRP, forest cover is not directly related to surface water chemistry; in the NE, greater developed land (and less forest) is correlated with higher surface water ANC, Ca plus Mg, pH, and sulfate.

8.6 MAPPED SOILS

8.6.1 Introduction

Soils are an important component of terrestrial ecosystems. They are the principal source of plant nutrients and provide a rooting medium for aboveground vegetation; they are the major site of within watershed decomposition reactions. Soils host a plenitude of chemical reactions, including adsorption, desorption, ion exchange, weathering, and precipitation reactions. These chemical reactions can affect the composition and quality of soil water and consequently subtending surface and ground waters. Soil physical properties, such as structure or architecture, the flowpath of soil water, the soil particle-size distribution, the depth to impermeable layers, and soil bulk density, are also important. In natural settings, the chemical and physical attributes of soils are inseparable. The objective of this analysis is to identify the relationships that exist between mapped soils and surface water chemistry on a regional basis.

Some soils are known to attenuate some of the effects of chronic sulfur deposition principally through sulfate adsorption and base cation supply reactions (e.g., cation exchange and mineral weathering). These reactions are important in isolation at the atomic level, however, as the scales become coarser (i.e., atomic to micro, micro to meso, meso to watershed, watershed to regional) the number of simultaneous, overlapping processes increases. At the regional scale the relationship between soil properties and soil water chemistry involves thousands of hectares of soils and the composition of

a large number of lakes or many kilometers of stream reaches. The relatively simple set of relationships (at the atomic level) becomes a complex set of diffuse relationships as the scale expands to the region. Recognition of the fact that soils *per se* integrate a large number of physical and chemical processes is the basis of the DDRP mapped soils analysis. In this analysis we use the proportion of different kinds of soils in watersheds, at a well-defined but regional scale, to identify relationships that exist between soils and the chemical composition of subtending surface waters.

8.6.2 Approach

As discussed in the Sections 4.1 and 4.2 and described in Lee et al. (1989a), a stratified random sample of watersheds was selected and mapped in the DDRP. Mapping followed strict protocols, and soil map units were regionally defined and correlated across the respective regions. The details of watershed selection, map unit correlation, and mapping can be found in Sections 5.2 and 5.4.

In the NE 592 kinds of soils were identified. These soils are the components of the 338 map units used to map the soils in the NE. In the SBRP 286 components and 176 map units were identified. Because it was not tractable to characterize this large number of soils it became apparent that a smaller set of soil units were needed to make regional soil characterization and sampling feasible. The result was the development of the soil "sampling classes". Soil components considered to have similar chemical and physical characteristics were grouped into unique classes that we termed a soil sampling class. In the NE, 38 different sampling classes were identified, and in the SBRP there were 12. Soil sampling classes were the basis for soil sampling and analytical characterization and served as our main link between the analytical data and the soils of the regions. They also serve as the basic units for relating mapped soils to surface waters in this analysis.

All watersheds are not completely covered by soils. Other non-soil cover is present and can, sometimes, extend over large areas. To completely assess the relationships between soils and surface water chemistry, such areas that occurred on our sample of watersheds were also identified during the mapping and were termed "miscellaneous land areas". Because these areas may influence the quantity and quality of surface waters they are included in this analysis. In the NE these include: rock outcrop (M01); pits, gravel (M02); rubble land (M03); and pits, quarry (M04). In the SBRP there were only two miscellaneous land areas: rock outcrop (MRO) and quarry pits (MPQ).

An overview of how this analysis was conducted is presented in Figure 8-8. After the soil maps were digitized, a summary of the soil map units and their extent on each watershed was obtained from the GIS for each region. The relative proportion of each map unit component had been estimated for the regions and entered into a mapping data file. Each map unit component had been assigned to a sampling class and, therefore, the proportion of each sampling class in the respective watersheds could be calculated. For example, 112 ha of map unit 134A was mapped on a particular watershed and map unit 134A was defined by three components (a, b, and c) with the following percentages: 80 percent component a, 15 percent component b, and 5 percent component c. Component a therefore accounts for 89.6 ha (112 ha x 0.80) of the 112 ha of map unit 134A while b and c account for 16.8 ha and 5.6 ha, respectively. This calculation was repeated for each map unit on a watershed basis and the results were pooled by sampling class. The proportions of the watersheds in the various soil sampling classes

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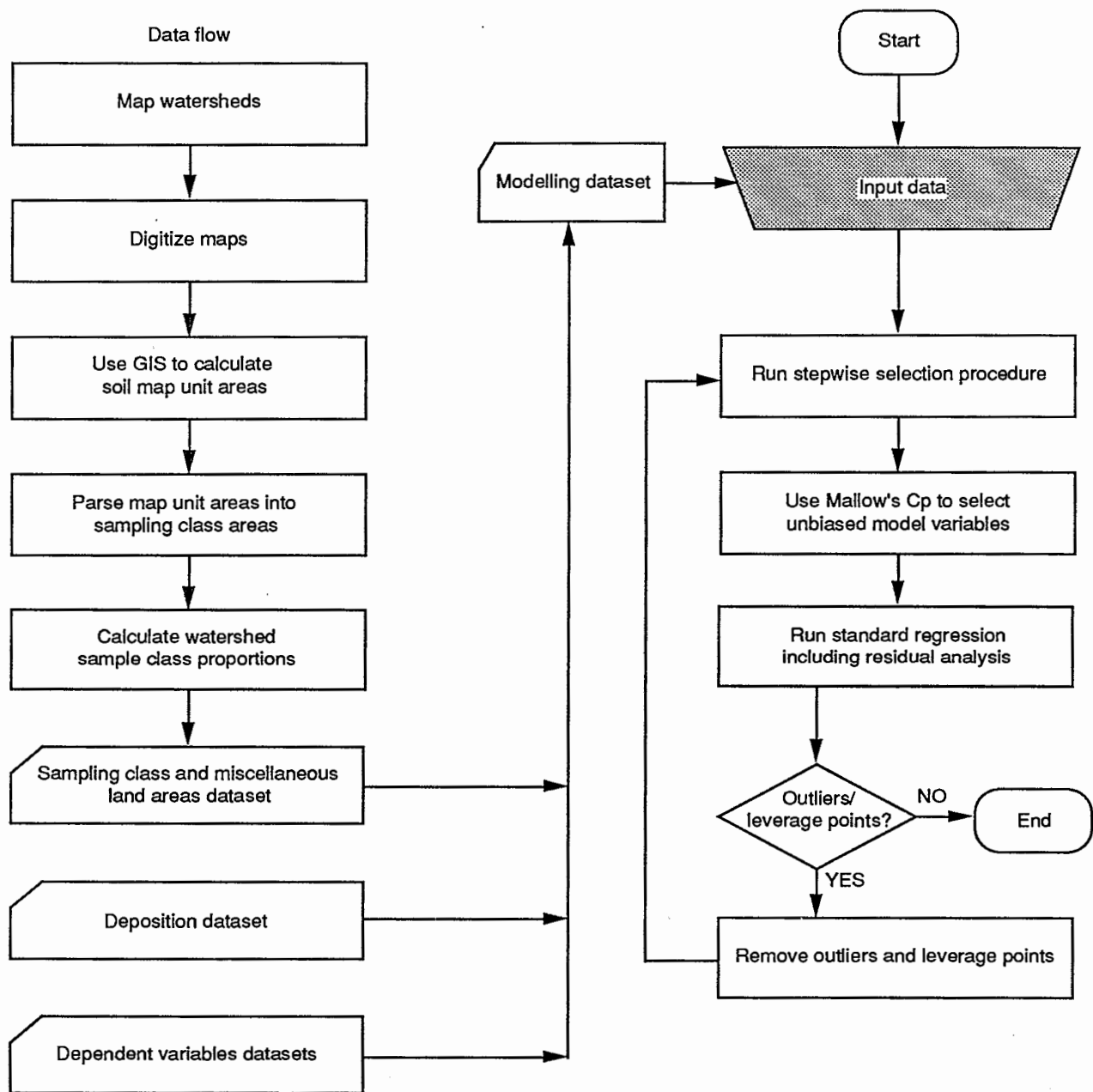
Figure 8-8. Data and regression model development flow diagrams.

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and miscellaneous land areas were calculated by dividing the extent of the soil sampling class or miscellaneous land area by the total area of the watershed.

With the GIS we can dissect or subdivide the watersheds to test various hypotheses. We are particularly interested in evaluating the effect of the riparian zone (near-lake or near-stream) on surface water chemistry. In the NE, two watershed buffer zones were considered in addition to the whole watershed area. One is limited to the area within the first 40-ft contour interval (called the 40-ft contour buffer zone) above the sampled lake. This buffer zone is used to delineate the near-lake soils and wetlands. The other includes the same 40-ft contour buffer zone plus a 30-m linear buffer on either side of any perennial (blue-line) stream and around contiguous wetlands. It also includes a 40-ft contour buffer zone around any other lakes or ponds that are on the watershed in addition to the sampled lake. Due to contour map distortions or errors there are only 144 watersheds in the 40-ft buffer zone dataset and 143 in the combined buffer dataset. Because the resource of interest in the SBRP is streams, elevational or contour buffer zones are not suitable, so linear buffer zones were used. These include the area within 100 m of the blue-line streams on the DDRP sample of watersheds in the SBRP. Because 2 of the 35 SBRP streams are not perennial, the SBRP buffer zone dataset has a sample size of 33. Tables 8-34 through 8-38 summarize the distributions of the soil sampling classes and miscellaneous land areas on the DDRP sample of watersheds. Table 8-34 is for whole watersheds in the NE, Table 8-35 is for the land within the 40-ft GIS contour buffer zone, and Table 8-36 is for the combined GIS buffer zones. Table 8-37 is for the whole watersheds in the SBRP, and Table 8-38 is for the GIS 100-m linear buffer zones.

Soils alone cannot explain all of the variation in surface water chemistry. Other factors such as deposition and in-lake or in-stream processes also influence surface water chemistry. Regional data on in-lake and in-stream processes do not exist, but deposition data do. For this analysis we include six variables from the long-term annual average data sets. The details of how these data were compiled are described in Section 5.6.3. The specific variables used in this analysis are discussed in Section 8.1.1. A total of 48 independent variables are used the NE (38 soil sampling classes plus 4 miscellaneous land areas plus 6 deposition variables) and 20 in the SBRP (12 soil sampling classes plus 2 miscellaneous land areas plus 6 deposition variables). The dependent variables include four surface water chemical measurements, sulfate (μeq L^{-1}), ANC (in μeq L^{-1}), Ca plus Mg (CAMG in μeq L^{-1}), and pH. A fifth variable, % S retention, is a calculated variable derived from deposition and surface water chemistry values (See Section 7 for details on how the percent sulfur retention values were calculated).

8.6.3 Sulfate and Sulfur Retention

The retention of sulfur by terrestrial ecosystems is an important mechanism that can delay the acidification of subtending surface waters. In the biogeochemical sulfur cycle there are two principal soil or sediment mediated sulfur retention mechanisms; sulfate adsorption and sulfate reduction. These mechanisms have been characterized and discussed in Sections 3.3, 7, and 9.2 in detail. Soils low in organic matter content having significant amounts of hydrous oxides of iron and aluminum will tend to retain sulfate via adsorption. Soils or sediments that are sufficiently wet to have anaerobic conditions retain sulfate via sulfate reduction.

Table 8-34. Summary Statistics for Percent Area Distribution of the 38 Soil Sampling Classes and the 4 Miscellaneous Land Areas on the DDRP Sample of 145 NE Lake Watersheds

SMPLCLAS	MEAN	STD_DEV	MIN	Q1[a]	MEDIAN	Q3[a]	MAX
E02	0.4	1.0	0.0	0.0	0.0	0.1	6.6
E03	5.4	19.6	0.0	0.0	0.0	0.0	99.9
E05	2.1	2.5	0.0	0.0	1.4	2.8	14.4
E06	0.2	1.0	0.0	0.0	0.0	0.0	7.3
H01	2.3	4.2	0.0	0.0	1.0	3.0	33.9
H02	1.0	3.2	0.0	0.0	0.0	0.1	19.2
H03	3.6	5.2	0.0	0.0	1.4	5.7	42.3
I01	1.5	3.3	0.0	0.0	0.3	1.8	26.7
I02	3.2	5.2	0.0	0.0	0.6	3.7	22.9
I05	1.5	4.6	0.0	0.0	0.0	0.0	27.0
I06	1.8	5.5	0.0	0.0	0.0	0.0	26.6
I09	1.4	6.0	0.0	0.0	0.0	0.0	48.8
I10	3.1	10.2	0.0	0.0	0.0	0.0	78.0
I11	1.3	5.0	0.0	0.0	0.0	0.0	39.8
I21	0.3	3.3	0.0	0.0	0.0	0.0	38.1
I25	4.3	11.1	0.0	0.0	0.0	0.0	47.0
I29	3.2	9.0	0.0	0.0	0.0	0.0	48.2
I30	0.5	1.9	0.0	0.0	0.0	0.0	13.2
I33	6.0	15.7	0.0	0.0	0.0	0.0	65.1
I37	0.3	0.8	0.0	0.0	0.0	0.3	4.8
I38	1.2	3.2	0.0	0.0	0.1	0.9	27.9
I40	1.1	7.0	0.0	0.0	0.0	0.0	79.9
I41	0.2	1.0	0.0	0.0	0.0	0.0	11.3
I42	0.2	1.2	0.0	0.0	0.0	0.0	13.4
I46	1.6	5.7	0.0	0.0	0.0	0.0	35.6
S01	0.3	1.0	0.0	0.0	0.0	0.1	7.8
S02	2.8	11.5	0.0	0.0	0.0	0.0	99.8
S05	0.7	2.0	0.0	0.0	0.0	0.1	17.6
S09	8.7	12.9	0.0	0.0	1.1	13.2	55.8
S10	1.9	5.9	0.0	0.0	0.0	0.1	46.0
S11	4.8	9.9	0.0	0.0	0.7	3.0	56.3
S12	6.8	8.8	0.0	0.0	3.3	12.4	36.4
S13	7.0	9.0	0.0	0.0	3.9	12.7	60.5
S14	9.0	12.7	0.0	0.0	1.2	15.5	52.4
S15	1.3	5.6	0.0	0.0	0.0	0.0	49.5
S16	2.5	7.6	0.0	0.0	0.0	0.0	34.6
S17	1.5	7.1	0.0	0.0	0.0	0.0	56.7
S18	1.6	5.5	0.0	0.0	0.0	0.0	29.5
M01	3.3	5.1	0.0	0.1	1.6	4.1	28.4
M02	0.1	0.7	0.0	0.0	0.0	0.0	7.0
M03	0.0	0.0	0.0	0.0	0.0	0.0	0.3
M04	0.0	0.1	0.0	0.0	0.0	0.0	0.9

[a] Q1 is the 25th percentile, and Q3 is the 75th percentile.

Table 8-35. Summary Statistics for the Percent Area Distribution of the 38 Soil Sampling Classes and the 4 Miscellaneous Land Areas in the GIS 40-ft Contour on the DDRP Sample of 145 NE Lake Watersheds

SMPLCLAS	MEAN	STD_DEV	MIN	Q1[a]	MEDIAN	Q3[a]	MAX
E02	1.6	4.1	0.0	0.0	0.0	0.1	20.2
E03	6.3	19.9	0.0	0.0	0.0	0.0	100.1
E05	1.0	1.6	0.0	0.0	0.2	1.6	11.1
E06	0.2	1.2	0.0	0.0	0.0	0.0	8.2
H01	1.2	3.0	0.0	0.0	0.0	0.8	19.0
H02	2.0	6.8	0.0	0.0	0.0	0.0	48.8
H03	10.1	12.5	0.0	0.0	3.0	18.9	60.0
I01	2.6	6.4	0.0	0.0	0.5	1.9	40.9
I02	3.7	7.3	0.0	0.0	0.6	3.1	39.9
I05	1.0	3.6	0.0	0.0	0.0	0.0	22.8
I06	1.1	4.0	0.0	0.0	0.0	0.0	22.2
I09	1.3	5.4	0.0	0.0	0.0	0.0	34.9
I10	2.4	8.0	0.0	0.0	0.0	0.0	73.9
I11	1.1	4.4	0.0	0.0	0.0	0.0	37.6
I21	0.3	3.0	0.0	0.0	0.0	0.0	34.9
I25	6.2	16.8	0.0	0.0	0.0	0.0	77.5
I29	2.0	6.2	0.0	0.0	0.0	0.0	33.0
I30	0.3	1.3	0.0	0.0	0.0	0.0	10.9
I33	4.8	13.8	0.0	0.0	0.0	0.0	75.8
I37	1.0	2.9	0.0	0.0	0.0	0.8	22.5
I38	2.3	5.6	0.0	0.0	0.0	1.4	43.9
I40	1.2	7.4	0.0	0.0	0.0	0.0	80.1
I41	0.3	1.4	0.0	0.0	0.0	0.0	11.5
I42	0.7	3.3	0.0	0.0	0.0	0.0	31.3
I46	2.6	10.1	0.0	0.0	0.0	0.0	66.1
S01	0.9	2.9	0.0	0.0	0.0	0.0	18.0
S02	6.6	19.1	0.0	0.0	0.0	0.0	99.9
S05	1.1	3.9	0.0	0.0	0.0	0.0	30.2
S09	6.0	13.0	0.0	0.0	0.0	4.6	69.8
S10	2.7	8.9	0.0	0.0	0.0	0.1	53.9
S11	4.4	10.3	0.0	0.0	0.0	2.1	49.2
S12	3.4	6.5	0.0	0.0	0.2	3.1	35.4
S13	3.3	6.7	0.0	0.0	0.0	3.8	59.4
S14	8.0	12.3	0.0	0.0	1.1	12.4	51.8
S15	0.6	3.4	0.0	0.0	0.0	0.0	38.0
S16	1.6	5.6	0.0	0.0	0.0	0.0	39.3
S17	1.1	6.8	0.0	0.0	0.0	0.0	60.9
S18	1.0	3.7	0.0	0.0	0.0	0.0	23.6
M01	1.6	3.4	0.0	0.0	0.2	1.6	24.8
M02	0.1	1.1	0.0	0.0	0.0	0.0	10.2
M03	0.0	0.1	0.0	0.0	0.0	0.0	1.2
M04	0.0	0.0	0.0	0.0	0.0	0.0	0.0

[a] Q1 is the 25th percentile, and Q3 is the 75th percentile.

Table 8-36. Summary Statistics for the Percent Area Distribution of the 38 Soil Sampling Classes and the 4 Miscellaneous Land Areas in the Combined GIS Buffers on the DDRP Sample of 145 NE Lake Watersheds

SMPLCLAS	MEAN	STD_DEV	MIN	Q1[a]	MEDIAN	Q3[a]	MAX
E02	1.5	3.8	0.0	0.0	0.0	0.1	19.4
E03	6.0	19.7	0.0	0.0	0.0	0.0	100.1
E05	1.1	1.7	0.0	0.0	0.3	1.6	11.5
E06	0.2	1.4	0.0	0.0	0.0	0.0	11.2
H01	1.4	3.2	0.0	0.0	0.0	1.1	20.4
H02	2.4	7.0	0.0	0.0	0.0	0.1	49.0
H03	9.6	11.5	0.0	0.0	3.3	17.3	60.0
I01	2.9	7.0	0.0	0.0	0.4	1.9	41.2
I02	4.4	7.7	0.0	0.0	0.8	4.1	39.9
I05	1.0	3.5	0.0	0.0	0.0	0.0	23.0
I06	1.1	3.8	0.0	0.0	0.0	0.0	22.0
I09	1.1	4.9	0.0	0.0	0.0	0.0	34.9
I10	2.5	8.6	0.0	0.0	0.0	0.0	73.9
I11	1.0	3.5	0.0	0.0	0.0	0.0	26.4
I21	0.2	2.4	0.0	0.0	0.0	0.0	27.9
I25	6.9	17.7	0.0	0.0	0.0	0.0	74.4
I29	1.7	5.3	0.0	0.0	0.0	0.0	32.7
I30	0.2	1.0	0.0	0.0	0.0	0.0	8.1
I33	4.6	12.6	0.0	0.0	0.0	0.0	62.5
I37	0.9	2.2	0.0	0.0	0.0	0.7	14.2
I38	2.5	5.6	0.0	0.0	0.0	1.7	43.5
I40	1.3	7.4	0.0	0.0	0.0	0.0	80.1
I41	0.2	1.2	0.0	0.0	0.0	0.0	11.5
I42	0.4	1.7	0.0	0.0	0.0	0.0	17.1
I46	2.7	10.3	0.0	0.0	0.0	0.0	65.6
S01	0.9	2.7	0.0	0.0	0.0	0.2	16.4
S02	5.6	17.4	0.0	0.0	0.0	0.0	100.2
S05	1.1	3.8	0.0	0.0	0.0	0.0	30.2
S09	6.1	12.8	0.0	0.0	0.3	6.1	69.8
S10	2.5	7.7	0.0	0.0	0.0	0.0	53.9
S11	4.1	9.6	0.0	0.0	0.1	2.2	51.9
S12	3.7	6.6	0.0	0.0	0.2	5.0	35.4
S13	3.5	6.7	0.0	0.0	0.0	4.7	59.4
S14	8.3	12.3	0.0	0.0	1.0	12.4	53.1
S15	0.7	2.8	0.0	0.0	0.0	0.0	24.4
S16	1.7	5.6	0.0	0.0	0.0	0.0	40.6
S17	1.1	7.0	0.0	0.0	0.0	0.0	64.9
S18	1.0	3.7	0.0	0.0	0.0	0.0	23.6
M01	1.7	3.5	0.0	0.0	0.3	1.6	25.1
M02	0.1	0.7	0.0	0.0	0.0	0.0	6.7
M03	0.0	0.1	0.0	0.0	0.0	0.0	0.8
M04	0.0	0.0	0.0	0.0	0.0	0.0	0.6

[a] Q1 is the 25th percentile, and Q3 is the 75th percentile.

Table 8-37. Summary Statistics for the Percent Area Distribution of the 12 Soil Sampling Classes and the 2 Miscellaneous Land Areas on the DDRP Sample of 35 SBRP Stream Watersheds

SMPLCLAS	MEAN	STD_DEV	MIN	Q1[a]	MEDIAN	Q3[a]	MAX
ACC	17.7	28.3	0.0	0.0	0.7	28.8	80.1
ACH	5.9	9.7	0.0	0.0	0.5	8.5	37.8
ACL	32.9	26.3	0.0	1.8	30.7	57.1	78.2
FL	2.5	3.1	0.0	0.0	0.9	4.0	10.7
FR	4.2	10.2	0.0	0.0	0.0	0.0	43.2
MSH	2.8	7.3	0.0	0.0	0.0	0.0	48.1
MSL	11.2	16.4	0.0	0.0	0.0	21.9	61.7
OTC	2.5	10.5	0.0	0.0	0.0	0.0	52.3
OTL	4.9	9.2	0.0	0.2	1.1	3.4	37.6
SHL	7.4	8.7	0.0	0.0	5.1	15.0	30.0
SKV	5.1	8.2	0.0	0.0	0.6	7.0	36.0
SKX	1.6	3.3	0.0	0.0	0.0	1.3	18.1
MPQ	0.1	0.5	0.0	0.0	0.0	0.0	2.8
MRO	1.2	1.9	0.0	0.0	0.7	1.5	15.0

[a] Q1 is the 25th percentile, and Q3 is the 75th percentile.

Table 8-38. Summary Statistics for the Percent Area Distribution of the 12 Soil Sampling Classes and the 2 Miscellaneous Land Areas in the 100-Meter Linear GIS Buffer on the DDRP Sample of 35 SBRP Stream Watersheds

SMPLCLAS	MEAN	STD_DEV	MIN	Q1[a]	MEDIAN	Q3[a]	MAX
ACC	5.1	10.9	0.0	0.0	0.7	1.8	40.7
ACH	10.6	14.8	0.0	0.0	0.9	24.9	43.7
ACL	24.6	20.7	0.0	0.1	25.0	36.6	71.0
FL	11.1	12.9	0.0	1.0	8.1	15.8	54.8
FR	2.9	7.2	0.0	0.0	0.0	0.0	27.6
MSH	4.4	10.1	0.0	0.0	0.0	0.0	59.0
MSL	10.1	14.2	0.0	0.0	0.0	17.6	42.0
OTC	6.8	19.9	0.0	0.0	0.0	0.0	79.1
OTL	5.2	6.7	0.0	0.6	2.0	6.1	24.4
SHL	6.4	8.3	0.0	0.2	2.8	12.8	28.8
SKV	10.7	14.4	0.0	0.0	3.0	16.4	50.8
SKX	1.0	2.3	0.0	0.0	0.0	0.0	11.7
MPQ	0.2	1.0	0.0	0.0	0.0	0.0	5.8
MRO	0.9	1.5	0.0	0.0	0.1	2.3	10.2

[a] Q1 is the 25th percentile, and Q3 is the 75th percentile.

Sulfate concentrations in the DDRP SBRP sample of streams are, in general, much lower than in the sample of lakes in the NE. However, the region as a whole has somewhat higher sulfur deposition than the NE. The deposition in the SBRP is more uniform than in the NE. Because the SBRP is a relatively small region with relatively uniform deposition, there is not a significant sulfate deposition gradient as in the NE. Unlike the NE the watersheds in the SBRP are not at sulfur steady state. A principal difference between the two regions is the soils. In the NE the soils are relatively young, having less profile and secondary mineral development. In the SBRP most soils are relatively older and more deeply weathered with abundant accumulations of secondary mineral phases (hydrous oxides of iron and aluminum).

8.6.3.1 Northeast

Following the procedures described above and in Section 8.1, several regression models were developed for the relationship between the independent variables (mapped soils and deposition) and lake sulfate. The results are presented in Table 8-39. The first whole watershed model for lake sulfate had an R^2 of 0.73. Two observations, however, had unusually high lake sulfate concentrations and wereidentified as being outlier and/or leverage points. These watersheds also had the only two occurrences of the miscellaneous land area, M04 -- quarry pits. This finding is consistent with the observation that major watershed disturbances, such as mining, may outweigh any surface water chemistry effects due to acidic deposition. Removing the watersheds with quarry pits and one other leverage point from the whole watershed analysis resulted in the model R^2 statistic dropping from 0.73 to 0.64. The variables in the regression model, however, remained the same, except for M04 which is now excluded. Table 8-39 shows the variables that were included in the lake sulfate regression models, indicated by the sign of their respective parameter estimates. These signs indicate either positive or negative correlation to the dependent variable. The inclusion of both wet and dry sulfate deposition in the regression models for the NE is not surprising. In the 142 observation, whole watershed model these two variables account for about 45 percent of the variability in lake sulfate. As discussed in Section 7, the NE is almost at sulfur steady state (i.e., input $\approx$ output) which explains why these two variables make such a large contribution to the explanatory power of the model.

In addition to sulfur deposition variables, eight soil sampling classes are included in the best whole watershed regression model for lake sulfate. Sampling classes E03, H03, and I33 were consistently included in the lake sulfate regression models. E03 is positively correlated with lake sulfate. This sampling class is characterized by coarse texture, poor development, and low sulfate adsorption capacity. These soils are excessively drained and seem to be a non-interacting conduit for drainage waters. Likewise, I06 and I11 are well drained and positively related with lake sulfate. These three soil sampling classes, however, generally occur only in Subregion 1D. Therefore, it is also plausible that these three sampling classes (E03, I06, and I) are surrogates for sea-salt sulfate contributions that may be underestimated in the LTA deposition dataset. Their inclusion in the regression model, may have little to do with their actual chemical and physical properties.

H03 was consistently negatively related to lake sulfate. The H03 soils are deep, wet, organic soils characterized by low pH (dysic). Because of the negative correlation, these soils are thought to be an active site of sulfur retention via biological processes (e.g., sulfate reduction), and would be expected to have a positive relationship with percent sulfur retention. The analysis indicates that sampling class

Table 8-39. Lake Sulfate and Percent S Retention Regression Models Developed for NE Lakes Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes) and Miscellaneous Land Areas (as a Percentage of Watershed Area) as Candidate Independent Variables[a]

	Lake Sulfate			Percent S Retention		
	Whole	40-ft	Comb.	Whole	40-ft	Comb.
SO4-Wet	+	+				
SO4-Dry	+	+	+			
Ca+Mg-Dry				-	-	-
E03	+	+	+			
H01				-	-	-
H03	-	-	-	+	+	+
I06	+					
I11	+					
I25	+		+			
I30		+				
I33	-	-	-		+	+
S02	-					
S12	+		+			
S17					+	+
S18		+	+	-	-	-
R^2	0.64	0.61	0.59	0.31	0.39	0.44
adjusted R^2	0.61	0.59	0.57	0.29	0.36	0.41
n-lakes[b]	142	141	141	141	142	140
p-model[c]	10	7	7	4	6	6
O/L[d]	3	3	2	4	2	3

[a] + and - refer to positive and negative parameter estimates, respectively
[b] n-lakes = number of observations used to develop the regression model
[c] p-model = number of regressor variables in model
[d] O/L = number of outlier or leverage points omitted

I25 is positively correlated with lake sulfate concentrations and that I33 is negatively related. Fragipans occur in the soils of both of these classes within 100 cm of the soil surface. The principal difference between these sampling classes is that I25 soils are very poorly to somewhat poorly drained while I33 soils are somewhat poorly drained to well drained and deep. Anaerobic conditions occur throughout the upper 100 cm of soil in the I25 class during some part of the year. Intuitively, this would suggest that this class of soils should have a negative relationship with lake sulfate concentrations rather than a positive one, because of the potential for sulfate reduction during the anaerobic periods. Other factors such as the landscape position of these soils and the timing and nature of the anaerobic periods may be responsible for the observed relationship.

The S12 class of soils is well drained, moderately deep, coarse-loamy Spodosols with relatively low base saturation and pH. Water moves rapidly through this class of soils and moves downhill at the bedrock contact with little opportunity for sulfur retention. There is a positive relationship between S12 soils and lake sulfate. The reason for the negative relationship between the S02 class and lake sulfate is unclear from this analysis; S02 soils may be a surrogate for another attribute.

In the NE the percent % S retention values range from -22 to +60, with a median value of -4. In contrast, in the SBRP the range is from -60 to +89, with a median value of 75 percent. In the NE the systems are almost at steady state with respect to sulfur. In contrast, the SBRP is effectively retaining most of the sulfur inputs. We would expect markedly different results in the regression analysis.

In the NE (see Table 8-39) the best whole watershed model explains only 31 percent of the variation in percent sulfur retention with a four-variable model. The best model is a six-variable model using the combined buffer data with an R^2 of 0.44. The sum of dry Ca and Mg deposition, H01, H03, and S18 was included in all three models; H03 soils have a positive parameter estimate. The H01 soils are thin (< 30 cm), organic soils overlaying bedrock or fragmental material that is freely drained. They are not wetland soils. They are probably active sites of organic matter decomposition and contribute sulfur from organic matter to the surface waters. The class H03, as described earlier, includes wetland soils that presumably retain sulfur via a sulfate reduction mechanism. Sampling class S18 soils are shallow and somewhat excessively drained. They are likely to be non-interacting conduits for drainage waters. The I33 and S17 classes are positively related to percent sulfur retention in the buffer zone models. The relationship with I33 was not as expected as was discussed with the lake sulfate results above. The reason for inclusion of dry Ca plus Mg deposition in the models is not known. It may be an artifact of the deposition data compilation or it may be functioning as a surrogate for another deposition variable.

8.6.3.2 Southern Blue Ridge Province

The regression models developed for the stream sulfate concentrations are summarized in Table 8-40. The results for seven models are included: four using the soils and miscellaneous land area distributions on the whole watersheds and three for the distributions in the 100 meter buffers.

The whole watershed model with 35 observations includes five variables that are all positively correlated with stream sulfate. One is the miscellaneous land area, MPQ. As noted in the NE, the occurrence of quarries on watersheds can have a significant effect on the subtending surface water chemistry. The effect on the surface water is dependent upon the type of geological strata being mined.

Table 8-40. Regression Models of Sulfate in SBRP Streams, Developed Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes) and Miscellaneous Land Areas (as a Percentage of Watershed Area) as Candidate Independent Variables[a]

	Whole Watersheds				100-m buffer zones		
Ca+Mg-Wet						-	
OTC	+	-			+		
ACH						-	
MSH						-	
SHL	+	+		+	+		+
OTL	+	+	+		+	+	+
MSL	+	+	+		+	+	+
MPQ	+						
R^2	0.84	0.63	0.45	0.30	0.82	0.66	0.57
adjusted R^2	0.82	0.58	0.42	0.28	0.79	0.59	0.52
n-streams[b]	35	33	32	31	33	31	30
p-model[c]	5	4	2	1	5	5	3
O/L[d]	none	2	3	4	none	2	3

[a] + and - refer to positive and negative parameter estimates, respectively
[b] n-lakes = number of observations used to develop the regression model
[c] p-model = number of regressor variables in model
[d] O/L = number of outlier or leverage points omitted

In the SBRP sample population of watersheds, there was one occurrence of MPQ. The surface water in this watershed had the highest observed value of stream sulfate concentration and the lowest % S retention. It is likely that the mining on this watershed has exposed sulfur-bearing materials which have subsequently oxidized and impacted the surface water. The Anakeesta Formation (King et al., 1968), which contains sulfur-bearing minerals is common in parts of the SBRP. Watershed disturbances, such as road construction and landslides, may expose these materials as well.

The SHL and OTL soils, as defined in Section 5, are both well drained and have relatively low organic matter content. SHL soils are shallow and OTL soils are deep. In general, the soils in these sampling classes have low sulfate adsorption capacities. The OTC soils, however, only occur on three watersheds in the SBRP DDRP sample, and in one instance they cover more than 50 percent of the watershed. These soils, while high in secondary clay minerals, have pH values that are unfavorable for sulfate adsorption and therefore do not retain sulfate to any significant degree. The watershed with the high OTC coverage also had the second highest stream sulfate concentration. In addition to low sulfate adsorption potential, it is likely that the calcareous parent material of the OTC is interbedded with sulfur-bearing materials. In the 33 observation, whole watershed model, the watersheds with more than 50 percent OTC coverage and the MPQ site are not included. The resulting model is the same as the 35 observation model, except that it no longer has MPQ and the sign on the OTC variable is negative. The sign reversal is probably caused by the low abundance of OTC on the two remaining OTCs. The 32 observation model has one OTC site remaining with 0.1 percent OTC coverage. In this mode, OTC was not a significant explanatory variable in this model. The 31 observation model only had one significant explanatory variable, the SHL sampling class. The soils in the SHL sampling class account for 30 percent of the variability in stream sulfate concentrations alone. These soils are well drained, low in clay, have moderate to rapid permeability, and are less than 50 cm deep. These four properties are characteristic of soils with short hydrologic contact times that have little or no effect on the chemistry of drainage waters passing through them. Surface waters in watersheds with an abundance of shallow soils will be more susceptible to acidification than watersheds with deep, moderately well-drained soils.

The soils in the MSL sampling class were consistently selected with positive parameter estimates in the stream sulfate regression models. This suggests that as the proportion of MSL soils on a watershed increases, the concentration of sulfate in the subjacent stream also increases. The soils in the MSL sampling class are, by definition, derived from metasediments and have low organic matter content. Chemically, they have only intermediate sulfate adsorption potential. The positive parameter estimates indicate, however, that these soils may be associated with sulfur-bearing materials.

The 33 observation, 100-m buffer model is similar to the 35 observation, whole watershed model, but has lower R^2 and adjusted R^2 values. In the 31 observation model, the ACH and MSH sampling classes both have negative parameter estimates. These soils as a group have relatively higher organic matter content in the surface layer than their ACC and MSL counterparts. This implies that, when these sampling classes occur in the near-stream zone, sulfate is retained. The 30 observation model has only three variables, SHL, OTL, and MSL, and explains approximately 60 percent of the variation in stream sulfate concentrations.

The regression model results for sulfur retention in the SBRP are presented in Table 8-41. The whole watershed model with 35 observations has an R^2 of 0.86. This R^2 is highly inflated by the presence

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of one watershed. This watershed was the only observation with a negative net sulfur retention (-66 percent). It is also the watershed with the quarry (MPQ), which serves as a source of sulfur. Omitting this watershed from the analysis produces a model with only one variable and an R^2 of 0.34. The remaining variable is the MSL sampling class, which is negatively correlated to percent sulfur retention. As proposed in the stream sulfate discussion above, the MSL sampling class soils are associated with sulfur-bearing parent materials that function as a source of sulfur. Omitting five more possible outlier/influence points only decreases the model R^2 from 0.34 to 0.33. The resulting model contains only the MSL sampling class. On a regional basis, these soils explain one third of the variation in sulfur retention and appear to be an important source of sulfur.

Three 100-m buffer, sulfur retention regression models are also presented in Table 8-41. The model with 33 observations and R^2 of 0.84 is biased by the watershed with the quarry. Omitting that watershed results in a three-variable model that accounts for 52 percent of the variation in sulfur retention. The variables in this model are all negatively correlated with sulfur retention. They include the OTC, SKX, and MSL sampling classes. The OTC and MSL have low and intermediate sulfate adsorption potentials, respectively, and may be sources of sulfur. The SKX soils are coarse textured, excessively drained Inceptisols formed in metasedimentary residuum. They may be a minor sulfur source, but more likely they are non-interacting soils with short hydrologic contact times. Omitting a second watershed, this one with 79 percent of the 100-m buffer zone area in the OTC sampling class, produces a two-variable model that explains 45 percent of the variation in sulfur retention. In addition to the MSL sampling class (negative parameter estimate), the MSH sampling class is included in this model. Based on the soil sampling class definitions, the only difference between these two sampling classes is their organic matter content and thickness of the surface layers; the MSH is high in organic matter and the MSL is low. In general, the MSH soils are well drained; however, where they occur in the near-stream areas (within 100 m of the stream) they may be saturated with water at depths 100 cm or more below the soil surface for a sufficient period to create anaerobic conditions that can potentially retain sulfur via sulfate reduction. Because of the distribution of the MSH sampling class soils, they may also be a surrogate for watersheds with high sulfate adsorption capacity soils.

8.6.3.3 Regional Comparisons

In the NE sulfur deposition explains the majority of the variability in lake sulfate concentrations. The central tendency for watersheds in the NE is to be at sulfur steady state where sulfur input $\approx$ sulfur outputs. The capacity of these systems to retain sulfur effectively is inherently low (Section 9.2), and has been exhausted (i.e., low or negative sulfur retention). In the SBRP where sulfur retention is high and the watersheds are retaining most of the sulfur inputs, sulfate deposition is not yet significantly related to stream sulfate concentrations.

In the NE there is evidence to suggest that localized sources of sulfur deposition, not accounted for in the LTA deposition dataset, may be contributing to higher sulfate concentrations in the near-coastal watersheds in Subregion 1D. This additional sulfur deposition is probably derived from wind-blown sea-salt aerosols. In both regions there were also indications that at least one of the soil sampling classes is functioning as a sulfur source or is a surrogate for a source of sulfur.

Table 8-41. Regression Models of Percent Sulfur Retention In SBRP Stream Watersheds Developed Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes), and Miscellaneous Land Areas (as a Percentage of Watershed Area) as Candidate Independent Variables[a]

	Whole Watersheds			100-m buffer zones		
OTC	-			-	-	
SKX				-	-	
MSH	+				+	
MSL	-	-	-	-	-	-
MPQ	-			-		
R^2	0.86	0.34	0.33	0.84	0.52	0.45
adjusted R^2	0.84	0.32	0.30	0.81	0.47	0.41
n-streams[b]	35	34	29	33	32	31
p-model[c]	4	1	1	4	3	2
O/L[d]	none	1	6	none	1	2

[a] + and - refer to positive and negative parameter estimates, respectively
[b] n-lakes = number of observations used to develop the regression model
[c] p-model = number of regressor variables in model
[d] O/L = number of outlier or leverage points omitted

Very poorly drained soils and acidic Histosols were positively related to sulfur retention; sulfate reduction is the likely mechanism. A stronger relationship was found when these soils occurred in the near-lake or near-stream areas in the NE. These soils may be responsible for most of the sulfur retention in the NE (See Sections 8.5 and 9.2).

Shallow soils with short hydrologic contact times serve as non-interacting drainage water conduits in both regions. It was also noted in both regions that the surface water in watersheds with a major watershed disturbance, such as a quarry, have higher concentrations of sulfate. The extent of this effectdepends on the nature of the geologic strata being disturbed and the magnitude and location of the disturbance.

8.6.4 ANC, Ca plus Mg, and pH

Acid neutralizing capacity (ANC) is an important measure of the potential of surface waters to buffer the input of acidic deposition. Systems with zero or negative ANC are already acidic and with low ANC are likely to be vulnerable to acid inputs. Systems with high ANC are strongly buffered (capacity protected) against acid inputs and are therefore not likely to become acidic, even at current levels of deposition, for some time, possibly centuries.

ANC is the principal indicator of surface water buffering. Related to ANC are the sum of base cations (Ca, Mg, K, Na) and the surface water pH. In this analysis, the sum of the principal base cations, Ca and Mg, is considered.

8.6.4.1 Northeast

In the NE region, regression models were developed that explain approximately one-half of the variability in ANC (Table 8-42). The best whole watershed model has six variables, including wet sulfate deposition. Sulfur deposition is negatively correlated with ANC. The remaining variables are sampling class variables and are all positively related to lake ANC. Soils in sampling classes I01, I11, I25, and I46 (very poorly drained and poorly drained Inceptisols) are among the classes with the highest base saturation and pH values. It follows that these soils are sources of base cations and supply subtending surface waters with base cations and buffer lake ANC. The soils in sampling class I06 are shallow, and in general, low in pH and base saturation. Their contribution to ANC is questionable; they may be functioning as a surrogate for another variable.

The best ANC model is developed with combined buffer data, explaining 54 percent of the variation in lake ANC with nine variables. Sulfate deposition and the I05 sampling class are the only variables in the model negatively correlated with ANC. I05 occurs mainly in Subregion 1D and may serve as a surrogate for sea-salt contributions of sulfur. Sampling classes I01, I11, I25, I46, and I06 are in this model as well as the whole watershed ANC model. This model also includes sampling classes S01 and S18 as variables, both having positive parameter estimates. The soils in both of these sampling classes have intermediate base saturation (~20 percent) and pH (~4.6). S01 soils are deep and are widely distributed across the region in small amounts. S18 soils are very shallow with a lithic or paralithic contact within 50 cm. The S18 sampling class occurs only in Subregion 1E.

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Table 8-42. Lake ANC and the Sum of Lake Calcium and Magnesium Regression Models Developed for NE Lakes Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes) and Miscellaneous Land Areas (as a Percentage of Watershed Area) as Candidate Independent Variables[a]

	Lake ANC			Lake Ca plus Mg		
	Whole	40-ft	Comb.	Whole	40-ft	Comb.
SO4-Wet	-	-	-			
H-Wet				-	-	-
E06		+			+	+
H01		-				
H02		+				+
I01	+	+	+	+		+
I05			-	-	-	-
I06	+		+	+	+	+
I09		+				
I11	+	+	+	+	+	+
I25	+	+	+	+	+	+
I46	+	+	+	+	+	+
S01			+			
S18		+	+		+	+
M04				+		
R^2	0.48	0.47	0.54	0.56	0.49	0.55
adjusted R^2	0.46	0.43	0.51	0.54	0.46	0.52
n-lakes[b]	145	144	142	145	144	143
p-model[c]	6	10	9	8	8	10
O/L[d]	none	none	1	none	none	none

[a] + and - refer to positive and negative parameter estimates, respectively
[b] n-lakes = number of observations used to develop the regression model
[c] p-model = number of regressor variables in model
[d] O/L = number of outlier or leverage points omitted

Because lake Ca plus Mg is strongly related to ANC (r = 0.94), the regression models developed for Ca plus Mg are similar to those for ANC and have comparable R^2 values. Sampling class I05 and wet hydrogen deposition (H-Wet) have negative parameter estimates. I05 was discussed above. H-WET is strongly correlated with wet sulfate deposition (r = 0.92) and was substituted for the wet sulfate deposition variable included in the ANC models. In the whole watershed model of Ca plus Mg, the miscellaneous land area M04 (quarries) was included in the model. These watershed disturbances also increase the amount of Ca and Mg in the subtending surface waters in addition to increasing the levels of sulfate. In fact, the levels of Ca plus Mg and sulfate are quite similar in these watersheds, and both have fairly high ANCs. Ca and Mg appear to be the cations accompanying the mobile anion sulfate. As long as the soils are not being depleted of base cations, this situation is little cause for concern.

The lake pH regression models were simpler than the ANC and Ca plus Mg models because they have fewer variables and similar R^2 values (Table 8-43). In all three models wet sulfate deposition had negative parameter estimates while the sampling classes I09 and I25 had positive parameter estimates. These results seem to be reasonable. Soils in the I25 sampling class have a relatively high base status, which accounts for the positive correlation with lake pH. The I09 soils are also positively related to pH, but are lower base status soils than the I25 soils. H03 is also included in the whole watershed model with a positive parameter estimate. Soils in the H03 sampling class are deep, wet, organic soils principally located in wetlands. These soils are dysic, meaning that the pH of undried samples is less than 4.5 (in 0.01 M $CaCl_2$). Because pH is an intensity variable (i.e., concentration) the pH of the last soil that drainage water passes through before it reaches the lake may initially control the pH of the lake water. If there are extensive wetlands surrounding a lake including H03 soils, the H03 soils may be the last soil that the drainage waters pass through; the pH of the lake will therefore be similar to the pH of the H03.

The combined buffer model for lake pH had the highest R^2 and adjusted R^2 values, 0.49 and 0.46, respectively, of the three regression models. As in the whole watershed model, the combined buffer model includes wet sulfate deposition and the sampling classes I09 and I25. Additionally, it has E05 and I05 with negative parameter estimates and E06 and H02 with positive parameter estimates. H03 was not included as an important variable in either of the buffer models. The soils in the E05 sampling class are poorly developed, very shallow (< 25 cm), underlain by hard bedrock, and also have one of the lowest aggregate pH values. Because of their chemical and physical characteristics, an increasing abundance of E05 soils will lead to lower lake pH values. The characteristics of the soils in the E06 sampling class are the direct result of human activities. They are deep soils that lack pedogenic development due to significant anthropogenic disturbance such as road construction. They are classed as Udorthents. In general, they have moderate to high base saturation and moderate pH. Because of recent disturbance, they may have abundant fresh weatherable mineral faces that supply base cations at a higher rate than other soils in the region.

8.6.4.2 Southern Blue Ridge Province

ANC in the SBRP is generally higher than in the NE. The median ANC value for the region is 120 μeq L^{-1}. In the NE the median is 56 μeq L^{-1}. Because of the chemical characteristics of the soils in the SBRP (i.e., higher sulfate adsorption capacities), these systems are not close to steady state with respect to sulfur inputs and outputs. The soils in the region are retaining a significant proportion of the

Table 8-43. Lake pH Regression Models Developed for NE Lakes Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes) and Miscellaneous Land Areas (as a Percentage of Watershed Area) as Candidate Independent Variables[a]

	Lake pH		
	Whole	40-ft	Comb.
SO4-Wet	-	-	-
E05		-	-
E06			+
H02		+	+
H03	-		
I05		-	-
I09	+	+	+
I25	+	+	+
R^2	0.45	0.45	0.49
adjusted R^2	0.44	0.42	0.46
n-lakes[b]	144	144	142
p-model[c]	4	6	7
O/L[d]	1	none	1

[a] + and - refer to positive and negative parameter estimates, respectively
[b] n-lakes = number of observations used to develop the regression model
[c] p-model = number of regressor variables in model
[d] O/L = number of outlier or leverage points omitted

sulfur in deposition, and at present, appear to be delaying the acidification of the surface waters in the region. The ANC of these surface waters and the factors that control it are, therefore, very important.

Regression models of the SBRP stream ANCs using the mapped soils, mapped miscellaneous land areas, and wet and dry deposition are presented in Table 8-44. The whole watershed regression models with 35, 34, and 33 observations all have very high R^2 values, 0.92, 0.86, and 0.943, respectively. These large R^2 values are due to the presence of observations with very high ANC (>1000 μeq L^{-1}) values. Two of the three sites are associated with the OTC sampling class and its calcareous parent materials. These three systems are probably capacity protected against acidification. Omitting them from the analysis and leaving 32 observations results in a three-variable model that explains 47 percent of the variation in stream ANC. One of the 32 watersheds has 0.1 percent OTC. Because of the strong positive relationship between calcareous materials and ANC, OTC has been included by the stepwise procedure as a variable. The FL sampling class is also included with a positive parameter estimate. The soils in this sampling class occur on flood plains. Compared to the other sampling classes in the SBRP, the soils in the FL sampling class have the third highest base saturation and the second highest pH. Omitting a fourth influence point results in a one-variable regression model for stream ANC that has an R^2 of 0.40. The single variable is the FL sampling class.

Unlike the NE, there is little or no indication that the DDRP sample of streams in the SBRP are contaminated with Na from road salt or sea salt additions. Therefore, in addition to considering the sum of stream Ca and Mg concentrations as a dependent variable, we have included an analysis of the sum of the four principal base cations (Ca + Mg + Na + K), the sum of base cations (SOBC). In this section and the two sections that follow, additional analyses of the relationship between these watershed attributes and SOBC are included.

The initial 100-m buffer models of stream ANC are similar to the whole watershed models. Dropping outlier/influence points results in a two-variable model that accounts for 92 percent of the variation in stream ANC. The two variables are OTC and FL. The OTC accounts for most of the explanatory power. Omitting all of the high ANC sites from this analysis does not produce an unbiased model.

The results of the Ca plus Mg analysis are presented in Table 8-45. Inclusion of all 35 observations results in a four-variable regression model with an R^2 of 0.90. However, as in the ANC analysis this model is strongly influenced by three observations with exceptionally high values of Ca plus Mg. These are the same three with high ANC. Omitting them from the analysis results in a two-variable model with an R^2 of 0.42. The two variables are FL and MPQ. Analysis of the residuals and influence diagnostics indicate that the MPQ is an influence point. Omitting it and developing a model based upon 31 observations results in a one-variable model. The variable is the FL sampling class. This is the identical model developed for ANC with the same 31 observations.

The results for the 100-m Ca plus Mg model follow the pattern set by the whole watershed. Inclusion of all 33 observations results in a model with a high R^2 but with two strong influence points. Omitting these two observations and rerunning the analysis leads to a higher R^2 model that has four variables. At the same time another influence point is identified. Omitting this observation results in a two-variable model with yet another influence point. This time, however, eliminating it and proceeding with the analysis does not produce an unbiased model.

Table 8-44. Regression Models of ANC in SBRP Stream Watersheds, Developed Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes) and Miscellaneous Land Areas (as a Percentage of Watershed Area) as Candidate Independent Variables[a]

	Whole Watersheds					100-m buffer zones		
Ca+Mg-Dry			-	-				
OTC	+	+	+	+		+	+	+
SKV	-	-				-		
SKX						+		
FL			+	+	+			+
MSH						-		
SHL						-		
OTL	+	+				+	+	
MSL	+	+				+	+	
R^2	0.92	0.86	0.943	0.47	0.40	0.91	0.933	0.924
adjusted R^2	0.90	0.84	0.938	0.41	0.38	0.88	0.926	0.919
n-streams[b]	35	34	33	32	31	33	32	31
p-model[c]	4	4	3	3	1	7	3	2
O/L[d]	none	1	2	3	4	none	1	2

[a] + and - refer to positive and negative parameter estimates, respectively
[b] n-lakes = number of observations used to develop the regression model
[c] p-model = number of regressor variables in model
[d] O/L = number of outlier or leverage points omitted

Table 8-45. Regression Models of Calcium Plus Magnesium in SBRP Streams, Developed Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes) and Miscellaneous Land Areas (as a Percentage of Watershed Area) as a Candidate Independent Variables

	Whole Watersheds			100-m buffer zones		
OTC	+			+	+	+
SKV	-					
SKX				+		
FL		+	+	+	+	
MSH				-		
OTL	+			+	+	
MSL	+			+		
MPQ		+				+
R^2	0.90	0.42	0.25	0.88	0.96	0.922
adjusted R^2	0.89	0.38	0.22	0.86	0.95	0.916
n-streams[b]	35	32	31	33	32	30
p-model[c]	4	2	1	5	4	2
O/L[d]	none	3	4	none	1	3

[a] + and - refer to positive and negative parameter estimates, respectively
[b] n-lakes = number of observations used to develop the regression model
[c] p-model = number of regressor variables in model
[d] O/L = number of outlier or leverage points omitted

The results of the whole watershed and 100-m buffer zone regression analyses for SOBC are presented in Table 8-46. The whole watershed model, including all 35 SBRP systems, produced a four-parameter model with an R^2 of 0.91. Included in this model is the calcareous sampling class OTC (positively related to SOBC). It follows that the presence of significant amounts of calcareous material can increase the levels of base cations that may be transported to the surface water. Systems with high SOBCs and ANCs are likely to be capacity protected against acidification. Analysis of the residuals found that three systems, all with ANC and SOBC greater than 1000 μeq L^{-1} were strong influence points. Dropping these and rerunning the analysis produces a three-parameter model with an R^2 of 0.50. This model also had significant influence points remaining. Omitting these resulted in a five-parameter model built on the data from 28 systems. This unbiased model explains 75 percent of the observed variation in SOBC. Five independent variables were included in this model. Ca and Mg in dry deposition and the SKX and ACL soils were included with negative parameter estimates. The FL and ACC soils were also included but with positive parameter estimates.

The soils in both the SKX and ACL sampling classes tend to be low base status. The SKX soils are formed in residuum and the ACL soils are formed in either residuum or alluvium. The presence of these soils on a watershed is indicative of highly weathered, low base status soils, and lower base status surface waters. In contrast, the soils in the FL class are relatively high base status and are associated with the higher base status surface waters. The ACC soils are very similar to the ACL soils and are differentiated by their particle-size families: the ACC soils are clayey and the ACL soils are either fine-loamy or coarse-loamy. The presence of the ACC soils may be indicative of readily weatherable primary minerals, while the FL soils may represent hydrologic convergence zones where base cation enriched drainage waters and sediments accumulate.

Table 8-46 includes three regression models developed for SOBC using deposition and the soils and miscellaneous land areas within 100 m of the sampled stream. The FL sampling class is included, with a positive parameter estimate, in the three models. The unbiased model (i.e., without outliers and/or leverage points) had four parameters, all with positive parameter estimates and an R^2 of 0.79. Included were the FR, FL, MSL, and OTL sampling class soils. All parameter estimates were positive, indicating that the soils in these classes are all associated with higher base status surface waters. The FR and MSL are typically low base status soils, while FL and OTL are some of the highest base status soils in the region. Because of their low base status and positive correlation to SOBC, the FR and MSL classes may be surrogates for other watershed attributes that supply base cations to the streams.

The buffer zone model explains slightly more of the variability in SOBC than the whole watershed model. This lends support to the hypothesis that the near-channel soils may have the greatest effects on surface water chemistry for some variables.

Stream pHs in the SBRP are higher than the northeastern lake pHs with a central tendency near circumneutrality. The regression models for stream pH developed with all 35 whole watershed observations and with all 33 100-m buffer observations are identical in that they include the same variables. As with stream ANCs and the concentrations of Ca plus Mg, stream pH is strongly influenced by the presence of calcareous soils. The results of the stream pH analysis are presented in Table 8-47. Omitting the two highest OTC sites and one other observation with high influence diagnostics, produces a model with two variables that explains 38 percent of the observed variation in stream pH.

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Table 8-46. Regression Models of SOBC[a] in SBRP Streams, Developed Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes) and Miscellaneous Land Areas (as a Percentage of Watershed Area) as Candidate Independent Variables[b]

	Whole Watersheds			100-m buffer zones		
Ca+Mg-Dry			-		-	
FR					+	+
OTC	+					
SKV	-					
SKX			-			
FL		+	+	+	+	+
MSL	+				+	+
OTL	+	+			+	+
ACL			-			
ACC			+			
MPQ		+		+	+	
R^2	0.91	0.50	0.75	0.41	0.74	0.79
adjusted R^2	0.90	0.44	0.70	0.36	0.65	0.74
n-streams[c]	35	32	28	30	28	25
p-model[d]	4	3	5	2	7	5
O/L[e]	none	3	4	3	5	8

[a] SOBC = sum of base cations (Ca + Mg + Na + K)
[b] + and - refer to positive and negative parameter estimates, respectively
[c] n-streams = number of observations used to develop the regression model
[d] p-model = number of regressor variables in model
[e] O/L = number of outlier or leverage points omitted

Table 8-47. Regression Models of Stream pH in SBRP Streams, Developed Using Deposition, Mapped Soils (as a Percentage of Watershed Area in Soil Sampling Classes) and Miscellaneous Land Areas (as a Percentage of Watershed Area) as Candidate Independent Variables[a]

	Whole Watersheds		100-m buffer zones				
SO4-Wet					-		
Ca+Mg-Dry							-
FR					-		-
OTC	+		+	+		+	
SKV	-		-				
SHL		+					
OTL	+	+	+	+	+		
MSL	+		+				
ACC	-		-				
R^2	0.67	0.42	0.68	0.38	0.39	0.47	0.29
adjusted R^2	0.61	0.39	0.63	0.34	0.31	0.45	0.23
n-streams[b]	35	33	33	31	30	29	28
p-model[c]	5	2	5	2	3	1	2
O/L[d]	none	2	none	2	3	4	5

[a] + and - refer to positive and negative parameter estimates, respectively
[b] n-lakes = number of observations used to develop the regression model
[c] p-model = number of regressor variables in model
[d] O/L = number of outlier or leverage points omitted

The two variables are the OTL and SHL sampling classes. After the OTC sampling class, the OTL class has the highest base saturation in the region. The SHL class consists of shallow Inceptisols and Ultisolswith moderate base saturation (~11%) and alone only accounts for approximately 3 percent of the variation in stream pH. By far, the OTL sampling class soils are more important in explaining the variability in stream pH.

Using only the soils and miscellaneous land areas within 100 m of the streams and the deposition data results in a final model with two variables that has an R^2 of 0.29. One of the variables is the sampling class FR, and the other is the sum of the dry Ca and Mg deposition. Both have negative parameter estimates. The negative parameter estimate on the FR is because, in the region as a whole, the soils in the FR sampling class have the lowest pHs and base saturation. The negative relationship with Ca and Mg in dry deposition does not seem reasonable. This variable may be a surrogate for another independent variable.

8.6.4.3 Regional Comparisons

Because ANC, Ca plus Mg, and pH are interrelated, the resulting regression models within each region are often similar. The median ANC and pH values in the northeastern lakes are lower than in the SBRP streams even though the median Ca plus Mg concentrations are higher. This is a direct result of elevated lake sulfate concentrations in the NE.

Results from both regions show that soils with high base saturation, especially those derived from calcareous parent materials (SBRP), are associated with surface waters that have higher values of ANC, base cations, and pH. Both lake and stream resources are susceptible to the effects of major watershed disturbances (e.g., quarries). When these disturbances are present, the subtending surface waters will have elevated base cation concentrations as well as elevated sulfate levels. In most cases the increase in sulfate is balanced with concomitant increases in base cations. Therefore, the ANCs are not generally negatively impacted by the water disturbance.

In the NE, poorly drained (wetland), organic soils that are acidic appear to decrease lake pH. This is probably due in part to organic acids from these soils. In the SBRP frigid soils (FR sampling class) are associated with lower pH surface waters. These soils are low pH and low base status. As was observed in the northeastern sulfate analysis above, the coastal watersheds appear to have occult sources of deposition that result in lower surface water ANCs, pHs, and Ca plus Mg.

In the NE the whole watershed regression models generally had about the same explanatory power as the models developed using buffer zone data. In the SBRP, however, the models developed using buffer zone data usually had more explanatory power; the only exception was for stream pH. This suggests that in stream watersheds, the near-channel zones have a greater effect on surface water chemistry for some variables than the rest of the watershed. To test this hypothesis definitively, however, would require finer resolution mapping data than those obtained in the DDRP.

8.6.5 Summary and Conclusions

The difference in soils between the two regions accounts for most of the observed differences seen in sulfate and sulfur retention. Compared to the soils of the SBRP the soils in the NE are young, shallow, less developed, and have a lower overall capacity to retain sulfur. In contrast, the soils in the SBRP are, in general, deep and highly weathered, with abundant secondary mineral phases that provide considerable sulfur retention capacities.

The major conclusions of this analysis are:

- In the NE, where sulfur retention on average is low, sulfur deposition explains more of the observed variation in lake sulfate concentrations than any other independent variable.

- In the SBRP, where the majority of sulfur inputs are retained by watershed soils, sulfur deposition is not yet significantly related to stream sulfate concentrations.

- Local sources of sulfur deposition from sea salt may be negatively affecting the surface water chemistry in the near-coastal watersheds in Subregion 1D of the NE.

- Wetland soils or soils that are wet part of the year promote sulfur retention via sulfate reduction reactions.

- Shallow soils with short hydrologic contact times and low sulfate adsorption capacities do not interact sufficiently with drainage waters to affect their chemistry. Watersheds with these types of soils in areas of high sulfur deposition are likely to be susceptible to surface water acidification.

- Soils with high base saturation are associated with higher surface water ANC, pH, and base cations.

- Poorly drained, acidic organic soils in the NE and frigid soils in the SBRP are associated with lower pH surface waters. In the NE this relationship may be due in part to the result of the organic acids in these soils. The frigid soils are low pH and low base status.

- Using only mapped soils information from the near-stream areas in the SBRP to develop regression models generally produced models with more explanatory power than those developed using only information from the whole watershed.

This type of analysis has been shown to be a useful tool for regionally assessing the relationships between surface waters and soils, miscellaneous land areas, and deposition. Although these attributes alone cannot account for all the variability in the observed data, there are some instances in which they do account for most of it. Care must be exercised in evaluating the resulting regression models.

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Inclusion of outliers and leverage points may result in models that are heavily biased. Sample populations with small sample sizes are particularly susceptible to bias.

This analysis demonstrates the utility of soil sampling classes in characterizing the soils across large geographic regions. It has helped us to assess the concept of soil sampling classes and may lead to some revisions in the way classes are differentiated.

8.7 ANALYSES OF DEPTH TO BEDROCK

8.7.1 Introduction

One of the important findings of the Integrated Lake/Watershed Acidification Study (ILWAS) (Newton and April, 1982; Goldstein et al., 1984) was that the depth of soil and surficial geological materials have a significant effect on the quality of subtending surface waters. The ILWAS scientists found that the difference in lake pH between Woods (pH 4.4-5.1) and Panther (pH 5-7.5) Lakes could be attributed to the difference in the depths of surficial materials on these watersheds.

In addition to depth, the chemical and physical characteristics of the surficial materials are also important. The latter affects the hydrologic flow path and the hydrologic contact time, which in turn affect the length of time to react with the drainage waters. Short hydrologic contact times produce little alteration in the chemistry of the drainage waters. The chemical characteristics of the surficial material are also important. Materials without weatherable primary minerals will have little beneficial effect on acidic inputs, even though they may be deep. Our objective in this analysis is to test this depth-to-bedrock hypothesis on a regional basis.

8.7.2 Approach

A depth-to-bedrock map was prepared during the mapping phase of the DDRP by assigning a depth-to-bedrock class to all soil map delineations. The procedure used in the NE was presented in Section 5.4.1.2 and for the SBRP in Section 5.4.2.2. In addition to the depth-to-bedrock maps, depth to bedrock was recorded for each soil component in the soils database for each region (Sections 5.4.1.1.2 and 5.4.2.1.2). The soils databases, therefore, provided an alternative approach to estimate the extent of depth-to-bedrock classes on watersheds and subsequently subregions and regions. Using these data rather than the data from the depth-to-bedrock maps provides a more precise method to estimate the proportion of depth-to-bedrock classes.

The depth-to-bedrock classes developed for this analysis from the soils data for the NE and SBRP are listed in Table 8-48. Note that the numbering of the classes proceeds from the rock outcrop (I) to the very deep (VI), and that depth classes V and VI indicate deeper soils for the SBRP than for the NE. In both regions, depth class I represents rock outcrop on the watersheds.

The depth of each soil (component) is recorded in the soil component file. As described in Section 8.6.2, the mapped soils are linked to the soil component file. This file contains component-specific information, including soil depth. Using this soil depth information we calculated the percentage of each

Table 8-48. Depth-to-Bedrock Classes for the Northeast and the Southern Blue Ridge Province

Northeast Region

Class	Depth range (cm)	Definition
NE_I		Rock outcrop
NE_II	10 - 25	Very shallow
NE_III	25 - 50	Shallow
NE_IV	50 - 100	Moderately deep
NE_V	100 - 150	Deep
NE_VI	150 +	Very deep

Southern Blue Ridge Province

Class	Depth range (cm)	Definition
SE_I		Rock outcrop
SE_II	10 - 25	Very shallow
SE_III	25 - 50	Shallow
SE_IV	50 - 100	Moderately deep
SE_V	100 - 200	Deep
SE_VI	200 - 500	Very deep

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watershed in each of the depth categories. These percentages are used as the independent depth-to-bedrock variables in the following analysis. The LTA sulfate and hydrogen deposition estimates, both wet and dry, are also used as candidate explanatory variables.

The descriptive statistics on the proportion of these depth classes for both NE and SBRP are presented in Table 8-49. In general, the NE has higher proportions of shallower soils than does the SBRP. The proportions of deeper soils are not strictly comparable between the regions, because depth classes V and VI are not the same across regions.

Within the NE, Subregions 1A and 1E have the highest percentages of rock outcrop, and Subregions 1C and 1D have the lowest. Subregion 1A has the highest percentage of very shallow and shallow soils, while Subregions 1D and 1B have the lowest. Subregions 1D and 1C have the highest proportions of the very deep soils, and Subregion 1A has the lowest proportion.

The statistical analyses used in the section are discussed in Section 8.1.2. Residual analysis revealed heteroscedasticity in the residuals for ANC and base cations for both regions. We, therefore, log-transformed these dependent variables in the analyses for depth-to-bedrock relationships.

8.7.3 Sulfate and Percent Sulfur Retention

8.7.3.1 Northeast

In the NE, depth to bedrock seems to have little effect on surface water sulfate (Table 8-50). Surface water sulfate is dominated by wet and dry sulfate deposition. The positive correlation between percent sulfur retention and dry sulfate deposition may represent a spurious correlation due to the formulation for percent retention.

8.7.3.2 Southern Blue Ridge Province

In the SBRP, depth to bedrock has a significant effect on sulfate dynamics. The percent of shallow soils (SE_III) has a strong positive relationship with surface water sulfate and a strong negative relationship with percent sulfur retention (Table 8-51). This suggests that, as the percent of shallow soils increases and the percent of deep soils decreases, the amount of sulfate adsorption decreases. This decrease in sulfate adsorption may be due to several factors. The deep soils have more mass and, hence, more total sulfate adsorption capacity. The deep soils may also have higher contact times and different flowpaths for the soil water.

8.7.3.3 Comparison of Regions

It appears that in-lake sulfate in the NE is predominantly controlled by atmospheric deposition and not by the depth of surficial material. In the SBRP, the shallow (25 - 50 cm) category of depth to bedrock accounts for about 32 percent of the variability in observed stream sulfate concentrations and more than 40 percent of the variability in watershed sulfur retention estimates. These results imply that shallow soils play an important role in regional sulfur dynamics in the SBRP and that they are often associated with higher stream water sulfate concentrations and lower watershed sulfur retention.

Table 8-49. Regional and Subregional Statistics for Percentage of Watershed Coverage of the Depth-to-Bedrock Classes

NE	Average	Median	Minimum	Maximum
NE_I	3.3	1.6	0.0	28.4
NE_II	4.2	2.3	0.0	42.8
NE_III	10.8	10.3	0.0	60.5
NE_IV	13.2	11.2	0.0	56.7
NE_V	0.4	0.0	0.0	64.8
NE_VI	67.8	70.0	2.8	100.0

Subregion 1A	Average	Median	Minimum	Maximum
NE_I	4.8	2.8	0.0	18.1
NE_II	8.1	6.8	0.0	21.3
NE_III	17.9	15.6	0.0	34.9
NE_IV	17.8	16.0	0.0	36.4
NE_V	0.0	0.0	0.0	0.0
NE_VI	51.5	55.6	12.1	100.0

Subregion 1B	Average	Median	Minimum	Maximum
NE_I	3.5	0.0	0.0	24.0
NE_II	1.8	0.0	0.0	12.7
NE_III	7.3	3.8	0.3	26.6
NE_IV	20.6	14.5	6.7	48.2
NE_V	0.0	0.0	0.0	0.0
NE_VI	66.7	67.5	26.1	92.8

Subregion 1C	Average	Median	Minimum	Maximum
NE_I	1.9	1.7	0.0	8.6
NE_II	3.4	2.8	0.0	10.0
NE_III	9.9	10.6	0.0	22.6
NE_IV	10.1	9.9	0.0	32.2
NE_V	0.0	0.0	0.0	0.1
NE_VI	75.5	73.3	32.7	100.0

Table 8-49. (Continued)

Subregion 1D	Average	Median	Minimum	Maximum
NE_I	2.2	0.3	0.0	12.8
NE_II	0.9	0.1	0.0	4.4
NE_III	4.1	1.0	0.0	22.4
NE_IV	5.7	1.4	0.0	27.0
NE_V	0.0	0.0	0.0	0.0
NE_VI	86.5	96.6	33.2	100.0

Subregion 1E	Average	Median	Minimum	Maximum
NE_I	4.0	1.6	0.0	28.4
NE_II	5.7	2.0	0.0	42.8
NE_III	12.4	10.8	0.0	60.5
NE_IV	11.3	7.6	0.0	56.7
NE_V	1.9	0.0	0.0	64.8
NE_VI	64.8	70.0	2.8	100.0

SBRP	Average	Median	Minimum	Maximum
SE_I	1.2	0.7	0.0	15.0
SE_II	0.0	0.0	0.0	2.6
SE_III	10.1	6.6	0.0	30.0
SE_IV	23.7	19.3	0.0	53.8
SE_V	14.6	7.1	0.0	58.3
SE_VI	50.2	38.2	12.6	99.0

Table 8-50. Results for NE of Regressions of Surface Water Chemistry on Depth-to-Bedrock Classes and Deposition Estimates

Water Chemistry Variable	R^2	Adjusted R^2	Variable in Model	Regression Sign	Signif.[a] Level
Sulfate	0.2723	0.2621	wet SO4 dep.	+	**
			dry SO4 dep.	+	*
Percent Sulfur Retention	0.1051	0.0983	dry SO4 dep.	+	***
Log(ANC+100)	0.2603	0.2446	wet SO4 dep.	-	***
			dry SO4 dep.	+	***
			NE_II	-	*
Log(Ca+Mg)	0.2481	0.2211	dry SO4 dep.	+	***
			wet SO4 dep.	-	***
			NE_V	-	**
			NE_II	-	**
			NE_VI	-	S
pH	0.3203	0.3058	wet SO4 dep.	-	***
			dry SO4 dep.	+	***
			NE_II	-	**

[a] S = significant at 0.15 level
 * = significant at 0.05 level
 ** = significant at 0.01 level
 *** = significant at 0.001 level

8.7.4 ANC, Ca plus Mg and pH

In this part of the depth-to-bedrock analysis we consider the relationships between the proportion of watershed coverage in the various depth-to-bedrock categories and the non-sulfur dependent variables. Unlike the NE, there is little or no indication that the DDRP sample of streams in the SBRP are contaminated with Na from road salt or sea salt. Therefore, in addition to considering the sum of stream Ca plus Mg as a dependent variable, we have included an analysis of SOBC (Ca + Mg + Na + K). Due to the behavior of the residuals of the regressions, both ANC and base cations were log-transformed to remove heteroscedasticity. One hundred (100) was added to the ANC before transforming, in order to avoid problems in taking the logarithm of non-positive numbers.

Wet sulfate deposition was negatively correlated with ANC, and dry sulfate deposition was positively correlated with ANC (Table 8-50). Wet sulfate deposition was introduced in the regression model first, and it presumably represents decreases in alkalinity of the surface waters with increasing deposition of sulfate. The second deposition variable may be a correction to an overfitting with wet sulfate deposition, or it may be a surrogate for some explanatory variable not included in the model. Since there are some high ANC sites in Subregion 1B, it could also represent a geographic effect, as discussed in Section 8.2. The very shallow soils represented by NE_11 (10-25 cm) are negatively correlated with ANC (Table 8-50). This results suggests that as the proportion of soils deeper than 25 cm increases, the capacity for cation exchange increases and ANC of the surface waters increases. It also suggests that these soils may have short hydrologic contact and therefore little or no effect on drainage water chemistry.

A similar behavior in the explanatory variables is seen for Ca plus Mg. Dry sulfate deposition is positively correlated with in-lake base cations. This correlation may represent increased cation exchange and leaching due to acidic deposition in a system at or near sulfur steady state. A second deposition variable, wet sulfate, is introduced with a negative parameter in the model later. As discussed previously, this may be a surrogate for some other variable or variables estimate or possibly a geographic effect. Three of the depth-to-bedrock classes were included with negative parameter estimates. Included were the deep (NE_V, 100 - 150 cm), the very deep (NE_VI, > 150 cm), and the very shallow (NE_II, 1 - 25 cm) depth categories. This result is contrary to the hypothesis suggested by the ILWAS project outlined in Section 8.7.1, that the deeper the surficial geologic material (i.e., the deeper the depth to bedrock) the higher the pH, ANC, and base cation status of the surface water. Our result implies the opposite relationship, on a regional basis. Overall, our model accounts for only about 25 percent of the variability in Ca plus Mg. Therefore, factors other than depth to bedrock are likely to account for most of the variability in Ca plus Mg.

The regression model for lake pH contained the same set of parameters as the model developed for ANC. This model, however, had a higher R^2 (0.32) than the one developed for ANC (0.26). Again, as wet sulfate deposition increases, surface water pH decreases. Likewise, as the proportion of the watershed with shallow soils increases, we can expect lower lake water pH.

8.7.4.1 Southern Blue Ridge Province

Due to the behavior of the residuals of the regressions, the dependent variables ANC, Ca plus Mg, and SOBC were log-transformed to remove heteroscedasticity. The regression models developed

for these transformed variables are presented in Table 8-51. In each of these models, the depth class SE_V (100 - 200 cm) was included with a negative parameter estimate. In the SOBC model it was the only parameter included and explained 22 percent of the observed variability. Both the ANC and Ca plus Mg models included a deposition variable. The estimate of dry hydrogen ion deposition was included (positive parameter estimate) in the ANC model, whereas wet sulfate deposition was included (negative parameter estimate) in the Ca plus Mg model. The reasons these variables were included in these models are unclear.

The negative relationships between depth class SE_V (100 - 200 cm) and ANC, Ca plus Mg, and SOBC suggest that this depth class represents surficial material that is highly weathered and therefore deep, with little or no weatherable minerals. In the SBRP, because the soils and surficial materials are old and highly weathered, unweathered primary minerals may be prevalent only at the bedrock:soil interface, in the saprolite. It is reasonable to assume that as these saprolites get farther from the soil surface, the weathering rates (cation supply rates) may actually decrease because they are farther removed from diurnal and other environmental influences. Because of this, watersheds with abundant deep, highly weathered soils, will probably be associated with lower ANC, pH, and base status surface waters.

The regression model for stream pH only included the estimate of dry hydrogen deposition and only accounts for about 15 percent of the observed variability in stream pH. Dry deposition has a positive parameter estimate, implying that as it increases so does stream pH. This apparent relationship is unreasonable; therefore, dry hydrogen deposition is probably functioning as a surrogate for another variable that is positively related to stream pH.

8.7.4.2 Comparison of Regions

In the NE, wet and dry sulfate deposition are important factors included in the depth-to-bedrock regression models developed for ANC, Ca plus Mg, and pH. In these models, the very shallow (NE_II, 1 - 25 cm) depth-to-bedrock categories were consistently negatively related to the dependent variables. This implies that as the proportion of the watershed in the very shallow depth categories increases (i.e., lower proportion of deeper material), we can expect the ANC, Ca plus Mg, and pH to decrease. This is a reasonable result since shallower surficial materials are generally indicative of lower base cation supply capacities.

In the SBRP the deep depth-to-bedrock category was negatively related to ANC, Ca plus Mg, and SOBC. This result suggests that this depth class represents surficial material that is highly weathered and deep, with little or no weatherable minerals. As the proportion of the watershed in this deep material increases, we can expect ANC, Ca plus Mg, and SOBC to be lower. The regression model for stream pH did not include any depth-to-bedrock variables.

8.7.5 Summary and Conclusions

Depth to bedrock appears to have an important effect on sulfate dynamics in the SBRP, but not in the NE. An important reason for this difference is that, in general, NE watersheds are at sulfate steady

Table 8-51. Results for SBRP of Regressions of Surface Water Chemistry on Depth-to-Bedrock Classes and Deposition Estimates

Water Chemistry Variable	R^2	Adjusted R^2	Variable in model	Regression Sign	Signif.[a] Level
Sulfate	0.3200	0.2966	SE_III	+	***
Percent Sulfur Retention	0.4211	0.4004	SE_III	-	***
Log(ANC)	0.3140	0.2667	dry H dep.	+	*
			SE_V	-	*
Log(Ca+Mg)	0.2740	0.2239	SE_V	-	**
			wet SO4 dep.	-	S
Log(SOBC)	0.2202	0.1933	SE_V	-	*
pH	0.1494	0.1210	dry H dep.	+	*

[a] S   = significant at 0.15 level
*   = significant at 0.05 level
**   = significant at 0.01 level
***   = significant at 0.001 level

state, whereas the SBRP sites are not. In both regions, depth to bedrock appears to be related to cation supply dynamics but in opposite ways. In the NE the shallower surficial material is associated with lower base status surface waters. In the SBRP the deeper material is also related to lower base status surface waters. In the NE as the proportion of the watershed in the very shallow depth categories increases (i.e., lower proportion of deeper material) we can expect the ANC, sum of Ca plus Mg concentrations, and pH to decrease. In the SBRP it is hypothesized that the deep class of surficial material represents highly weathered materials with little or no weatherable minerals remaining. As the proportion of the watershed in this class of material increases, lower base status surface waters can be expected.

8.8 INTEGRATED ANALYSIS OF ALL MAPPED VARIABLES

8.8.1 Introduction

Each of the preceding sections has considered the relationship between an isolated set of independent watershed variables and the chemistry of the subtending surface waters. These analyses considered the relationships of surface water chemistry to atmospheric deposition only (Section 8.2), derived hydrologic parameters (Section 8.3), mapped bedrock geology (Section 8.4), mapped landuse/vegetation (Section 8.5), mapped soils (Section 8.6), and depth to bedrock (Section 8.7). None of these attributes alone can explain all of the variability in the observed chemistry. The chemistry of surface waters is the integrated result of many interacting factors, including those just mentioned.

In this analysis we combine the data from Sections 8.2-8.7 to develop regression models that more fully account for the variability in the observed dependent variable data. Our objective is to identify the most important relationships that exist between watershed physical characteristics and surface water chemistry. In Section 8.10 we include the soil chemical and physical data. In the analysis presented in this section, we do not consider any of the watershed buffer zone data.

8.8.2 Approach

The approach used in this analysis follows that described in Sections 8.1.1 and 8.1.2 with the following exception. Because the number of explanatory variables in this analysis exceeded the number of watersheds in the SBRP, Mallow's C_p statistic could not be used as a model selection criterion; Akaike's information criterion was used instead. After each model was developed we performed residual analysis on it, checking for leverage points and outliers, as well as for the standard regression assumptions as described in Section 8.1.2.

8.8.3 Sulfate and Sulfur Retention

8.8.3.1 Northeast

In the NE there is a strong relationship between wet sulfate deposition and sulfate concentration in the lakes (Table 8-52). Because the watersheds are in general at sulfur steady state, the surface waters tend to reflect the sulfur chemistry of atmospheric deposition. The negative relationship between aquatic sulfate and precipitation indicates dilution effects caused by increased rainfall and runoff.

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Table 8-52. Regression Models of Surface Water Sulfate and Sulfur Retention in the NE Lake Watersheds Using Deposition, Derived Hydrologic Parameters, Bedrock Geology Reaction Classes, Depth To Bedrock, Mapped Landuse/Vegetation, and Mapped Soils as Candidate Regressor Variables

Variable[a]	R^2	Adjusted R^2	Variable in Model	Regression Sign	Signif.[b] Level
Sulfate	0.7223	0.6962	WET SULFATE DEP.	+	***
(n = 141)			M04	+	***
			PRECIPITATION	-	***
			FACTOR9	+	***
			H03	-	***
			FACTOR4	+	**
			E06	+	S
			H2O_WS	+	S
			M03	-	S
			PERIN	-	S
			TOTSTRM	+	S
			REL_RAT	-	S
S Retention	0.4710	0.4360	FACTOR5	+	**
(n = 129)			I46	-	***
			NE_II	-	***
			FACTOR12	-	***
			ATKBMEAN	+	***
			MAXREL	+	*
			H03	+	*

[a] n = number of observations included in regression model
[b] S = significant at 0.15 level
* = significant at 0.05 level
** = significant at 0.01 level
*** = significant at 0.001 level

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Anthropogenic factors also strongly affect the sulfate concentrations. The miscellaneous land area M04 (quarries) and the soil sampling class E06 (made land) both represent sources of sulfur from anthropogenic watershed disturbances (Table 8-52). The positive correlation with Factor 9 also represents anthropogenic sources: Factor 9 indicates increasing cabin count, urbanization, and quarries. The positive correlation between lake sulfate and Factor 4 (agricultural land, and cropland and pasture land) results from some combination of anthropogenic amendments (e.g., lime, fertilizers) to the soil and preference for conducting agricultural activities on fertile soils, which are likely to have higher pH and thus reduced anion adsorption capacities. If these soils are limed or amended with phosphate, displacement of sulfate from adsorption sites may result in increased sulfate moving into surface waters.

The correlations with the soil sample class H03 indicate that reduction of sulfate and retention of sulfur by wetlands (Table 8-52) are also important. The positive relationship with H2O_WS (the water bodies to watershed area ratio) suggests that in-lake sulfate reduction has a greater effect on sulfur budgets in those watersheds with high watershed to lake area ratios and long lake hydrologic residence times (see Section 3.3.7.2). An alternative explanation could be that this relationship reflects lessopportunity for precipitation to contact soils and hence more control of sulfate concentration by the deposition.

The first variable selected by the stepwise regression for sulfur retention is Factor 5, which represents wetlands (Table 8-52). This correlation reiterates the importance of wetlands in the biogeochemical sulfur cycle on a regional basis. The same rationale applies to the inclusion of soil sampling class H03, a wetland soil, with a positive parameter estimate.

The very shallow (10 - 25 cm), NE_II, depth-to-bedrock class was included in the sulfur retention model with a negative parameter estimate. This result implies that as the proportion of watershed coverage in very shallow surficial materials increases, watershed sulfur retention decreases. This is apparently due to a concomitant decreased watershed sulfate adsorption (sulfur retention) capacity. Alternatively, NE_II is highly correlated with the presence of both H01 and E05 on a watershed. H01 is a relatively dry Histosol in which mineralization of organic matter and consequently sulfur production could occur. The H01 soils are usually associated with high elevations and may be indicative of cloud interception (i.e., increased deposition). Factor 12 (rainfall and runoff) was included with a negative relationship with retention (Table 8-52), suggesting a dilution effect due to increased runoff.

8.8.3.2 Southern Blue Ridge Province

The first variable selected by the stepwise regression procedure is SE_III, in the regression model of stream sulfate concentration (the shallow depth class) (Table 8-53). This is indicative of the overall reduced sulfate adsorption capacity of shallower soils. The two depth classes SE_VI (very deep soils) and SE_V (deep soils) which are brought in later in the stepwise procedure probably represent corrections to the overfitting of SE_III in the regression. Since the amount of adsorption is not linearly related to the proportion of shallow soils on a watershed, it is reasonable that the extents of SE_VI and SE_V are used to correct for the regression estimate for SE_III.

Runoff has a negative relationship with stream sulfate concentration, indicating a dilution effect from increased precipitation. The sample class MSL has a positive relationship with stream sulfate

concentration (Table 8-53). This same sample class also has a negative relationship with sulfur retention in the first two SBRP sulfur retention models. Considered together, these results suggest that MSL may be related to or indicative of sulfur-bearing parent material. This relationship was also noted and discussed in Section 8.6. Factor 8 (open land and pasture) has a positive relationship with stream sulfate concentrations, suggesting that anthropogenic additions or the activities of livestock are impacting stream sulfate concentrations as discussed in the previous section.

The sample class ACC has a negative relationship with stream sulfate concentration. Soils in this sample are derived from acid crystalline parent materials. They are clayey and have high sulfate adsorption capacities. Thus, we expect the extent of these soils to be negatively related to in-stream sulfate. MAX, the maximum bedrock sensitivity number on a watershed, is negatively related to sulfate in the subtending waters (Table 8-53). In the SBRP this relationship is expected because deeper soils are associated with more extensively weathered parent materials, which in turn results in increased amounts of iron and aluminum oxides, the principal sites of sulfate adsorption. More weatherable bedrock produces more of the deeper, finer textured soils abundant in iron and aluminum.

In the three successive models for sulfur retention, we see explanatory variables similar to those selected for the stream sulfate concentration regression models. The first model for sulfur retention was a model developed with 32 SBRP watersheds. The residual analysis identified one watershed as a strong leverage point due to its unusual negative sulfur retention and the singular presence of MPQ (quarry) on the site. In the second model another site was identified as an outlier and was also excluded. This watershed also appears to have an internal source of sulfur. The variables that appear in the first two models and not in the third model are probably site-specific or are included due to correlations with other variables.

The miscellaneous land class MPQ (miscellaneous pits and quarries) is negatively correlated with sulfur retention in the first model (Table 8-53), indicating an internal source of sulfur, as previously discussed. The sample classes MSL and FL are also negatively related to percent sulfur retention in the first two models (Table 8-53). This result may indicate that one or both of these sample classes occasionally has weatherable sulfur-bearing parent material. The soils in the FL sampling class have low sulfur retention (adsorption) capacities.

The depth-to-bedrock classes SE_III and SE_VI are negatively related to sulfur retention in all three models, and SE_V is also negatively related to retention in the final model (Table 8-53). As discussed previously, SE_III may be indicative of the lower capacity of shallower soils to adsorb sulfate, and the signs for SE_V and SE_VI suggest that they appear in the regressions as nonlinearity corrections for overestimating the regression parameter for SE_III.

The bedrock geology variable H5up is positively related to sulfur retention in the first two models, but not in the third (Table 8-53). This result indicates, as does the negative relationship between sulfate concentration and MAX, that more weatherable bedrock geologies tend to produce deeper soils with higher sulfate adsorption capacities. H5up does not appear in the 30-observation regression model.

Table 8-53. Regression Models of Surface Water Sulfate and Sulfur Retention in the SBRP Stream Watersheds Using Deposition, Derived Hydrologic Parameters, Bedrock Geology Reaction Classes, Depth To Bedrock, Mapped Landuse/Vegetation, and Mapped Soils as Candidate Regressor Variables

Variable[a]	R^2	Adjusted R^2	Variable in Model	Regression Sign	Signif.[b] Level
Sulfate (n = 31)	0.8496	0.7744	SE_III	+	***
			RUNOFF	-	S
			MSL	+	***
			SE_VI	+	***
			FACTOR8	+	*
			ACC	-	S
			REL_RAT	-	**
			SE_V	+	**
			MAX	-	*
			SKX	-	S
S Retention (n = 32)	0.9297	0.9052	MPQ	-	***
			MSL	-	***
			SE_III	-	***
			SE_VI	-	S
			DRY SULFATE DEP.	+	**
			H5UP	+	**
			DRY H DEP.	-	*
			FL	-	S
S Retention (n = 31)	0.6893	0.5948	MSL	-	***
			SE_III	-	***
			SE_VI	-	S
			DRY SULFATE DEP.	+	**
			H5UP	+	**
			DRY H DEP.	-	*
			FL	-	S
S Retention (n=30)	0.5835	0.5168	SE_III	-	***
			SE_VI	-	**
			SE_V	-	S
			ACC	+	S

[a] n = number of observations included in regression model
[b] S = significant at 0.15 level
* = significant at 0.05 level
** = significant at 0.01 level
*** = significant at 0.001 level

The first two models suggest some possible indicators of internal sources of sulfate (e.g., MSL, MPQ), and the final model indicates the importance of soil depth and soil type. The sample class ACCis positively related to sulfur retention, indicating that very clayey soils, derived from acid crystalline parent materials, are strong adsorbers of sulfate.

8.8.3.3 Regional Comparisons

In the NE, the surface water sulfate concentrations are strongly affected by sulfur deposition. In the SBRP, however, the watersheds are not at sulfur steady state, and hence do not mirror trends in deposition as readily as the northeastern sites do. In both regions, watershed disturbance and agricultural practices may outweigh the effects of deposition on surface water chemistry. Some soils have distinct relationships with stream sulfate concentrations and watershed sulfur retention and may be indicative of internal watershed sulfur sources. The northeastern lakes display more obvious effects of wetlands than do streams in the SBRP, where extensive wetlands are relatively uncommon. Effects due to soil depth and bedrock geology are more pronounced in the SBRP. In the NE, sulfur retention seems to be primarily controlled by extent and type of wetlands. In the SBRP, sulfur retention is controlled by the soil mass (i.e., oxyanion adsorption capacity) available to adsorb sulfate and the extent of types of soils that adsorb more strongly.

8.8.4 ANC, Ca plus Mg, and pH

8.8.4.1 Northeast

The regression model for ANC in northeastern watersheds indicates that surface water ANC is primarily driven by watershed-specific variables. The first variable in the model is Factor 4, the extent of pasture and cropland in the watershed, which has a positive relationship with surface water ANC (Table 8-54). This relationship may represent an increase in base cations through the use of soil amendments (i.e., lime), and it may also be indicative of the selection of high base status soils for agricultural activities. The soil sampling class I46 was also included with a positive relationship with ANC (Table 8-54), which is expected, because the soils in this sampling class are high base status. Their typical base saturation is over 75 percent, and their average pH is the highest of all northeastern soil sampling classes. Factor 12 (precipitation and runoff) has a negative relationship with surface water ANC (Table 8-54), indicating a dilution effect in the surface waters produced by increased runoff.

MAX, the highest value of the bedrock sensitivity code on a watershed, has a positive relationship with ANC (Table 8-54). The higher bedrock sensitivity numbers are associated with lithologies, such as carbonates, that can buffer soils and surface water against changes in ANC.

The first variable in the regression model of Ca plus Mg is Factor 4 (pasture and cropland), as in the model for ANC (Table 8-54). Again, this result probably indicates preference for agricultural development on higher base status soils and the introduction of soil amendments. Factor 12 (precipitation and runoff) again has a negative relationship with surface water ANC and Ca plus Mg, indicating a chemical dilution.

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Table 8-54. Regression Models of Surface Water ANC, Ca plus Mg, and pH in the NE Lake Watersheds Using Deposition, Derived Hydrologic Parameters, Bedrock Geology Reaction Classes, Depth To Bedrock, Mapped Landuse/Vegetation, and Mapped Soils as Candidate Regressor Variables

Variable[a]	R^2	Adjusted R^2	Variable in Model	Regression Sign	Signif.[b] Level
ANC (n = 138)	0.4860	0.4666	FACTOR4	+	***
			I46	+	***
			FACTOR12	-	**
			ATKBMEAN	+	**
			MAX	+	*
Ca+Mg (n = 142)	0.5877	0.5662	FACTOR4	+	***
			FACTOR12	-	***
			I46	+	***
			M04	+	***
			I25	+	***
			M01	+	***
			H01	-	*
pH (n = 143)	0.4621	0.4383	FACTOR4	+	***
			FACTOR12	-	*
			WET SULFATE DEP.	-	***
			H03	-	***
			FACTOR1	+	**
			DRY SULFATE DEP.	+	*

[a] n = number of observations included in regression model
[b] S = significant at 0.15 level
 * = significant at 0.05 level
 ** = significant at 0.01 level
 *** = significant at 0.001 level

The soil sampling classes I46 and I25 are positively related to Ca plus Mg (Table 8-54). Both of these sampling classes have soils with high base status and high pH. Soil-water flowing through these soils would be expected to have more exchange of acid cations for base cations and to contribute base cations to the surface waters. The miscellaneous land area M04 is also positively related to surface water Ca plus Mg (Table 8-54). M04 (pits, quarries) has been shown previously to be related to increases in lake and stream sulfate concentrations (Section 8.6 and 8.8.3). Apparently base cations accompany sulfate to the surface waters.

The sample class H01 is negatively related to Ca plus Mg (Table 8-54). The soils that make up this class are thin mantles of organic material overlaying rock outcrop or rock fragments. These soils generally occur on steep mountain slopes at high elevations. Precipitation falling on these soils flows rapidly from these areas to drainage ways that feed directly into the surface waters. The lower mass available for cation exchange and the reduced soil contact could account for the lower base cations in the surface waters.

Surface water pH is positively related to Factor 4 (pasture and cropland) and negatively related to Factor 12 (precipitation and runoff), as are ANC and Ca plus Mg (Table 8-54). As discussed previously, Factor 4 probably reflects preference for agricultural development on higher base status soils and introduction of soil amendments. Factor 12 again indicates the dilution effect of increased precipitation. Wet sulfate deposition has a negative relationship with surface water pH (Table 8-54), indicating the ability of increased sulfate deposition to lower the pH of subtending surface waters.

The soil sampling class H03 has a negative relationship with lake pH (Table 8-54). The soils in this soil sampling class are dysic (low pH) wetland soils. By definition, they have low pH, typically less than 4.5. These soils may be contributing organic acids and thus affecting the pH of the surface waters. Also, these soils can be the last soil that the drainage waters pass through before reaching the lake. Because of their position in the watershed, these soils may therefore have a significant ultimate effect on surface water chemistry.

The model developed for lake pH includes Factor 1 with a positive parameter estimate. Factor 1 represents developed land. This factor incorporates effects due to waste disposal sites, pits and quarries, cabins, urban commercial land, and urban residential land. The positive relationship with pH (Table 8-54) may indicate that the relationship is primarily driven by the base cation influx associated with some anthropogenic disturbance, such as pits or quarries. The positive relationship between surface water pH and dry sulfur deposition suggests that this explanatory variable is a surrogate for some other factor.

8.8.4.2 Southern Blue Ridge Province

The three SBRP sites with high ANC are excluded in order to make the analysis more comparable with the results from the NE and to adhere to the DDRP design. If these sites were included the squared correlations for ANC and Ca plus Mg would have been over 90 percent, and the squared correlation for pH would have been over 70 percent. These increases in explained variability are all due to the presence of highly weatherable bedrock with large amounts of carbonates and calcareous soils on these watersheds.

The model for surface water ANC shows a positive relationship with the sample class FL and a negative relationship with runoff (Table 8-55). The sample class FL is composed of flooded soils that are near the stream channels and have fairly high base status and pH compared to the other soils in the region. These soils may be the last soil that the drainage waters pass through before reaching the surface waters. In the near-stream channel position, these soils may have a significant effect on stream chemistry. The negative relationship with runoff suggests chemical dilution.

Two regression models were developed for Ca plus Mg in SBRP streams. The first was developed with 32 observations. The second is based upon 29 observations after residuals analysis of the first model identified one outlier and two leverage points. In both models, the sample class FL has a positive relationship with stream base cations (Table 8-55), as it does with ANC. Runoff is negatively related to stream base cations (Table 8-55). Both of these have been discussed previously.

In the first Ca plus Mg model, H5up is positively related to base cations. The higher values of the sensitivity scale are associated with carbonate bedrocks that weather more easily and contribute base cations to drainage waters. In both models for Ca plus Mg, there is a positive relationship with Factor 3 (Table 8-55). Factor 3 represents larger proportions of cropland, land under horticulture, and open land as defined by the SCS. As in the NE, this result may reflect the impact of soil amendments on surface water chemistry, and it may indicate that agriculture is conducted on fertile, high base status, flood plain soils. In the second model, Factor 4 (open land, urban development, and wetlands) is positively related to stream base cations. The relationship with SCS open land and development indicates anthropogenic sources of base cations to the surface waters. DDENSITY, a measure of drainage density, is negatively related to stream base cation concentration. Higher drainage densities usually indicate a faster runoff response and, hence, lower soil interaction. With less soil contact, the base cation supply would tend to be lower. In the second model, wet sulfate deposition is negatively related to base cation concentration. This may be a surrogate for increased precipitation and thus might represent a dilution effect.

Unlike the NE, there is little or no indication that the DDRP sample of streams in the SBRP is contaminated with sodium (Na) from road-salt or sea-salt additions. Therefore, in addition to considering the stream Ca plus Mg as a dependent variable, we have included an analysis of the sum of the four principal base cations, Ca + Mg + Na + K, (SOBC). The regression model developed for SOBC explains about 92 percent of the observed variation in SOBC and contains three highly significant variables with positive parameter estimates. These are Factor 3 (larger proportions of cropland, horticultural activities, or open land), SE_VI (very deep depth-to-bedrock category, 200 - 500 cm), and the OTL soil sampling class. As mentioned previously, Factor 3 is indicative of the preference of high base status soils for agricultural purposes, which tend to be located near streams in the flood plain. In conjunction with this, soil amendments may result in increased surface water base cation concentrations. The very deep depth-to-bedrock category (SE_VI) is synonymous with near channel, flood plain soils. These zones are also where base cation enriched drainage waters and sediments accumulate. The soils in the OTL soil sampling class are generally very high base status soils, and are therefore associated with higher base status surface waters.

In the model for surface water pH, there is a negative relationship with runoff (Table 8-55). The soil sampling class FR is negatively related to stream pH (Table 8-55). The sampling class FR is composed of the frigid soils, which have the lowest pH and base status soils in the region. When they

Table 8-55. Regression Models of Surface Water ANC, Ca plus Mg, and pH in the SBRP Stream Watersheds Using Deposition, Derived Hydrologic Parameters, Bedrock Geology Reaction Classes, Depth To Bedrock, Mapped Landuse/Vegetation, and Mapped Soils as Candidate Regressor Variables

Variable[a]	R^2	Adjusted R^2	Variable in Model	Regression Sign	Signif.[b] Level
ANC (n = 32)	0.4531	0.4154	FL	+	***
			RUNOFF	-	**
Ca+Mg (n = 32)	0.6714	0.6227	FL	+	**
			RUNOFF	-	**
			H5UP	+	***
			FACTOR3	+	*
Ca+Mg (n = 29)	0.7101	0.6471	FL	+	***
			FACTOR3	+	**
			FACTOR4	+	S
			DDENSITY	-	*
			WET SULFATE DEP.	-	S
SOBC (n = 25)	0.9285	0.8927	FACTOR3	+	***
			SE_VI	+	***
			OTL	+	***
			WET SULFATE DEP.	-	**
			WET H DEP.	+	*
			ACC	-	*
			MSL	+	*
			SKV	-	S
pH (n=32)	0.4312	0.3470	RUNOFF	-	*
			FR	-	*
			STRMORD	+	*
			DRY H DEP.	+	S

[a] n = number of observations included in regression model
[b] S = significant at 0.15 level
 * = significant at 0.05 level
 ** = significant at 0.01 level
 *** = significant at 0.001 level

occur, the drainage water pH would be expected to be reduced. Also, the proportion of these soils is negatively correlated with the proportion of FL, the flooded soils with high base status and high pH.

STRMORD, the maximum Horton stream order on the watershed, is positively related to stream pH (Table 8-55). Larger values of stream order tend to be associated with larger watersheds. These sites have longer flow paths and more soil contact, which would elevate the pH of the drainage waters. Dry hydrogen deposition is positively related to stream pH in the regression model (Table 8-55). The sign of the relationship indicates that dry hydrogen deposition is probably a surrogate for another variable.

8.8.4.3 Regional Comparisons

In both regions, watershed-specific factors appear to be more important than atmospheric deposition on the base status and pH of surface water. The effects of bedrock lithology and presence of agricultural land appear across both regions. The base status of soils and their contact time also affect the surface water ANC.

8.8.5 Summary and Conclusions

The specific conclusions of these analyses are:

- The effect of deposition on surface water chemistry is much more distinct in the NE than in the SBRP.

- Major watershed disturbances, such as quarries and urbanization, result in increased surface water sulfate concentrations. They also produce higher base status surface waters.

- Land use, especially near-lake or near-stream agricultural activities (e.g. lime and fertilizer amendments) may outweigh the effects of deposition on surface water chemistry.

- In the NE, wetland soils are associated with sulfur retention.

- Shallow soils are negatively related to sulfur retention in both the NE and SBRP. This is probably caused by their decreased capacity to adsorb sulfate.

- In the SBRP, easily weathered parent materials produce abundant iron and aluminum .oxyhydroxides. Soils formed in these types of parent materials are usually deep and have large sulfate adsorption capacities.

- In the SBRP, the very deep depth-to-bedrock category of surficial material is synonymous with near channel, flood plain soils. These zones are also where base cation enriched drainage waters and sediments accumulate. These zones are therefore associated with higher ANC surface waters.

8.9 SOIL PHYSICAL AND CHEMICAL CHARACTERISTICS

8.9.1 Introduction

This section evaluates the relationships between surface water chemistry and the soil physical and chemical characteristics that were measured by the analytical laboratories as part of the DDRP soil survey. Section 2 outlined the hypothesized basis for control of surface water chemistry by soil chemical characteristics, i.e., sulfate retention and base cation supply. Section 3 discussed the influences of these soil chemical characteristics in greater detail. This section uses an empirical approach to evaluate whether the hypothesized mechanisms of soil chemical influence on surface water chemistry are supported by relationships between measured soil chemical and physical data and water chemistry data.

Relationships between soil characteristics and surface water chemistry are evaluated in this section using bivariate correlations and multiple regressions. The dependent variables are discussed in Section 8.1.2.

8.9.2 Approach

The candidate independent or explanatory variables considered in this section are those that were measured at the soil analytical laboratories on soil samples taken during the DDRP soil survey. A complete list of the measured physical and chemical characteristics was given in Table 5-22. Summary statistics for the subset of those variables that were used in this section are given in Section 8.9.4.

The soil samples analyzed by the DDRP were from individual subhorizons of pedons sampled randomly from areas of occurrence of predefined sampling classes as described in Section 5.5. As many as seven and as few as zero pedons were sampled on each watershed. In order for the data to be used in the empirical analyses, they were aggregated through the sampling class framework and single values calculated for each watershed according to the mass and the area of occurrence (from the mapped data, Section 5.4) of each sampling class on each watershed. This procedure is described in more detail in Section 8.9.3.

There are questions about how data should be aggregated from single points in a heterogeneous watershed or landscape to represent the entire study area. The related issues have been discussed in detail by Johnson et al. (1988b). For these Level I analyses the aggregation should yield a value that is representative of the soils that influence the chemistry of water draining into the lake or stream as measured by the index sample. The index sample (defined in Section 5.3) represents water that has passed through the watersheds over different time periods and along different flow paths. For example, some portion of the water in northeastern lakes passed slowly through the deeper soils of the watersheds and entered the lakes or streams draining into the lakes as baseflow; another portion flowed rapidly through shallow soils as quickflow draining directly into the lakes or streams because the deeper soils were saturated. Thus, under some hydrologic conditions, characteristics of the deeper soils on much or all of each watershed might be relevant; under spring runoff, frozen, or storm conditions, the attributes of the shallow soils or soils closest to the lakes or streams might be more important. Since the SBRP stream samples were collected during baseflow conditions, the influence of shallow hydrologic flowpaths

should be relatively less important than in the NE, and characteristics of deeper soils over most of the watersheds should be most relevant.

The soils data have been aggregated two different ways to evaluate whether the characteristics of soils over the entire watershed or soils closest to the lake or stream are more closely associated with the surface water chemistry. The first aggregation results in watershed values, weighted by area of occurrence of each sampling class, representing all of the soils on the watershed. The second aggregation results in watershed values representing the area of occurrence of each sampling class within mapped buffer zones around the lakes and streams. The development of the buffer zones is discussed in Section 5.4.1.7.5. The aggregation procedures are discussed in more detail in Section 8.9.3.

The concept of capacity and intensity variables needs to be considered in these Level I analyses. Capacity variables include the pool of exchangeable calcium, cation exchange capacity, or sulfate adsorption capacity, for example. They represent either pools of available ions that may be exchanged for other ions in solution or sinks that may remove ions from solution. The size of these pools or sinks determines how long a process such as base cation leaching or sulfate adsorption can occur before the pool or sink is depleted and other processes begin to occur. Intensity variables, such as pH, base saturation, and equilibrium soil solution sulfate concentration, represent concentrations of ions that are readily exchangeable and that quickly reach equilibrium with water in contact with the soil. In the absence of in-stream or in-lake changes and deposition directly to the stream or lake, surface water should reflect the values of the intensity variables of the soil with which it was last in contact. For the correlation and regression analyses presented here, both capacity and intensity variables were selected as candidate variables to evaluate the importance of each in relationships with the index chemistry variables.

8.9.2.1 Statistical Methods

A multiple linear regression modelling approach was used to estimate the value of a response or dependent variable as a linear function of a set of predictor variables. Figure 8-9 illustrates the steps used to develop the regression models. This section provides a brief summary of the modelling approach.

The DDRP database contains information on 145 lake watersheds in the NE and 35 stream watersheds in the SBRP. Prior to regression analysis, the distributions of the selected dependent (i.e., surface water chemistry) variables were examined for obvious outliers. Based on this examination, two northeastern watersheds with high lake sulfate concentrations were dropped. In the SBRP three watersheds were eliminated due to high stream alkalinity and an additional watershed was removed because of high sulfate. Each of the watersheds deleted due to high sulfate concentrations had open pits or quarries on a small portion of the watershed. The three SBRP watersheds had ANC > 1200 μeq L^{-1} probably due to the presence of carbonate bedrock.

Candidate explanatory variables were chosen in a two-stage procedure. First, explanatory variables common to both the NE and SBRP were selected to facilitate comparison of the regression models for the two regions. This selection was based on hypothesized relationships and nonparametric correlations
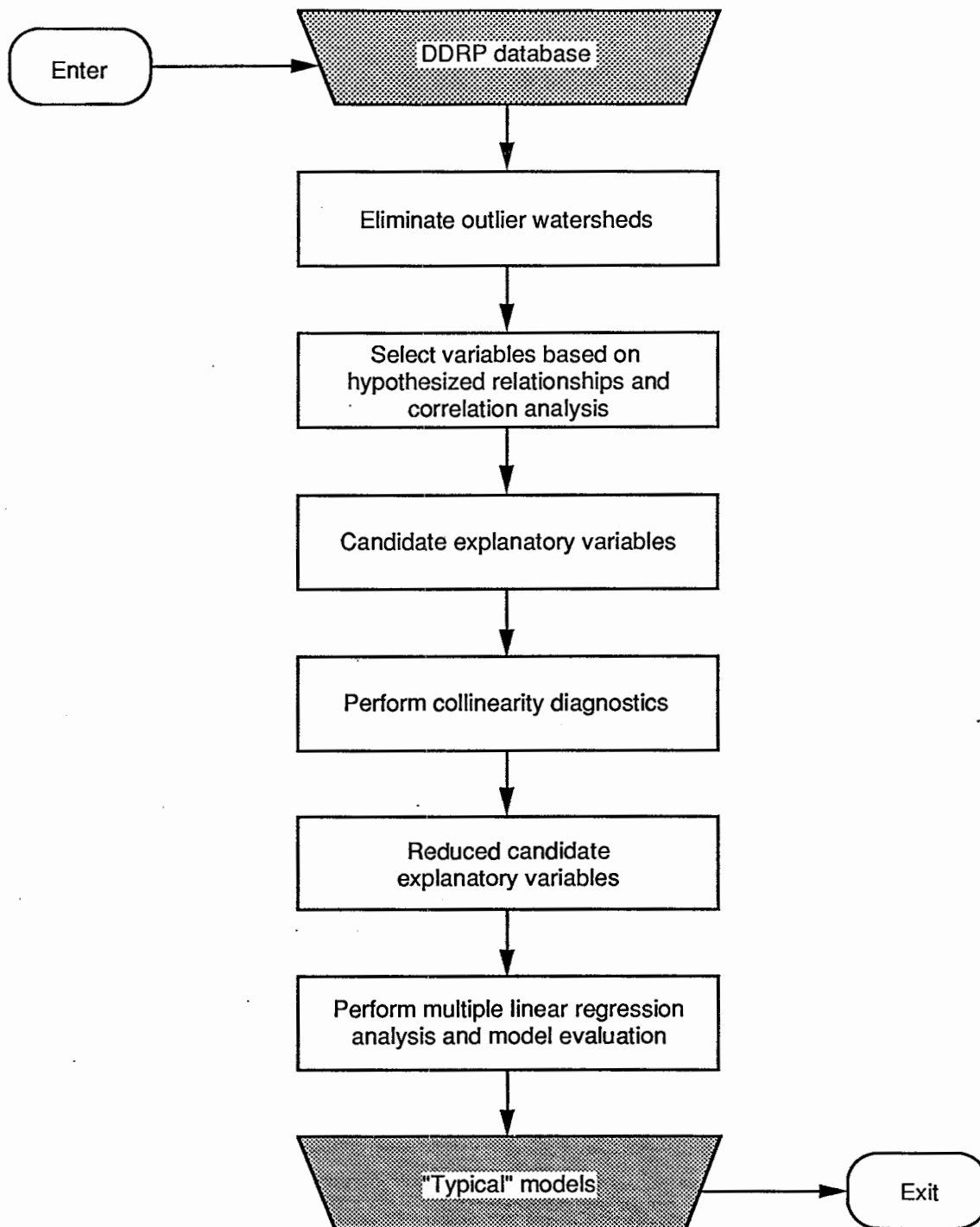
Figure 8-9. Model development procedure.

between the dependent and predictor variables. At least one soil base cation, pH, sulfate, aluminum, and particle size variable was included in the initial set of predictors. Ammonium chloride-extracted base cations were selected over the ammonium acetate extractions to be consistent with the Level II and III Analyses. Concentrations were used instead of pools because of the collinearity introduced into the pool estimates when multiplying the concentrations by a common mass.

In building and interpreting multiple regression models it is important to recognize that few independent, i.e., explanatory, variables in watersheds are statistically independent. Soil pH, base saturation, and exchangeable calcium are usually correlated with each other, as are total carbon, extractable aluminum, extractable sulfate, and sulfate isotherm parameters. Candidate variables were selected from the list in Table 5-22 to eliminate highly correlated variables (those having $|r| > 0.95$).

The second step in variable selection used the collinearity diagnostics from the regression procedure (REG) in SAS (SAS Institute, Inc., 1988) to identify highly collinear predictor variables in the initial set. When a predictor variable is nearly a linear combination of other predictor variables, parameter estimates for these variable coefficients are unstable and have high uncertainty (Draper and Smith, 1981). The collinearity diagnostics available in the REG procedure test for near-linear dependencies among sets of predictors. The intercept was not included in the analysis because zero values for the predictor variables were generally not within the range of the data (Freund and Littell, 1986). The diagnostics were applied iteratively to the initial set of predictors. At each step, the maximum condition number was examined and if it exceeded 30, one of the identified collinear variables was dropped. Preference was given to keeping a collinear variable that (1) was more mechanistic, i.e., potentially causal, than other collinear variables; (2) was considered a more reliable measure; and (3) was the only remaining variable of its type (e.g., hydrologic, deposition, vegetation) (Hunsaker et al., 1986a). Stepwise regression was then performed, as described in Section 8.1.2.

8.9.3 Aggregation of Soil Data

8.9.3.1 Introduction

Previous regional analyses of relationships between watershed characteristics and surface water chemistry in areas with varying levels of acidic deposition have generally been data limited so aggregation within watersheds was not an issue (e.g., Rapp et al., 1985; Nair 1984; Eilers et al., 1983). Hunsaker et al. (1986a), however, used more intensive soils data and maps for the Adirondacks and found that different aggregation procedures resulted in different associations between soil characteristics and surface water chemistry.

There are no universally accepted or generalized procedures for aggregating watershed components to obtain a weighted watershed average or characteristic value. Therefore, there is a variety of aggregation procedures that might satisfy the objective of the Level I Analyses.

One issue considered in aggregating data for modelling relationships between soil chemistry and surface water chemistry was the distinction between intensity and capacity variables. Water chemistry at any point in time is controlled by intensity variables such as soil pH, base saturation, or aluminum solubility. The effect of intensity variables on water chemistry is dependent on the relative cross-sectional

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area of the soil through which water flows just prior to emerging as surface water. Therefore, aggregation of intensity variables should give greater weight to that portion of the soil last encountered by the water. Because of the difficulty in quantifying lateral versus vertical flow through watershed soils, we have not succeeded in defining an ideal aggregation scheme for intensity variables, and the method for capacity variables (below) was used.

Changes in water chemistry over time are dependent on capacity variables such as soil cation exchange capacity, amounts of weatherable minerals present, or amount of soluble aluminum present. Unlike intensity variables, the effect of capacity variables is proportional to the mass of soil which the water contacts before emerging as surface water. Consequently, the capacity variables were aggregated, weighting by the mass of soil contacted by the water.

Because aquatic chemistry represents the integrated response of an entire watershed, one aggregation approach was to define the watershed-level quantity as a weighted combination of the sampling classes that occur on the entire watershed. This weighting scheme used the percentage composition of the watershed in terms of the sampling classes (i.e., each sampling class was weighted by its areal fraction on the watershed).

Another aggregation approach was to consider only those soils in the immediate vicinity of the lake or stream. Physical and chemical characteristics of the soils in these zones might exhibit a much stronger relationship with water chemistry than the aggregation of all watershed soils. For the NE a combined buffer around the lake and streams draining into the lake was delineated; in the SBRP the area within a 100-m zone along each side of the stream was determined (see Section 5.4.1.2 for details on development of the buffers). In both regions the sampling class composition of the buffers was calculated and the areal fractions were used as weights in calculating aggregated soil chemistry data for the buffers.

It should be noted that there are a number of approaches in addition to the two described here that could be used to obtain an aggregated watershed estimate. Possible approaches include weighting by hydrologic group, bedrock type, or vegetation type. However, given the sample design used for the DDRP, the aggregation approaches used for these Level I Analyses all involve weighting by the area of the sampling classes on all or part of the watershed.

8.9.3.2 Aggregation of Soil Data

Extensive discussion among the DDRP investigators resulted in the formulation of a common aggregation approach that appeared to be applicable for each level of analysis (Johnson et al., 1988b) This approach was to

(1)   weight each horizon by its mass per unit area [thickness x bulk density x (1 - coarse fragments)] to obtain a mass-weighted average for each pedon,

(2)   weight the pedon values by their mass per unit area to obtain a sampling class weighted average, and

(3) weight the sampling class value by the product of mass per unit area and areal proportion of the sampling class on the watershed to obtain a watershed-weighted average.

Mass weighting was necessary for capacity variables (e.g., cation exchange capacity, sulfate adsorption capacity) because these variables represent the amount of soil potentially available to react with acidic deposition. Mass weighting was also used for aggregation of intensity variables (e.g., pH, base saturation) because a more appropriate method was not obvious.

Coefficients for sulfate isotherms describe the partitioning of sulfate between adsorbed and dissolved phases within the soil. Because the coefficients are derived from a function fitted to a set of observations, the techniques used to obtain watershed estimates for these coefficients differ from the aggregation methods described above.

The procedure involved fitting the extended Langmuir equation to isotherms for individual samples using a nonlinear least squares routine. Estimates of net adsorbed sulfate at a set of reference points were obtained for each sample using the fitted function, and these estimates were mass weighted to sampling class. An isotherm was fit to the sampling class values, and net adsorbed sulfate was estimated at the set of reference points. The net adsorbed sulfate values generated using the sampling class isotherm coefficients were aggregated for each watershed, using the product of the sampling class mass and the areal fraction of the sampling class on the watershed as a weight. Finally, an isotherm was fit to the watershed estimates and the coefficients were derived from the fitted function.

8.9.3.3 Assessment of the DDRP Aggregation Approach

There are several assumptions inherent in the sampling class approach to soil characterization described in Section 5.5.1. One important assumption is that soil components within a sampling class are sufficiently similar so that any sample from a particular class can be used to characterize that class. A consequence is that there may be a significant sample location effect that could inflate the estimate of the sampling class variance. The following two sections describe procedures for evaluating the occurrence and importance of watershed effects. Additional discussion of these results can be found in Turner et al., in review.

The sampling class definitions grouped soils having similar taxonomy or physical properties with the assumption that chemistry of soils in a sampling class would also be similar. Comparison of the variance within sampling classes to the variance between sampling classes, as estimated by a variance components analysis, revealed that for most soil variables the within-class variance was equal to or greater than the between-class variance (Table 8-56). Subsequent aggregation to watersheds resulted in very little variance among watersheds, i.e., the watershed values for most chemical parameters were very similar for most watersheds. The significance of this result depends on the spatial scale of the variation. If the observed within-sampling-class variance occurred on the scale of meters (i.e., as if all pedons for a sampling class were sampled on the same watershed), then the sampling class aggregation scheme has accomplished a desirable smoothing of the data and it would appear that soils in the DDRP regions are fairly uniform, especially in the SBRP. If, on the other hand, the observed within-sampling-class variation occurred on the scale of kilometers, then aggregating through sampling class to watershed

Table 8-56. Standard Deviations Within and Among Northeast Sampling Classes Estimated from B Master Horizon Data.

Variable[a]	Within Replicate	Within Sampling Classes	Among Sampling Classes	Percent Variation Explained by Sampling Class
SAND	5.437	12.861	15.642	60
CLAY	1.557	4.032	4.752	58
FRAG	6.747	12.221	9.184	36
AC_KCL	0.155	0.359	0.326	45
CA_CL	0.213	0.552	0.538	49
SBC_CL	0.155	0.402	0.409	51
BS_CL	0.121	0.354	0.346	49
CEC_CL	0.095	0.228	0.214	47
AC_BACL	0.156	0.295	0.310	52
PH_01M	0.139	0.369	0.272	35
PH_H2O	0.144	0.416	0.370 *	44
C_TOT	0.270	0.327	0.375	57
N_TOT	0.310	0.305	0.305	50
S_TOT	0.152	0.266	0.195	43
AL_KCL	0.162	0.423	0.367	43
AL_PYP	0.142	0.265	0.274	52
AL_CD	0.135	0.259	0.286	55
SO4_H2O	0.118	0.200	0.219	55
SO4_PO4	0.173	0.338	0.381	56
SO4_B1[b]	.	0.247	0.212	42
SO4_B2[b]	.	0.187	0.055 *	8
SO4_XIN[b]	.	0.228	0.228	50
SO4_SLP[b]	.	0.307	0.297	48

[a] Variable labels and units are found in Table 8-59. All variables
   except SAND, CLAY, and FRAG are $\log_{10}$.

[b] Within replicate estimates not available.

* Within variation significantly larger than among variation (p = 0.05).

has averaged out real watershed-to-watershed differences. Under this assumption, the uniformity of the watershed estimates indicates that they are biased toward the regional mean.

The DDRP sampling design was not intended to directly answer the question of the scale of variation. DDRP soil sampling was statistically designed to characterize sampling classes, not watersheds. Given the available data we can, however, ask whether there is a watershed effect, i.e., do the values for a specific variable from all pedons sampled on a watershed tend to be above or below their respective sampling class means? Analyses described below revealed significant watershed effects for most variables in both the NE and SBRP.

8.9.3.4 Estimation of Watershed Effect

A weighted, unbalanced analysis of variance model that partitions the variability of a given soil parameter into a sampling class effect, a watershed effect, and a residual error was used to assess the watershed-specific effect on each variable. The statistical model used in this analysis was:

$$y_{ij} = a_i + b_j + e_{ij},$$
<div align="right">(Equation 8-1)</div>

where y_{ij} is the pedon value for a given soil parameter from sampling class i on watershed j, a_i and b_j are estimates of the sampling class and watershed effects, and e_{ij} is the residual error.

Horizon data were aggregated to the pedon prior to watershed effect analysis in order to avoid the occurrence of missing values which would result from using only subhorizon or master horizon data, since not all pedons sampled had all horizons. Weighted pedon averages for capacity and intensity variables were calculated using the aggregation approach described in Section 8.9.3.3.

It should be noted that this model does not contain a term for the sampling class by watershed interaction. Since only one pedon was sampled in a sampling class on a watershed, there were not enough data to estimate the interaction term. Furthermore, only a small percentage of the possible sampling class by watershed combinations was actually sampled in each region. Also, the model does not contain an intercept in order to avoid the difficulties encountered in using an intercept model with unbalanced data (Searle, 1987).

For the Northeast, there were 38 a_i effects, one for each sampling class. The OTC sampling class was not included in the SBRP analysis, because the watersheds which contained OTC were outliers with respect to stream alkalinity and were dropped from the analysis (see Section 8.9.2). Therefore, the SBRP model contained 11 sampling class effects. The parameterization of the model required that the number of watershed effects, b_j, be one less than the number of sampled watersheds. This parameterization ensured that the model was of full rank and that the estimates of sampling class and watershed effects were unbiased. For the Northeast this resulted in 135 b_j terms, since only 136 of the 145 watersheds were sampled. In the SBRP, three watersheds were dropped due to extreme values for stream ANC and the model for this region contained 31 watershed effects.

The analyses were conducted using the SAS REG regression procedure (SAS Institute, Inc., 1988). Binary indicator variables (0 or 1) were used to classify each pedon into the appropriate sampling class and watershed. The sampling class estimates obtained from the regression model were aggregated to watershed, weighting by the areal fraction of sampling class on the watershed and, for capacity variables,

the product of the areal fraction and the sampling class mass. The resulting unadjusted watershed estimate was modified by adding the estimate of the watershed effect to give an adjusted watershed value. The adjusted watershed values were then used as explanatory variables in the analyses described in Sections 8.9.4 to 8.9.6.

8.9.3.5 Evaluation of Watershed Effect

There was a significant watershed effect for most variables (Table 8-57), and therefore the watershed effect adjustment was applied uniformly to all of the data. The watershed effect adjustment had little effect on the means of the watershed estimates but the variance was generally much greater for the adjusted values (Table 8-57). This result was expected given the large within-sampling-class variance. Variance that had been averaged out in the sampling class aggregation was reintroduced as a watershed effect. The variability in the distributions of the adjusted values was more like our expectations of the variability of natural systems (Figure 8-10). Figure 8-11 illustrates the difference in the watershed means and standard errors for pH in 0.01 M $CaCl_2$. Note that the adjusted watershed means are more variable from watershed to watershed than the unadjusted means. The uncertainty of the adjusted means, however, is higher than that of the unadjusted means. The actual variance probably lies between these two estimates.

Because the watershed effect was significant, the watershed-effect-adjusted soil chemistry was used in the following Level I regression analyses. The large uncertainty of the adjusted estimates limits the predictive power of the soil variables in the regression analyses. Future surveys should be designed to reduce this uncertainty.

8.9.4 Regional Soil Characterization

Soil physical and chemical properties were expected to vary between the NE and SBRP and among the subregions of the NE. In this section, soils are characterized using data for measured soil variables regionalized to the target populations. Means and standard errors for these variables are presented for each of the northeastern subregions, for the NE as a whole, and for the SBRP in Table 8-58. The regionalized means are averages of the adjusted watershed values weighted by the inverses of the watershed inclusion probabilities. The standard error of the regionalized mean is the weighted standard error calculated from the adjusted watershed values weighted by the inverses of the watershed inclusion probabilities. Values were calculated for the whole watershed, for the combined buffer zone in the NE, and for a 100-m buffer zone in the SBRP (see Section 5.4.1.2 for detailed description of the buffer zones). For base cations, only values from the 1.0 N NH_4 Cl extraction were used in these analyses, as these are the values of interest to the modelling efforts. Data obtained using the 1.0 N NH_4 Cl and 1.0 N NH_4 OAc extractions were found to be highly correlated, so similarities may be inferred. Values in Table 8-58, as well as the cumulative distribution frequencies shown in Section 5.5.6, can be used to characterize the DDRP soils.

Watersheds from the five subregions of the NE differ in the primary soil properties that were hypothesized to affect surface water chemistry (Sections 2 and 3, Church and Turner, 1986). For the whole-watershed aggregation, base saturation (BS_CL) ranges from 17 to 30 percent, with the Adirondacks (1A) and Southern New England (1D) soils having the lowest mean base saturation. Cation

Table 8-57. Means and Standard Deviations of Soil Characteristics by Aggregation Method and Region

	NE			
Variable	Unadjusted		Adjusted	
	Mean	Std. Dev.	Mean	Std.Dev.
SAND *	65.5	13.2	65.0	17.9
CLAY *	5.17	3.82	5.21	6.33
SOILDEN *	1.27	0.17	1.27	0.22
CA_CL	1.92	1.52	2.10	5.81
MG_CL *	0.45	0.37	0.39	1.09
BS_CL *	20.3	9.72	19.6	20.9
CEC_CL *	6.40	2.93	7.11	6.75
PH_01M *	4.02	0.13	4.28	0.42
AL_PYP	0.29	0.12	0.29	0.19
C_TOT *	4.00	2.70	4.08	4.72
SO4_H2O	9.66	3.82	9.57	8.22
SO4_PO4	29.0	10.7	28.9	18.9

	SBRP			
Variable	Unadjusted		Adjusted	
	Mean	Std. Dev.	Mean	Std.Dev.
SAND *	54.7	2.13	55.1	12.1
CLAY *	18.3	2.56	16.7	5.69
SOILDEN *	1.31	0.07	1.27	0.13
CA_CL	0.26	0.06	0.37	0.40
MG_CL *	0.23	0.03	0.24	0.15
BS_CL *	11.03	1.98	12.3	9.04
CEC_CL *	6.81	0.86	7.30	3.19
PH_01M *	4.32	0.06	4.37	0.20
AL_PYP	0.25	0.09	0.29	0.21
C_TOT	0.93	0.44	1.21	1.13
SO4_H2O	8.82	1.28	9.42	4.61
SO4_PO4	84.9	10.6	82.8	36.0

* Watershed effect significant at p < 0.01.
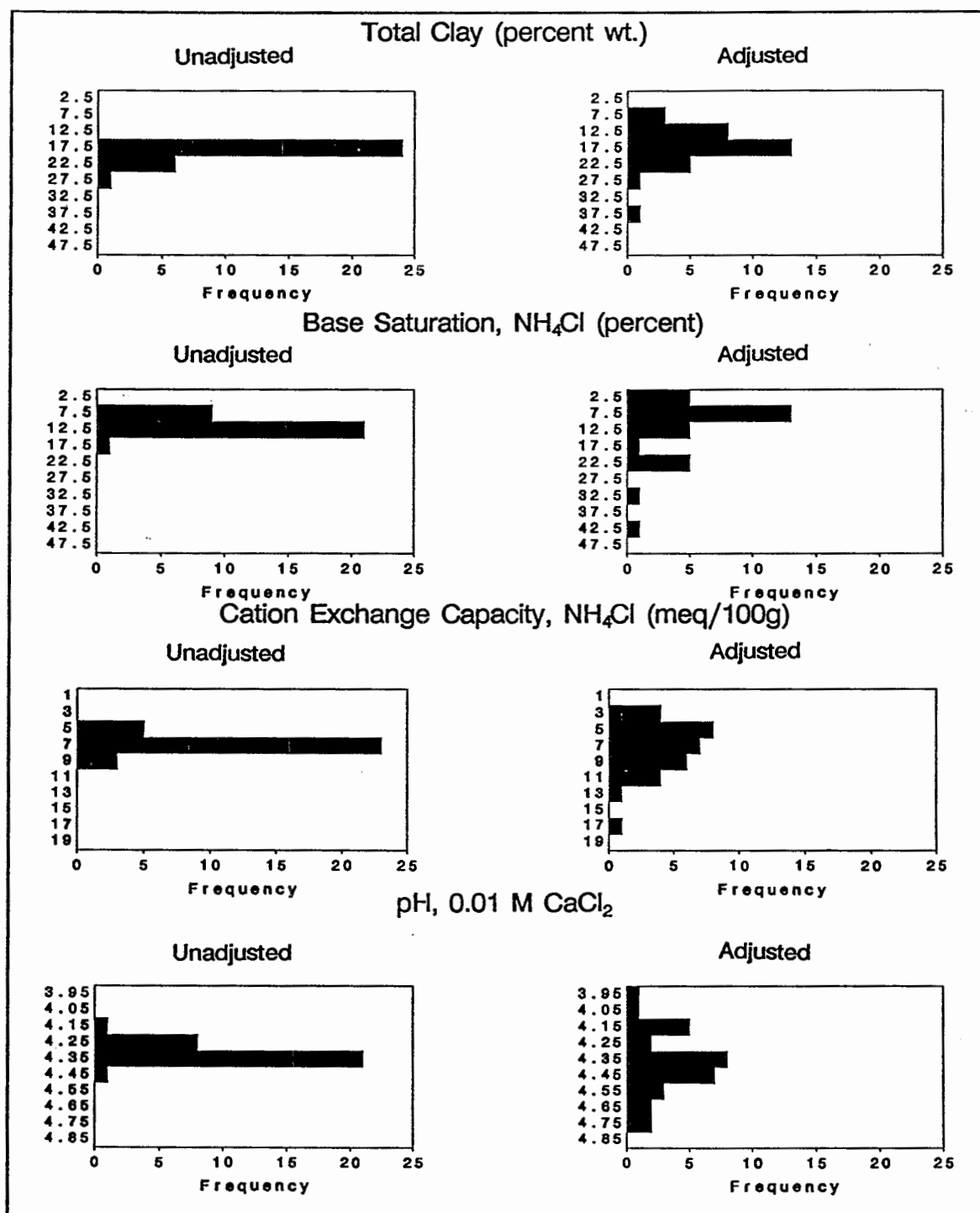
Figure 8-10. Histograms of unadjusted and adjusted watershed means for selected SBRP soils variables. The values on the vertical axes denote interval midpoints of the soil variables.

Figure 8-11. The mean pH ± 2 standard errors for the SBRP watersheds estimated using the common aggregation (bars) and the watershed effects adjusted aggregation (lines) illustrate the lack of variation among the common aggregation values.

Table 8-58. Population Means and Standard Errors for Selected Variables, by Subregion/Region and Aggregation (Watershed Adjusted Data)

	Mean ± Standard Error by DDRP Subregion/Region						
	NE Subregion[a]					Overall	
Variable/ Aggregation [b]	1A	1B	1C	1D	1E	NE	SBRP

Soil Physical Properties

Variable/Aggregation	1A	1B	1C	1D	1E	NE	SBRP
SAND							
WS [c]	69.60 ± 3.03	45.52 ± 1.77	68.15 ± 2.82	78.15 ± 2.19	53.56 ± 2.18	62.17 ± 1.32	50.35 ± 1.48
BUF	73.87 ± 2.45	45.47 ± 1.76	71.11 ± 3.10	79.42 ± 2.59	54.70 ± 2.64	64.04 ± 1.51	52.19 ± 1.48
SILT							
WS	27.65 ± 2.38	41.67 ± 1.39	28.30 ± 2.22	19.72 ± 1.73	37.64 ± 1.72	31.67 ± 1.04	30.04 ± 0.95
BUF	23.55 ± 1.93	41.84 ± 1.39	24.58 ± 2.44	18.81 ± 2.04	35.28 ± 2.08	29.37 ± 1.19	30.89 ± 0.93
CLAY							
WS	2.69 ± 1.01	12.85 ± 0.59	3.68 ± 0.95	2.08 ± 0.73	8.69 ± 0.73	6.15 ± 0.44	19.61 ± 1.03
BUF	2.68 ± 0.82	12.80 ± 0.59	4.33 ± 1.04	1.75 ± 0.87	9.80 ± 0.89	6.53 ± 0.51	16.92 ± 1.01
FRAG							
WS	19.88 ± 3.03	25.41 ± 1.88	25.28 ± 2.62	19.10 ± 2.25	21.47 ± 2.05	22.38 ± 1.27	19.40 ± 1.89
BUF	20.95 ± 2.45	24.32 ± 1.88	27.39 ± 2.83	18.47 ± 2.59	22.92 ± 2.72	23.08 ± 1.47	25.32 ± 1.71
THKA							
WS	70.14 ± 5.69	90.52 ± 3.95	77.18 ± 5.08	108.33 ± 4.99	76.58 ± 3.87	82.42 ± 2.53	102.31 ± 7.73
BUF	85.19 ± 4.44	101.35 ± 4.14	81.84 ± 5.25	111.11 ± 5.68	81.03 ± 4.74	90.19 ± 2.69	103.79 ± 7.05
SOILDEN							
WS	1.21 ± 0.03	1.50 ± 0.02	1.16 ± 0.03	1.41 ± 0.03	1.23 ± 0.03	1.29 ± 0.02	1.30 ± 0.02
BUF	1.21 ± 0.03	1.50 ± 0.02	1.08 ± 0.04	1.38 ± 0.03	1.15 ± 0.03	1.25 ± 0.02	1.25 ± 0.02

Soil Chemical Properties

Variable/Aggregation	1A	1B	1C	1D	1E	NE	SBRP
CA_CL							
WS	4.87 ± 2.10	2.28 ± 1.15	1.36 ± 2.00	2.96 ± 1.34	2.04 ± 1.35	2.65 ± 0.87	0.30 ± 0.07
BUF	4.95 ± 1.72	3.31 ± 1.15	2.40 ± 1.98	3.94 ± 1.55	2.82 ± 1.52	3.44 ± 0.85	0.41 ± 0.07
MG_CL							
WS	0.47 ± 0.32	0.74 ± 0.17	0.20 ± 0.30	0.26 ± 0.20	0.53 ± 0.20	0.44 ± 0.13	0.27 ± 0.03
BUF	0.69 ± 0.26	0.93 ± 0.17	0.58 ± 0.30	0.40 ± 0.23	0.93 ± 0.23	0.73 ± 0.13	0.21 ± 0.03
K_CL							
WS	0.06 ± 0.01	0.10 ± 0.01	0.08 ± 0.01	0.05 ± 0.01	0.13 ± 0.01	0.09 ± 0.01	0.15 ± 0.01
BUF	0.06 ± 0.01	0.10 ± 0.01	0.10 ± 0.01	0.05 ± 0.01	0.14 ± 0.01	0.09 ± 0.01	0.14 ± 0.01
NA_CL							
WS	0.03 ± 0.02	0.05 ± 0.01	0.05 ± 0.02	0.03 ± 0.01	0.07 ± 0.01	0.04 ± 0.01	0.02 ± 0.00
BUF	0.06 ± 0.02	0.06 ± 0.01	0.10 ± 0.02	0.04 ± 0.01	0.12 ± 0.02	0.08 ± 0.01	0.03 ± 0.00
BS_CL							
WS	18.44 ± 3.94	29.10 ± 3.22	22.25 ± 3.77	17.49 ± 3.73	25.39 ± 2.95	22.80 ± 1.91	11.83 ± 1.35
BUF	23.30 ± 3.19	35.17 ± 3.30	30.21 ± 3.90	20.13 ± 4.24	30.49 ± 3.58	28.29 ± 2.11	12.27 ± 1.23
CEC_CL							
WS	9.89 ± 1.60	8.93 ± 0.88	6.27 ± 1.52	3.98 ± 1.03	7.92 ± 1.03	7.60 ± 0.66	7.17 ± 0.48
BUF	10.82 ± 1.31	9.59 ± 0.88	9.44 ± 1.50	5.08 ± 1.19	10.64 ± 1.15	9.43 ± 0.65	7.86 ± 0.45
AC_BACL							
WS	19.82 ± 2.88	10.66 ± 1.58	18.95 ± 2.73	10.04 ± 1.83	17.67 ± 1.85	16.03 ± 1.20	10.60 ± 0.81
BUF	19.72 ± 2.36	11.19 ± 1.57	24.57 ± 2.71	12.46 ± 2.12	23.06 ± 2.07	18.94 ± 1.16	11.90 ± 0.80
PH_01M							
WS	4.22 ± 0.09	4.37 ± 0.06	4.40 ± 0.08	4.35 ± 0.08	4.43 ± 0.06	4.36 ± 0.04	4.34 ± 0.05
BUF	4.38 ± 0.07	4.47 ± 0.07	4.50 ± 0.08	4.38 ± 0.09	4.53 ± 0.08	4.46 ± 0.04	4.38 ± 0.05
PH_H2O							
WS	4.80 ± 0.10	5.01 ± 0.07	4.96 ± 0.09	4.83 ± 0.09	5.01 ± 0.07	4.93 ± 0.04	5.08 ± 0.06
BUF	4.97 ± 0.08	5.14 ± 0.07	5.08 ± 0.09	4.86 ± 0.10	5.10 ± 0.08	5.04 ± 0.05	5.12 ± 0.05
AL_AO							
WS	0.86 ± 0.06	0.23 ± 0.04	0.54 ± 0.06	0.24 ± 0.04	0.43 ± 0.04	0.48 ± 0.03	0.26 ± 0.03
BUF	0.66 ± 0.05	0.21 ± 0.03	0.39 ± 0.06	0.23 ± 0.05	0.36 ± 0.05	0.38 ± 0.03	0.32 ± 0.03

Table 8-58. (Continued)

	Mean ± Standard Error by DDRP Subregion/Region						
	NE Subregion					Overall	
Variable/ Aggregation	1A	1B	1C	1D	1E	NE	SBRP
AL_CD							
WS	0.47 ± 0.05	0.20 ± 0.03	0.31 ± 0.05	0.15 ± 0.03	0.26 ± 0.03	0.29 ± 0.02	0.45 ± 0.03
BUF	0.37 ± 0.04	0.19 ± 0.03	0.25 ± 0.05	0.15 ± 0.04	0.23 ± 0.04	0.24 ± 0.02	0.42 ± 0.03
AL_PYP							
WS	0.43 ± 0.04	0.18 ± 0.02	0.27 ± 0.03	0.19 ± 0.02	0.24 ± 0.02	0.27 ± 0.01	0.26 ± 0.03
BUF	0.36 ± 0.03	0.18 ± 0.02	0.23 ± 0.03	0.18 ± 0.03	0.22 ± 0.03	0.24 ± 0.01	0.32 ± 0.03
ALPOT							
WS	7.46 ± 0.22	7.82 ± 0.15	7.54 ± 0.19	8.19 ± 0.19	7.49 ± 0.15	7.66 ± 0.10	7.22 ± 0.19
BUF	7.71 ± 0.17	8.11 ± 0.16	7.83 ± 0.20	8.32 ± 0.21	7.83 ± 0.18	7.93 ± 0.10	7.41 ± 0.18
LIMEPOT							
WS	2.60 ± 0.09	2.68 ± 0.06	2.71 ± 0.08	2.73 ± 0.08	2.74 ± 0.06	2.69 ± 0.04	2.51 ± 0.05
BUF	2.76 ± 0.07	2.80 ± 0.06	2.86 ± 0.08	2.79 ± 0.09	2.86 ± 0.07	2.82 ± 0.04	2.58 ± 0.05
C_TOT							
WS	5.21 ± 1.35	1.90 ± 0.74	4.68 ± 1.28	3.19 ± 0.86	3.84 ± 0.87	3.86 ± 0.56	1.16 ± 0.20
BUF	5.62 ± 1.11	2.56 ± 0.74	7.07 ± 1.27	4.36 ± 1.00	5.97 ± 0.97	5.26 ± 0.55	1.42 ± 0.20
SO4_H2O							
WS	7.77 ± 4.10	13.84 ± 2.25	8.35 ± 3.90	11.98 ± 2.65	7.24 ± 2.64	9.49 ± 1.70	9.68 ± 0.63
BUF	8.27 ± 3.35	13.82 ± 2.24	9.99 ± 3.86	13.07 ± 3.08	8.88 ± 2.95	10.51 ± 1.66	10.28 ± 0.62
SO4_PO4							
WS	26.57 ± 6.06	23.20 ± 3.32	28.90 ± 5.76	40.53 ± 3.86	25.71 ± 3.89	28.24 ± 2.52	87.91 ± 7.12
BUF	24.90 ± 4.96	21.75 ± 3.31	31.98 ± 5.70	41.63 ± 4.46	30.29 ± 4.37	29.54 ± 2.45	82.10 ± 7.02
SO4_EMX [d]							
WS	3052.2 ± .	2165.3 ± .	2623.7 ± .	1750.4 ± .	2338.1 ± .	2436.5 ± .	5362.4 ± .
SO4_B2 [d]							
WS	870.8 ± .	952.7 ± .	891.1 ± .	1116.6 ± .	872.2 ± .	925.6 ± .	175.4 ± .
SO4_XIN [d]							
WS	120.93 ± .	289.84 ± .	125.49 ± .	255.83 ± .	133.59 ± .	175.22 ± .	38.59 ± .
SO4_SLP [d]							
WS	3.15 ± .	1.74 ± .	2.61 ± .	1.31 ± .	2.38 ± .	2.33 ± .	32.75 ± .

Surface Water Chemistry							
SO416							
WS	115.46 ± 3.54	155.16 ± 8.52	92.33 ± 4.99	129.28 ± 6.46	73.90 ± 4.21	109.54 ± 3.58	29.69 ± 4.00
SO4_NRET							
WS	-0.12 ± 0.04	0.11 ± 0.05	-0.00 ± 0.07	-0.13 ± 0.05	-0.13 ± 0.07	-0.05 ± 0.03	0.72 ± 0.03
CAMG16							
WS	183.63 ± 20.80	327.00 ± 32.82	191.65 ± 19.46	206.01 ± 26.23	205.03 ± 19.68	220.22 ± 11.47	121.55 ± 15.17
SOBC							
WS	230.82 ± 24.75	441.98 ± 44.41	292.30 ± 24.59	507.77 ± 42.57	292.49 ± 19.68	337.53 ± 16.12	204.63 ± 22.40
CM_IO							
WS	1.00 ± 0.12	1.63 ± 0.17	1.06 ± 0.13	1.03 ± 0.16	1.23 ± 0.13	1.19 ± 0.07	0.69 ± 0.11
ALKA [e]							
WS	80.81 ± 19.29	191.83 ± 31.27	117.04 ± 19.33	94.60 ± 23.07	140.02 ± 18.60	125.60 ± 10.45	128.79 ± 16.26
PHEQ11							
WS	6.50 ± 0.16	7.15 ± 0.19	7.01 ± 0.13	6.73 ± 0.21	7.16 ± 0.09	6.93 ± 0.07	7.26 ± 0.05

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.

[b] Variable labels and units are found in Table 8-60.

[c] For each variable, WS refers to the entire watershed and BUF refers to the buffer zone.

[d] Error estimates were unavailable.

[e] ALKANEW in the NE, ALKA11 in the SBRP

exchange capacity (CEC_CL) is lowest in Southern New England, with a mean approximately half that of the northeastern regional mean. The highest levels of water-extractable sulfate (SO4_H2O) are found in the two more southern subregions (Poconos/Catskills, 1B, and Southern New England); phosphate-extractable sulfate is highest in the Southern New England soils. Sulfate isotherms also differ among the subregions. Sulfate adsorption capacity (SO4_EMX) is highest for soils in the Adirondack Subregion and lowest in Southern New England. The Southern New England soils are also characterized by the highest half-saturation constant (SO4_B2) and the second largest equilibrium soil solution concentration (SO4_XIN). Thus, the adsorption curve for the Southern New England soils is flatter and lower than that for the other subregions. Soils in the Poconos/Catskills Subregion have similar isotherm parameters to the Southern New England soils, except for a significantly higher sulfate adsorption capacity. Sulfate isotherms for soils from the three northern subregions are distinct from those of the southern subregions.

Other soil properties also vary among the subregions. Exchangeable acidity (AC_BACL) is relatively high in the Adirondacks soils, which are also characterized by the highest sum of base cations and the highest cation exchange capacity. In general, extractable aluminum (AL_AO, AL_CD, AL_PYP) also is highest in the Adirondacks soils. Soils of the Poconos/Catskills Subregion are finer-textured relative to the other subregions and have a higher mean bulk density (SOILDEN). Soils in the Southern New England watersheds have higher sand content. The relatively low mean CEC may be related to the higher sand content of these soils. Soils in the Maine (1E) Subregion are similar to the Adirondacks and Central New England (1C) soils, with relatively high levels of exchangeable acidity and total carbon. Spodosols represent a large proportion of the soils in these three northern subregions, which may partially explain these observations. Soil pH varies relatively little among the five subregions.

Comparing regional watershed means for the NE and SBRP, a few differences are notable. Soils in the NE are characterized by higher concentrations of bases and base saturation, higher acidity, and much lower clay content and phosphate-extractable sulfate. Carbon content of northeastern soils is also higher than SBRP soils. Sulfate isotherm parameters also differ significantly between the two regions, with the SBRP exhibiting significantly higher maximum adsorption capacity and significantly lower equilibrium soil solution sulfate concentrations than the northeastern soils.

Mean values for soils within the buffer zones are similar to the whole-watershed means for most variables. Differences exist for the base cation variables (CA_CL, MG_CL, K_CL, NA_CL, BS_CL), where levels are higher in the buffers relative to the whole watershed. As these buffers represent areas of convergent flow (variable hydrologic source areas, riparian zones), this is as expected. Soils in the buffer zones have higher total carbon content and slightly higher water-extractable sulfate levels. In the Central New England and Maine Subregions, the mean extractable acidity of the buffer soils is higher relative to the whole watershed mean. Differences between buffers and whole watershed values are generally larger in the NE than in the SBRP.

8.9.5 Sulfate and Sulfur Retention

This section and Section 8.9.6 discuss the statistical relationships between measured soil physical and chemical properties and water chemistry for the DDRP watersheds. These relationships are also evaluated in terms of potential cause-effect controls on water chemistry. Tables 8-59 and 8-60 show the

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Table 8-59. Non-parametric Correlations Between Lake Chemistry Variables and Selected Soil Properties for the NE DDRP Watersheds

		Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 143				
Variable	Units	SO416[a]	SO4_NRET	CAMG16	ALKANEW	PHEQ11
Soil Physical Properties						
SAND Sand, total	percent			-0.34086 0.0001	-0.33012 0.0001	-0.31760 0.0001
SILT Silt, total	percent			0.31267 0.0001	0.31272 0.0001	0.30011 0.0003
CLAY Clay, total	percent			0.30097 0.0003	0.25367 0.0022	0.24658 0.0030
FRAG Fragments > 2mm diameter	percent					
THKA Thickness adjusted for FRAG	cm		0.22660 0.0065			
SOILDEN Bulk density	g/cc	0.18434 0.0275	0.16098 0.0548	0.20719 0.0130	0.18355 0.0282	0.18659 0.0257
Soil Chemical Properties						
CA_CL Exchangeable calcium (NH4 Cl)	meq/100g			0.22554 0.0068	0.20727 0.0130	0.21764 0.0090
MG_CL Exchangeable magnesium (NH4 Cl)	meq/100g			0.24922 0.0027	0.22041 0.0082	0.21303 0.0106
K_CL Exchangeable potassium (NH4 Cl)	meq/100g			0.33975 0.0001	0.35981 0.0001	0.34094 0.0001
NA_CL Exchangeable sodium (NH4 Cl)	meq/100g					
SBC_CL Sum of base cations (NH4 Cl)	meq/100g	-0.20633 0.0134		0.17816 0.0333	0.19769 0.0179	0.20094 0.0161
BS_CLM Base saturation	percent			0.35370 0.0001	0.32607 0.0001	0.31892 0.0001
CEC_CL Cation exchange capacity	meq/100g					

[a] SO416 is the lake sulfate concentration, SO4_NRET is watershed sulfur retention, CAMG16 is the lake sum of base cation concentration, ALKA11 is the lake acid neutralizing capacity, and PHEQ11 is the air-equilibrated stream pH.

Table 8-59.   (Continued)

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 143

Variable	Units	SO416	SO4_NRET	CAMG16	ALKANEW	PHEQ11
AC_BACL Acidity, total exchangeable	meq/100g					
PH_01M pH (0.01 M CaCl2)		-0.26116 0.0016	0.20045 0.0164	0.34515 0.0001	0.50310 0.0001	0.50717 0.0001
PH_H2O pH (deionized water)		-0.24556 0.0031	0.19831 0.0176	0.39852 0.0001	0.55995 0.0001	0.56159 0.0001
AL_AO Aluminum, acid oxalate extr.	percent		-0.22581 0.0067	-0.29118 0.0004	-0.22259 0.0075	-0.22549 0.0068
AL_CD Aluminum, citrate dithionite extr.	percent		-0.30041 0.0003	-0.17679 0.03470	-0.19756 0.0180	-0.21248 0.0108
AL_PYP Aluminum, pyrophosphate extr.	percent		-0.31004 0.0002	-0.23970 0.0039	-0.24274 0.0035	-0.25233 0.0024
ALPOT Aluminum potential (pH - $1/3$ pAl)						
LIMEPOT Lime potential (pH - ½pCa)		-0.22764 0.0063	0.18844 0.0242	0.31191 0.0001	0.45409 0.0001	0.45649 0.0001
C_TOT Carbon, total	percent					
SO4_H2O Sulfate, water extractable	mg S/kg		0.21355 0.0104			
SO4_PO4 Sulfate, phosphate extractable	mg S/kg				-0.16690 0.0463	
SO4_EMX Adsorption asymptote	ueq/kg		-0.17203 0.0399	-0.31713 0.0001	-0.26774 0.0012	-0.26759 0.0012
SO4_B2 Half saturation constant	ueq/L	0.26265 0.0015		0.20137 0.0159		
SO4_XIN Zero net adsorption concentration	ueq/L	0.32235 0.0001		0.33774 0.0001	0.17842 0.0330	0.17229 0.0396
SO4_SLP Zero net adsorption, slope	L/kg	-0.17347 0.0383		-0.34564 0.0001	-0.23617 0.0045	-0.23432 0.0049

Table 8-60. Non-parametric Correlations Between Stream Chemistry Variables and Selected Soil Properties for the SBRP DDRP Watersheds

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 31

Variable	Units	SO416[a]	SO4_NRET	SOBC	ALKA11	PHEQ11
Soil Physical Properties						
SAND Sand, total	percent					
SILT Silt, total	percent	0.42863 0.0161				
CLAY Clay, total	percent					
FRAG Fragments > 2mm diameter	percent			-0.40161 0.0251	-0.45121 0.0108	
THKA Thickness adjusted for FRAG	cm	-0.37742 0.0363				
SOILDEN Bulk density	g/cc					
Soil Chemical Properties						
CA_CL Exchangeable calcium (NH4 Cl)	meq/100g	0.58790 0.0005	-0.40766 0.0228	0.51532 0.0030	0.41331 0.0208	0.51734 0.0029
MG_CL Exchangeable magnesium (NH4 Cl)	meq/100g			0.49597 0.0045	0.44315 0.0125	0.35363 0.0510
K_CL Exchangeable potassium (NH4 Cl)	meq/100g					
NA_CL Exchangeable sodium (NH4 Cl)	meq/100g					
SBC_CL Sum of base cations (NH4 Cl)	meq/100g	0.48226 0.0060				
BS_CLM Base saturation	percent			0.54597 0.0015	0.52823 0.0023	0.50444 0.0038
CEC_CL Cation exchange capacity (NH4 Cl)	meq/100g					

[a] SO416 is the stream sulfate concentration, SO4_NRET is watershed sulfur retention, SOBC is the stream sum of base cation concentration, ALKA11 is the stream acid neutralizing capacity, and PHEQ11 is the air-equilibrated stream pH.

Table 8-60. (Continued)

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 31

Variable	Units	SO416	SO4_NRET	SOBC	ALKA11	PHEQ11
AC_BACL Total exchangeable acidity	meq/100g				-0.36169 0.0456	
PH_01M pH (0.01M CaCl2)					0.37298 0.0388	0.46169 0.0089
PH_H2O pH (deionized water)						
AL_AO Aluminum, acid oxalate extr.	percent			-0.35524 0.0499	-0.36653 0.0426	
AL_CD Aluminum, citrate dithionite extr.	percent					
AL_PYP Aluminum, pyrophosphate extr.	percent			-0.48589 0.0056	-0.48710 0.0055	-0.41774 0.0194
ALPOT Aluminum potential (pH - $1/3$ pAl)		0.36573 0.0430	-0.38790 0.0311			
LIMEPOT Lime potential (pH - ½pCa)						0.39194 0.0292
C_TOT Carbon, total	percent					
SO4_H2O Sulfate, water extractable	mg S/kg	0.43427 0.0146				
SO4_PO4 Sulfate, phosphate extractable	mgS/k					
SO4_EMX Adsorption asymptote	ueq/kg	-0.49395 0.0047	0.46976 0.0077			
SO4_B2 Half saturation constant	ueq/L			-0.44032 0.0132	-0.44476 0.0122	
SO4_XIN Zero net adsorption concentration	ueq/L				-0.42702 0.0166	
SO4_SLP Zero net adsorption, slope	L/kg			0.41129 0.0215	0.44758 0.0116	

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nonparametric Spearman correlations between selected soil properties and each of the water chemistry variables considered. Results of stepwise multiple regressions for sulfate and sulfur retention are given in Tables 8-61 and 8-62.

8.9.5.1 Northeast

8.9.5.1.1 Whole watershed aggregation -

The coefficients of determination, or R^2, range from 0 to 0.56 for sulfate and from 0.12 to 0.64 for sulfur retention in the northeastern subregions. Bivariate correlations between soil properties and sulfate or sulfur retention are generally not high. The strongest correlation is between lake sulfate concentration and the zero net adsorption concentration (or equilibrium soil solution sulfate concentration) from the sulfate isotherms. This relationship makes sense mechanistically, i.e., since northeastern watersheds are generally near steady state with respect to sulfur deposition, soil and lake sulfate concentrations both tend to reflect deposition. The highest correlation with sulfur retention is a negative one with extractable aluminum. Soils in the NE appear to be approaching a new equilibrium with lower sulfate deposition; soils rich in extractable aluminum have a large adsorbed sulfate pool that is now desorbing, resulting in an inverse relationship between extractable aluminum and sulfate retention. The correlations of sulfate and sulfur retention with soil pH and lime potential also fit this scenario. As would be expected, the correlations for sulfate and sulfur retention tend to be opposite in sign. A similar pattern of relationships is apparent in the multiple regression results, with some variation among the subregions. In the Poconos/Catskills (1B) and Southern New England (1D), sulfate is positively correlated with soil pH; in Central New England (1C) and in the region as a whole, however, the relationship with pH is negative. In the Adirondacks (1A) and the Poconos/Catskills, the two subregions with highest sulfate deposition, sulfate is correlated with the half-saturation concentration, a sulfate isotherm intensity factor that is highly correlated with the concentration at zero net adsorption. This relationship is consistent with the bivariate correlations. In the Poconos/Catskills, Central New England, and Southern New England, sulfate is correlated with extractable aluminum. This is consistent with the hypothesis that previously adsorbed sulfate may be desorbing from these soils. This scenario also is supported by the sulfur retention regressions; in most subregions and the NE overall, the greater the extractable aluminum in the soil, the lower the net retention.

8.9.5.1.2 Combined buffer aggregation -

Variables selected by the stepwise regressions for the northeastern watersheds aggregated for the combined buffers around the lakes and streams were the same as or similar to those selected for the whole watershed aggregation. The R^2 for sulfate improved significantly, with fewer variables in the model, but the R^2 for the sulfur retention model is lower. Buffer zone models were not run for the northeastern subregions. These results alone do not allow a conclusion to be drawn regarding the relative merits of each aggregation for these analyses.

Table 8-61. Results of Stepwise Multiple Regressions for DDRP Lake and Stream Sulfate Concentrations (SO416) Versus Soil Physical and Chemical Properties

Variable[b]	Whole Watersheds							Buffer Zone	
	Subregion[a]					Region		Region	
	1A[c]	1B	1C	1D	1E	NE	SBRP	NE	SBRP
SAND									
CLAY						5			
FRAG									
THKA									
SOILDEN						3			
CA_CL									
MG_CL							1		1
SBC_CL									
BS_CL		4(-)							
CEC_CL									
AC_BACL									
PH_01M		1	2(-)	2		2(-)			
AL_AO				3					
AL_CD			1			4			
AL_PYP		2				6		3	
ALPOT									
C_TOT	3		4(-)				4(-)		
SO4_H2O			3(-)	1(-)			3		3
SO4_PO4								4(-)	
SO4_EMX	2						2(-)	2	2(-)
SO4_B2	1	3				1			
SO4_XIN								1	
SO4_SLP									
R²	0.35	0.56	0.52	0.46	None Selected	0.27	0.66	0.43	0.62

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-60.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

Table 8-62. Results of Stepwise Multiple Regressions for DDRP Watershed Sulfur Retention (SO4_NRET) Versus Soil Physical and Chemical Properties

Variable[b]	Whole Watersheds							Buffer Zone	
	Subregion[a]					Region		Region	
	1A[c]	1B	1C	1D	1E	NE	SBRP	NE	SBRP
SAND									
CLAY									
FRAG						5			
THKA						4			
SOILDEN									
CA_CL									
MG_CL	2(-)						2(-)		2(-)
SBC_CL									
BS_CL							3		3
CEC_CL									
AC_BACL			2		4				
PH_01M	1		6						
AL_AO					2				
AL_CD			1(-)	1(-)	1(-)	1(-)		1(-)	
AL_PYP		2(-)	3(-)					4(-)	
ALPOT									
C_TOT			4(-)						
SO4_H2O			5	2		2		2	
SO4_PO4		1							
SO4_EMX							1		1
SO4_B2						3(-)		3(-)	
SO4_XIN					3(-)				
SO4_SLP									
R^2	0.12	0.41	0.64	0.30	0.37	0.22	0.44	0.16	0.44

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-60.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

8.9.5.2 Southern Blue Ridge Province

8.9.5.2.1 Whole watershed aggregation -

Exchangeable magnesium and maximum sulfate adsorption capacity are most strongly related to sulfate and sulfur retention in the SBRP in the multiple linear regressions (Tables 8-61 and 8-62). R^2 for sulfate is 0.66, and 0.44 for sulfur retention. Higher exchangeable magnesium (and calcium, in the bivariate correlations) in the soil is correlated with higher sulfur in the water and lower sulfate retention by the soil; higher sulfate adsorption capacity is correlated with lower sulfate in the water and higher retention in the soil. Higher water-extractable sulfate in the soil is correlated with higher water sulfate. Higher base saturation soils are correlated with greater sulfur retention in the soil (though this may be spurious because there is no bivariate correlation between these variables). In this region where the soils have not yet reached equilibrium with atmospheric sulfur deposition, the adsorption capacity of the soil is a good explanatory variable of both retention and concentration in the drainage water. Water-extractable sulfate is a readily mobilized pool of sulfate, acting in the SBRP as the soil intensity variable associated with sulfate in the water. The reason for the strong relationship between exchangeable magnesium (and calcium) and sulfate is possibly due to higher base status soils generally having higher pH and hence lower sulfate adsorption, although there is no correlation between base saturation or pH and sulfate. Another possibility would be a sulfur-rich bedrock source that is weathering both bases and sulfur. This is supported by the correlation between the low organic meta-sedimentary MSL sampling class soils and stream sulfate (Section 8.6.3.2).

8.9.5.2.2 100-m buffer aggregation -

There is virtually no difference in the models selected for the 100-m buffer aggregation from those for the whole watershed in the SBRP. This suggests that estimated chemistry for the soils at the stream sides is not more strongly associated with spring baseflow chemistry than those in the whole watershed. Stream chemistry measured during stormflow, a time when the near-stream soils would be expected to be more hydrologically active, might be more strongly associated with 100-m buffer soil chemistry.

8.9.6 Ca plus Mg (SOBC), ANC, and pH

Results of stepwise multiple regression for Ca plus Mg concentrations (sum of base cations in the SBRP), ANC, and pH are given in Tables 8-63 through 8-65. This section summarizes the results and discusses potential cause-effect controls on surface water chemistry. The dependent water chemistry variables are all highly correlated with each other and therefore have very similar associations with soil physical and chemical properties. Of the four, pH is the most dissimilar because of its nonlinear relationship with ANC (Figure 5-7).

8.9.6.1 Northeast

8.9.6.1.1 Whole watershed aggregation -

The R^2 values range from 0.31 to 0.84 for the northeastern subregions. Soil pH is most commonly and most strongly associated with the water chemistry in most northeastern subregions and in the region

Table 8-63. Results of Stepwise Multiple Regressions for DDRP Lake Calcium plus Magnesium Concentrations (CAMG16) and Stream Sum of Base Cation Concentrations (SOBC) Versus Soil Physical and Chemical Properties

| Variable[b] | Whole Watersheds | | | | | | | Buffer Zone | |
| | Subregion[a] | | | | | Region | | Region | |
	1A[c]	1B	1C	1D	1E	NE	SBRP	NE	SBRP
SAND						4(-)			
CLAY						1			
FRAG									
THKA						5(-)			
SOILDEN						6			
CA_CL			3						
MG_CL					2(-)				
SBC_CL	3								
BS_CL					1		1	1	1
CEC_CL		2			3			5	
AC_BACL				2					
PH_01M	2	1	4	1		2		4	
AL_AO					4(-)				
AL_CD			2						
AL_PYP				5(-)	5				
ALPOT									
C_TOT									
SO4_H2O		1							
SO4_PO4				3(-)					
SO4_EMX						3(-)			
SO4_B2								3(-)	
SO4_XIN	1			4(-)				2	
SO4_SLP									
R^2	0.71	0.57	0.49	0.81	0.59	0.40	0.44	0.38	0.48

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-60.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

Table 8-64. Results of Stepwise Multiple Regressions for DDRP Lake and Stream ANC (ALKANEW and ALKA11) Versus Soil Physical and Chemical Properties

			Whole Watersheds					Buffer Zone	
			Subregion[a]				Region		Region
Variable[b]	1A[c]	1B	1C	1D	1E	NE	SBRP	NE	SBRP
SAND						3(-)			
CLAY						1			
FRAG									
THKA									
SOILDEN									
CA_CL			2			4			
MG_CL		3(-)	3(-)			5(-)			
SBC_CL	3								
BS_CL							1	1	1
CEC_CL		2						5	
AC_BACL				4					
PH_01M	2	1		1		2		2	
AL_AO					1(-)				
AL_CD			4	5(-)					
AL_PYP					2				
ALPOT									
C_TOT	4(-)								
SO4_H2O			1(-)						
SO4_PO4				3(-)					
SO4_EMX			5(-)		3(-)				
SO4_B2								4(-)	
SO4_XIN	1			2(-)				3	
SO4_SLP									
R^2	0.75	0.62	0.53	0.83	0.47	0.43	0.44	0.36	0.47

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-60.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

Table 8-65. Results of Stepwise Multiple Regressions for DDRP Lake and Stream pH (PHEQ11) Versus Soil Physical and Chemical Properties

| | Whole Watersheds | | | | | | | Buffer Zone | |
| | Subregion[a] | | | | | Region | | Region | |
Variable[b]	1A[c]	1B	1C	1D	1E	NE	SBRP	NE	SBRP
SAND						2(-)			
CLAY									
FRAG									2(-)
THKA									
SOILDEN									
CA_CL			4					2	
MG_CL			3(-)	2					
SBC_CL									
BS_CL							1		1
CEC_CL				3(-)					
AC_BACL									
PH_01M	1	1		1		1		1	
AL_AO		6(-)	2		2(-)				
AL_CD									
AL_PYP					4				
ALPOT							3		3
C_TOT		5							
SO4_H2O			1(-)						
SO4_PO4					3			3(-)	
SO4_EMX		2(-)			1(-)				
SO4_B2		4					2(-)		
SO4_XIN	2	3(-)							
SO4_SLP									
R²	0.33	0.84	0.64	0.46	0.71	0.31	0.45	0.30	0.48

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-60.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

overall. Exchangeable calcium, base saturation, and the sum of soil base cations are highly correlated with each other and are also commonly associated with the water chemistry. In the Poconos/Catskills Subregion, cation exchange capacity was selected by the stepwise regressions for ANC and Ca plus Mg; this region has the highest mean base saturation. In Southern New England, cation exchange capacity was selected for lake pH, but with a negative sign; that subregion has the lowest base saturation, i.e., it has a greater proportion of acidic cations on its exchange sites. The bivariate correlations (Table 8-59) also match the pattern seen in the multiple regressions; heavier, clay-rich soils high in exchangeable bases, pH, and base saturation are strongly correlated with higher bases, ANC, and pH in the water. These relationships lend support to the hypothesis that exchangeable bases in soils are important controls on the base cation supply to, and ANC of, surface waters.

A group of soil sulfate-related variables also is correlated with base cations, ANC, and pH of the northeastern DDRP lakes. The variables include intensity and capacity isotherm parameters, water and phosphate extractable sulfate, the different forms of extractable aluminum, and possibly exchangeable magnesium. The variables appear in different combinations and with different signs in the regressions for the different subregions. The bivariate correlations (Table 8-59) show strong positive correlations with sulfate concentration at zero net adsorption; i.e., high equilibrium sulfate concentration (which is correlated with sulfate deposition) is associated with high base cation supply for the region overall. The sulfate isotherm variables SO4_EMX and SO4_SLP are correlated with low base cation supply, ANC, and pH. In the regressions for the northeastern region as a whole, most of the sulfate-related chemical parameters are replaced by soil texture variables. The sandier soils are associated with lower base cations, ANC, and pH in surface water; the soils with higher clay content are associated with higher base cations, ANC, and pH in the water. Further work is needed to detail possible mechanisms and subregional differences in these relationships.

8.9.6.1.2 Combined buffer aggregation -

The variables selected by the stepwise regressions for the buffer zone aggregation are more similar to the variables selected for the subregion models than to those selected by the models for the whole region. However, they have slightly lower R^2 values than the whole-watershed models, and much lower R^2 values than the subregion models. Buffer zone models were not run for the subregions. These limited results suggest that the buffer zone aggregation does not help in explaining variability in the surface water chemistry.

8.9.6.2 Southern Blue Ridge Province

8.9.6.2.1 Whole watershed aggregation -

Base saturation is most highly associated with these SBRP stream chemistry variables. Other associated variables for pH include aluminum potential and the isotherm half-saturation constant. R^2 values range from 0.44 to 0.45, slightly higher than for the NE. The bivariate correlations are consistent with the multiple regression results. As for the NE, these relationships support the hypotheses that exchangeable bases and mobile sulfate are important regulators of surface water chemistry.

8.9.6.2.2 100-m buffer aggregation -

The models selected for the buffer zone aggregation are very similar to those for the entire watershed aggregation.

8.9.7 Evaluation of Alternative Aggregation Schemes

In order to examine the effect of the different aggregation schemes on the Level I Analysis results, we ran several regressions using soil chemistry variables from the unadjusted aggregation scheme. The results of these regressions are compared with the results from the watershed adjusted data in Tables 8-66 and 8-67. Prior to regression analysis, a collinearity analysis was conducted. Variables dropped as a result of this analysis are marked by X's in the tables. The remaining variables were used in stepwise regressions with ANC and sulfate as the response variables.

Examination of Tables 8-66 and 8-67 shows that many more candidate explanatory variables had to be dropped from the unadjusted data than from the adjusted data. There were fewer instances of multi-collinearity when using the watershed aggregation. Second, the regression models based on the adjusted data generally explained more variance in the response variables than did the models based on the unadjusted data. The only exception to this result is SO416 in the SBRP. The adjustment for watershed effect generally appears to increase the explanatory power of the soil chemistry variables.

8.9.8 Summary and Conclusions

8.9.8.1 Alternative Aggregation Schemes

The DDRP soil sampling and common aggregation scheme (unadjusted data) probably characterizes regional and subregional means of soil properties well. The common aggregation scheme appears to have limitations, however, in characterizing the regional distribution of soil properties or the soil properties of individual watersheds. The common aggregation scheme biases individual watershed values toward the regional mean value. An alternative aggregation approach that uses a regression model to adjust for watershed effects appears to adjust the problem of bias toward the regional mean but adds additional uncertainty to the estimates of watershed soil chemistry.

The common aggregation scheme was used for most Level II and III modeling because it was the only data available at the time. The correlations and regressions conducted here used the watershed-effects-adjusted data because they have the most explanatory power for surface water chemistry. Additional field work would be needed to assess which aggregation scheme most closely mimics reality. The characteristics of each aggregation scheme must be kept in mind when interpreting the results of the models.

Although the buffer zone and whole-watershed aggregation schemes do result in slightly different values for some of the soil physical and chemical variables, most differences are probably not significant. The buffer zone aggregation does not result in improved regression relationships for either the NE or SBRP, thus the advantage of using one aggregation scheme over the other for explaining index chemistry is unclear. The buffer zone aggregation was hypothesized to be more representative because it implicitly

Table 8-66. Results of Stepwise Multiple Regressions for DDRP Lake and Stream ANC (ALKANEW and ALKA11) Versus Unadjusted and Watershed Adjusted Soil Physical and Chemical Properties

Variable[a]	NE[b]		SBRP[b]	
	Unadjusted	Adjusted	Unadjusted	Adjusted
SAND	X	3(-)	X	
CLAY		1	X	
FRAG			X	
THKA			X	
SOILDEN			X	
CA_CL		4		
MG_CL		5(-)	X	
SBC_CL				
BS_CL	1		1	1
CEC_CL	2(-)		X	X
AC_BACL	X		X	
PH_01M		2		
AL_AO	X			
AL_CD			X	
AL_PYP	X		X	
ALPOT			X	
C_TOT	X		X	
SO4_H2O	X			
SO4_PO4			X	
SO4_EMX				
SO4_B2				
SO4_XIN			X	
SO4_SLP	X		2	X
R^2	0.33	0.43	0.29	0.44

[a] Variable labels and units are found in Table 8-60.
[b] X's indicate variables dropped in collinearity analysis. Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

Table 8-67. Results of Stepwise Multiple Regressions for DDRP Lake and Stream Sulfate (SO416) Versus Unadjusted and Watershed Adjusted Soil Physical and Chemical Properties

Variable[a]	NE[b] Unadjusted	NE[b] Adjusted	SBRP[b] Unadjusted	SBRP[b] Adjusted
SAND	X		X	
CLAY	4(-)	5	X	
FRAG			X	
THKA	5(-)		X	
SOILDEN		3	X	
CA_CL				
MG_CL			X	1
SBC_CL				
BS_CL				
CEC_CL			X	X
AC_BACL	X		X	
PH_01M		2(-)		
AL_AO	X			
AL_CD		4	X	
AL_PYP	X	6	X	
ALPOT			X	
C_TOT	X		X	
SO4_H2O	X			3
SO4_PO4	3(-)		X	
SO4_EMX	2		1(-)	2(-)
SO4_B2		1		
SO4_XIN	1		X	
SO4_SLP	X		2	X
R^2	0.47	0.27	0.32	0.62

[a] Variable labels and units are found in Table 8-60.
[b] X's indicate variables dropped in collinearity analysis. Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

weighted watershed values to take into account convergent flow and last hydrologic contact with the soil. However, from our analyses, the importance of these characteristics appear to be minor for explaining index water chemistry. This may be due to insufficient characterization of the buffer zones. Only soil mapping units greater than 6-10 acres were mapped; the effective buffer zones may be much smaller in size. A more thorough soil characterization and evaluation of watershed hydrology is necessary before the importance of buffer zones in controlling stream chemistry can be determined.

8.9.8.2 Sulfate and Sulfur Retention

The regression analyses indicated that the sulfate isotherm parameters are strongly related to surface water sulfate. In the NE the important parameters are the equilibrium sulfate concentration and the half saturation constant. This is consistent with the hypothesis that northeastern soils are near steady state with respect to sulfate adsorption. In the SBRP the adsorption asymptote and the extractable sulfate are important explanatory variables for stream sulfate concentration. These variables indicate soils that are actively adsorbing sulfate. Too much emphasis should not be placed on which particular isotherm parameters are selected in the regressions, since the isotherm parameters are themselves strongly correlated. It is significant, however, that the isotherm parameters are selected in both the NE and SBRP. Even in a region near steady state, the sulfate isotherm parameters yield information about concentrations of sulfate in the surface waters.

Variables relating to soil acidity and base status are also important but do not enter the regression models for the regions and subregions in a consistent manner. The relationship of surface water sulfate concentration and soil pH varies among the subregions of the NE and is not statistically significant for the SBRP watersheds. In general in the NE, high concentrations of sulfate in surface waters are associated with low pH and high extractable aluminum concentrations in the soils. In the SBRP, high sulfate concentrations are associated with high concentrations of base cations in the soils. The fact that the two regions are approaching soil sulfate equilibrium from different directions (declining deposition and desorption in the NE versus adsorption in the SBRP) may be responsible for the variability observed in the soil chemical relationships.

In general, the same soil variables that are important in predicting sulfate concentration are important in the regressions for sulfur net retention, but the coefficients of the variables have opposite signs. Values of sulfur retention are significantly higher in the SBRP then in the NE. This is consistent with the lower observed equilibrium sulfate concentration (Table 8-58).

8.9.8.3 Ca plus Mg (SOBC), ANC, and pH

Soil pH, exchangeable base cations, and texture are most strongly related to lake ANC, pH, and base cation concentrations in the NE. Soil base saturation has the strongest relationships in the SBRP. The sulfate isotherm parameters are more common as explanatory variables in the NE than the SBRP. This is consistent with the mobile anion hypothesis. The drainage water sulfate concentration, and therefore the sulfate isotherm parameters, is relatively less important in controlling ANC in the SBRP than in the NE.

Mean concentrations of Ca plus Mg are significantly higher in the NE than the SBRP, as expected since soils in the SBRP are older and more highly weathered. Northeastern soils also have a higher base

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saturation on average than those in the SBRP. The regressions and measured soil and surface water attributes support the hypothesis that soil base cation availability has a stronger effect on surface water ANC than other soil chemical properties.

8.9.9 Summary Conclusions

- Soil variables important in explaining surface water sulfate and watershed sulfur retention include soil sulfate concentration and adsorption capacity, extractable aluminum, soil pH, and texture.

- Soil variables important in explaining ANC, pH, and Ca plus Mg (sum of base cations) in surface water include soil base saturation, pH, soil sulfate concentration, and texture.

- Using a multiple regression modelling approach, measured soil chemical and physical properties alone can account for one quarter to three quarters of the variance in ANC, sulfate, and base cations in the lake and stream waters of the DDRP regions and subregions.

- The DDRP soils data aggregation scheme using soil sampling classes masks a significant watershed effect. The aggregation scheme probably accurately characterizes regional mean values, but it draws all data toward the mean, and may affect the distribution of modelling results. Those results also will be drawn toward the mean, underestimating the possible response of watersheds having soil characteristics at the sensitive end of the distribution.

- Aggregating soils by buffer zones near the lakes and streams does not generally result in better correlations with index values of surface water chemistry. Stronger associations would likely be observed between buffer zone soil characteristics and stormflow chemistry, when those soils are more hydrologically active.

8.10 EVALUATION OF ASSOCIATIONS BETWEEN WATERSHED ATTRIBUTES AND SURFACE WATER CHEMISTRY

8.10.1 Introduction

This section evaluates the relationships between surface water chemistry and all of the watershed attributes measured in the DDRP. Many watershed characteristics have been shown to explain a significant portion of the variance in surface water chemistry when considered individually or in groups of related variables (see Sections 8.2 through 8.9). The analyses in this section are designed to integrate and evaluate the various watershed attributes in explaining the variability in surface water chemistry. The results are important in assessing whether the DDRP Levels II and III modelling efforts are considering the variables most important in controlling surface water chemistry.

8.10.2 Approach

The candidate explanatory variables considered in this section include soil physical and chemical properties, climate and deposition, geology, hydrology, physiography, vegetation, and land use characteristics. Two basic categories of watershed attributes were used: average attribute values for a watershed and areal proportions of a watershed meeting specified criteria. Average attributes for each watershed include means for depth to bedrock, soil base saturation, soil permeability, deposition, precipitation, and runoff values, among others. Mean watershed attributes were calculated by averaging the values associated with mapped areas on a watershed and weighting by the areal fraction of the mapped area. An overview of the procedure for aggregating soil variables is given in Section 8.9.3, and a description for the other watershed attributes can be found in Turner et al. (1989).

Although average values provide an integrated estimate of an attribute at the watershed level, such values do not provide much information about the distribution of an attribute on a watershed. Furthermore, mean values cannot be calculated for many attributes such as vegetation cover type or geomorphic position. Therefore a second category of attributes was developed in order to estimate the proportion of watersheds meeting specified criteria. Watershed proportions were derived from the mapped data by summing the areal percentages of those mapping units on each watershed that satisfy the specified criterion.

Summary statistics for the subset of watershed attributes that were used in these analyses are given in Tables 8-58 and 8-68. Data derived from field mapping activities are described in Section 5.4.1.3, and the land use/wetland data obtained from photointerpretation are explained in Section 5.4.1.6. Deposition, precipitation, and runoff data were obtained as described in Sections 5.6 and 5.7. The regression modelling approach described in Section 8.9.2.2 was also used here.

8.10.3 Regional Characterization of Watershed Attributes

Characteristics of the sampled watersheds differ among the five subregions and between the two study regions. The characteristics can be grouped into four categories: climate/deposition variables, geologic parameters, hydrologic/physiographic descriptors, and land use/vegetation variables. Means and standard errors for these means are presented for each of the northeastern subregions, for the NE as a whole, and for the SBRP in Table 8-68.

8.10.3.1 Northeast Subregions

Long-term atmospheric deposition of ions varies among the five subregions, despite approximately equal precipitation amounts. Sodium and chloride deposition are highest in the Southern New England subregion, probably due to sea-salt deposition. The highest levels of calcium and magnesium deposition are found in the Adirondacks and Southern New England, and deposition of hydrogen ions and sulfate is highest in the Poconos/Catskills Subregion.

Table 8-68. Population Means and Standard Errors for Selected Variables, by Subregion/Region and Aggregation

Variable/ Aggregation [b]	NE Subregion [a] 1A	1B	1C	1D	1E	Overall NE	SBRP
			Deposition/Climate				
CA_LTD [c]							
WS	0.15 ± 0.01	0.10 ± 0.01	0.08 ± 0.01	0.10 ± 0.01	0.06 ± 0.01	0.10 ± 0.00	0.20 ± 0.02
MG_LTD							
WS	0.07 ± 0.00	0.06 ± 0.01	0.08 ± 0.01	0.15 ± 0.01	0.10 ± 0.01	0.09 ± 0.00	0.09 ± 0.01
NA_LTD							
WS	0.07 ± 0.01	0.10 ± 0.01	0.14 ± 0.02	0.49 ± 0.07	0.26 ± 0.03	0.20 ± 0.01	0.14 ± 0.01
K_LTD							
WS	0.03 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.02 ± 0.00	0.03 ± 0.00
CM_LTD							
WS	0.22 ± 0.01	0.16 ± 0.01	0.16 ± 0.01	0.26 ± 0.02	0.17 ± 0.01	0.19 ± 0.00	0.29 ± 0.02
NH4_LTD							
WS	0.25 ± 0.01	0.21 ± 0.01	0.15 ± 0.01	0.14 ± 0.01	0.11 ± 0.01	0.17 ± 0.00	0.22 ± 0.01
H_LTD							
WS	0.77 ± 0.01	1.14 ± 0.02	0.66 ± 0.01	0.72 ± 0.02	0.42 ± 0.01	0.72 ± 0.01	0.68 ± 0.03
SO4_LTD							
WS	0.73 ± 0.02	0.97 ± 0.02	0.61 ± 0.02	0.71 ± 0.02	0.46 ± 0.02	0.68 ± 0.01	0.84 ± 0.03
NO3_LTD							
WS	0.56 ± 0.01	0.60 ± 0.01	0.41 ± 0.01	0.43 ± 0.02	0.28 ± 0.01	0.45 ± 0.01	0.43 ± 0.01
CL_LTD							
WS	0.05 ± 0.00	0.10 ± 0.01	0.09 ± 0.01	0.48 ± 0.05	0.19 ± 0.02	0.16 ± 0.01	0.12 ± 0.01
PREC_L							
WS	108.30 ± 1.27	111.52 ± 1.29	109.05 ± 1.39	117.78 ± 1.51	110.30 ± 1.61	110.89 ± 0.65	145.40 ± 1.15
RNOF_T							
WS	70.26 ± 1.80	55.99 ± 1.69	63.00 ± 1.79	62.03 ± 1.69	69.69 ± 1.19	64.71 ± 0.89	82.06 ± 3.75
TMP_AVG							
WS	4.84 ± 0.14	8.29 ± 0.27	6.45 ± 0.28	9.18 ± 0.26	5.82 ± 0.22	6.68 ± 0.17	13.15 ± 0.26
COASTD							
WS	297.83 ± 6.25	128.57 ± 11.81	100.62 ± 6.87	22.54 ± 5.03	69.80 ± 13.74	128.63 ± 9.58	. ± .
			Geology				
GEO_SEN							
WS	2.71 ± 0.13	2.32 ± 0.15	2.70 ± 0.14	2.15 ± 0.08	2.80 ± 0.24	2.58 ± 0.08	2.15 ± 0.12
GEO_MAX							
WS	3.53 ± 0.23	2.70 ± 0.26	3.95 ± 0.27	2.67 ± 0.27	3.74 ± 0.34	3.40 ± 0.14	2.62 ± 0.25
GEO_GT4							
WS	0.82 ± 0.61	4.26 ± 3.55	3.59 ± 1.99	1.44 ± 1.16	20.33 ± 6.21	6.87 ± 1.80	.22 ± 0.32
			Physiography				
EL_MIN							
WS	530.33 ± 19.74	398.32 ± 24.88	294.97 ± 26.02	89.05 ± 22.25	160.08 ± 26.80	301.65 ± 17.98	566.48 ± 37.48
MAXREL							
WS	155.43 ± 15.92	96.37 ± 16.89	220.97 ± 25.11	42.36 ± 6.16	124.83 ± 15.41	134.80 ± 9.73	537.01 ± 93.21
SLP							
WS	20.02 ± 0.81	9.98 ± 0.95	14.39 ± 0.83	10.59 ± 1.02	13.01 ± 1.35	13.89 ± 0.57	37.75 ± 3.40
BUF	12.17 ± 0.89	7.65 ± 0.84	9.19 ± 0.82	9.87 ± 1.13	9.32 ± 1.04	9.66 ± 0.45	34.64 ± 2.89

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-70.
[c] For each variable, WS refers to the entire watershed and BUF refers to the buffer zone.

Table 8-68. (Continued)

Mean ± Standard Error by DDRP Subregion/Region

Variable/ Aggregation	NE Subregion					Overall	
	1A	1B	1C	1D	1E	NE	SBRP
ATNMEAN							
WS	7.90 ± 0.12	8.47 ± 0.14	8.31 ± 0.09	8.40 ± 0.14	8.29 ± 0.16	8.26 ± 0.06	7.81 ± 0.09
ATKBMEAN							
WS	0.91 ± 0.13	2.40 ± 0.11	0.77 ± 0.11	-0.82 ± 0.37	1.47 ± 0.19	1.03 ± 0.12	. ± .
GMP_FTN							
WS	20.31 ± 3.10	19.97 ± 3.08	28.28 ± 4.00	24.00 ± 5.21	31.99 ± 3.98	24.92 ± 1.79	3.17 ± 1.40
BUF	46.29 ± 4.89	40.15 ± 5.44	52.05 ± 4.88	36.36 ± 6.32	52.94 ± 4.86	46.58 ± 2.41	9.20 ± 3.34
LOW							
WS	5.65 ± 1.10	6.81 ± 1.49	6.68 ± 1.68	10.54 ± 2.19	5.38 ± 0.94	6.72 ± 0.67	2.33 ± 0.71
BUF	17.15 ± 3.30	19.02 ± 4.14	19.34 ± 3.11	17.40 ± 3.65	15.82 ± 2.26	17.68 ± 1.46	11.74 ± 2.90
Hydrology							
HYD_SLW							
WS	63.79 ± 3.31	90.67 ± 1.76	65.45 ± 3.66	32.87 ± 6.60	73.20 ± 4.55	67.01 ± 2.40	5.32 ± 1.78
BUF	70.49 ± 4.48	92.87 ± 2.08	68.95 ± 4.59	33.25 ± 6.69	73.58 ± 5.23	69.76 ± 2.69	4.65 ± 1.38
DRN_SLW							
WS	12.06 ± 1.79	42.82 ± 4.99	23.31 ± 3.34	11.75 ± 2.26	28.00 ± 3.59	24.04 ± 1.81	1.89 ± 0.60
BUF	27.41 ± 3.29	61.80 ± 4.43	43.26 ± 3.95	19.40 ± 3.46	43.75 ± 4.89	40.05 ± 2.26	7.87 ± 2.28
PERM							
WS	6.87 ± 1.07	2.36 ± 0.52	5.22 ± 0.71	21.74 ± 3.62	5.81 ± 1.21	7.52 ± 0.87	5.08 ± 0.45
BUF	7.75 ± 1.68	1.81 ± 0.44	8.19 ± 1.70	22.63 ± 3.34	6.59 ± 1.56	8.58 ± 1.00	5.16 ± 0.34
PRM_SLW							
WS	33.57 ± 3.71	61.57 ± 5.94	46.41 ± 3.50	13.33 ± 5.44	43.71 ± 4.06	41.18 ± 2.38	0.22 ± 0.16
BUF	39.08 ± 5.46	70.60 ± 6.00	42.53 ± 4.50	10.34 ± 3.96	44.82 ± 4.66	42.99 ± 2.78	0.69 ± 0.43
DEPTH							
WS	3.08 ± 0.76	1.74 ± 0.30	4.68 ± 0.67	15.44 ± 2.12	3.17 ± 0.62	4.96 ± 0.58	1.59 ± 0.13
BUF	4.73 ± 0.93	2.23 ± 0.35	7.18 ± 1.19	17.15 ± 1.97	4.55 ± 0.81	6.52 ± 0.65	2.01 ± 0.15
BRD_SHL							
WS	46.48 ± 3.96	33.15 ± 4.57	25.39 ± 2.32	13.22 ± 4.30	33.55 ± 4.83	31.91 ± 2.09	9.43 ± 2.26
BUF	25.66 ± 4.48	18.84 ± 3.06	12.24 ± 2.31	8.16 ± 3.21	21.09 ± 4.46	17.90 ± 1.81	8.69 ± 2.03
IPD_SHL							
WS	32.41 ± 2.85	46.30 ± 4.16	22.93 ± 3.71	8.98 ± 2.60	33.21 ± 4.62	29.73 ± 2.00	. ± .
BUF	19.53 ± 2.88	52.03 ± 5.17	15.40 ± 3.03	6.13 ± 2.03	26.75 ± 4.21	24.56 ± 2.14	. ± .
AREA_TER							
WS	356.54 ± 67.42	329.22 ± 78.84	671.77 ± 128.58	190.82 ± 34.91	681.50 ± 138.66	476.84 ± 51.34	966.91 ± 213.37
AREA_H2O							
WS	46.31 ± 12.79	26.87 ± 6.12	43.76 ± 7.11	31.67 ± 7.98	95.61 ± 25.33	52.00 ± 7.39	0.58 ± 0.39
WALA							
WS	19.38 ± 4.99	18.64 ± 5.75	28.75 ± 4.85	8.68 ± 1.47	15.26 ± 2.29	18.82 ± 2.02	. ± .
VOL							
WS	2.09 ± 1.33	0.87 ± 0.25	1.39 ± 0.58	0.74 ± 0.19	4.18 ± 1.81	2.03 ± 0.56	. ± .
DDENSITY							
WS	0.46 ± 0.11	0.69 ± 0.16	0.86 ± 0.18	0.32 ± 0.12	0.71 ± 0.14	0.63 ± 0.07	1.03 ± 0.17
STRORDER							
WS	1.92 ± 0.06	2.89 ± 0.07	3.00 ± 0.00	3.00 ± 0.00	3.66 ± 0.09	2.92 ± 0.06	2.23 ± 0.21
Land Use/Vegetation							
FOREST							
WS	96.13 ± 0.88	75.88 ± 4.71	91.41 ± 1.48	75.65 ± 3.90	89.37 ± 1.78	86.79 ± 1.36	90.20 ± 3.00
BUF	. ± .	. ± .	. ± .	. ± .	. ± .	. ± .	84.44 ± 4.51
CULTIV							
WS	0.00 ± 0.00	1.08 ± 0.68	0.44 ± 0.17	2.55 ± 1.41	3.38 ± 1.00	1.48 ± 0.36	1.77 ± 2.06
BUF	. ± .	. ± .	. ± .	. ± .	. ± .	. ± .	3.19 ± 2.73
PASTURE							
WS	0.11 ± 0.08	11.62 ± 4.24	2.67 ± 0.72	2.30 ± 1.42	1.72 ± 0.55	3.51 ± 0.87	6.84 ± 1.93
BUF	. ± .	. ± .	. ± .	. ± .	. ± .	. ± .	10.50 ± 3.29
DISTURB							
WS	0.41 ± 0.21	6.46 ± 1.61	0.57 ± 0.15	13.99 ± 3.54	0.80 ± 0.23	3.59 ± 0.74	1.10 ± 0.69
BUF	. ± .	. ± .	. ± .	. ± .	. ± .	. ± .	1.57 ± 0.69
WETLAND							
WS	3.35 ± 0.70	4.92 ± 1.11	4.92 ± 1.23	5.51 ± 1.26	4.73 ± 0.90	4.63 ± 0.47	0.03 ± 0.07
BUF	. ± .	. ± .	. ± .	. ± .	. ± .	. ± .	0.31 ± 0.55

Table 8-68.   (Continued)

Variable/ Aggregation	Mean ± Standard Error by DDRP Subregion/Region						
	NE Subregion					Overall	
	1A	1B	1C	1D	1E	NE	SBRP
VGT_CNF							
WS	16.00 ± 2.51	6.18 ± 1.46	19.19 ± 3.17	27.28 ± 6.48	32.81 ± 4.93	20.56 ± 1.97	4.71 ± 1.55
BUF	31.48 ± 4.52	11.55 ± 3.05	30.33 ± 5.16	29.31 ± 6.28	43.69 ± 6.01	30.19 ± 2.54	4.71 ± 2.04
VGT_DCD							
WS	72.80 ± 3.49	73.87 ± 4.95	45.21 ± 5.74	44.34 ± 7.69	33.21 ± 4.92	53.25 ± 2.82	36.75 ± 7.69
BUF	44.15 ± 4.94	66.25 ± 4.44	28.50 ± 5.42	42.93 ± 7.87	24.31 ± 4.68	39.91 ± 2.78	37.07 ± 5.71
VGT_DRY							
WS	0.46 ± 0.27	16.96 ± 4.86	4.28 ± 1.15	9.80 ± 3.60	7.84 ± 1.82	7.46 ± 1.22	9.49 ± 3.00
BUF	0.48 ± 0.37	15.44 ± 3.91	4.30 ± 1.58	6.62 ± 1.64	4.04 ± 1.13	5.84 ± 0.96	14.94 ± 4.53
VGT_WET							
WS	1.80 ± 0.57	2.56 ± 1.16	2.48 ± 0.69	4.27 ± 1.26	2.20 ± 0.59	2.50 ± 0.37	0.03 ± 0.05
BUF	7.88 ± 2.45	6.29 ± 2.67	8.57 ± 2.30	6.71 ± 1.74	7.08 ± 1.71	7.37 ± 1.01	0.12 ± 0.19

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Although differences in bedrock sensitivity (GEO_SEN), expressed using the DDRP weatherability index (see Section 8.4), are not large, in the Maine Subregion nearly 20 percent of the watershed area is of sensitivity class > 4 (GEO_GT4). This is larger than for any other subregion.

Elevation of the sample lakes (EL_MIN) is highest in the Adirondacks and lowest in Southern New England. Maximum relief (MAXREL) is highest in the Central New England Subregion and lowest in Southern New England. The percentage of watershed area in foot or toe slope (GMP_FTN) is highest in Maine. The highest percentage of land with poor drainage and permeability characteristics (HYD_SLW, DRN_SLW, PERM_SLW) is consistently found in the Poconos/Catskills Subregion and the lowest in the Southern New England Subregion. Soils in Southern New England have greatest mean depth to bedrock (DEPTH), relatively few shallow (< 50 cm) impermeable layers (IPD_SHL), and are generally coarser-textured than soils on watersheds in other subregions (see Section 8.9.4).

Vegetation and land use characteristics vary somewhat among the subregions. No appreciable area of cultivated land occurs in the Adirondacks watersheds. The Southern New England watersheds have the largest proportion of urban or disturbed land. Watersheds of the Southern New England and Maine Subregions contain the most coniferous cover, and deciduous forest coverage is greatest in the Adirondacks and Poconos/Catskills watersheds. The percent of open, dry vegetation (open, non-forested land that is not wetlands) is greatest in the Poconos/Catskills Subregion; the Adirondacks Subregion has almost no area of open, dry vegetation. The open, dry vegetation class often indicates pasture or abandoned farm land.

8.10.3.2 Northeast and Southern Blue Ridge Providence

Current atmospheric deposition is higher in the SBRP than in the NE. The mean annual temperature in the SBRP is nearly twice that of the NE. Northeastern watersheds generally contain more weatherable bedrock than the SBRP. Elevation, maximum relief, and slope are all higher in the SBRP. However, the minimum elevation in the SBRP is approximately equal to the minimum of the Adirondacks subregion. The northeastern watersheds include a higher percentage of "wet" or poorly drained soils (based on HYD_SLW, DRN_SLW, and PERM_SLW). Despite a greater mean depth of bedrock, the NE has a higher percentage of watershed area overlying shallow (<50 cm) bedrock. Watersheds are generally larger in the SBRP and contain larger percentages of area in pasture; watersheds in the NE have a greater percentage of wetlands and more coniferous vegetation.

The buffer zones are characterized by lower slopes, a higher percentage of foot and toe slopes, and a slightly higher percentage of land with "slow" drainage. For the Adirondacks and Poconos/ Catskills Subregions, the buffers also included more soils with hydrologic group C or D and permeability of ≤ 3. In general, soils in the buffer zones are slightly deeper, with a lower percentage of area with shallow bedrock relative to the whole watershed. The buffer zones contain a higher percentage of lowlands and more coniferous vegetation in the NE. In the NE the percent open, dry vegetation is slightly less in the buffer zones than in the whole watersheds, although the percent open, wet vegetation is higher. In the SBRP the percent area with open, dry vegetation is greater in the buffer zones than in the whole watersheds.

8.10.4 Sulfate and Sulfur Retention

This section and Section 8.10.5 discuss the statistical relationships between selected watershed attributes and the water chemistry for the DDRP regions. These relationships are evaluated in terms of potential cause-effect controls on surface water chemistry and identification of any important controlling factors which are not accounted for. Tables 8-69 and 8-70 show the nonparametric Spearman correlations between selected watershed attributes and each of the water chemistry variables considered. Correlations with soil properties were shown in Tables 8-59 and 8-60. Results of the stepwise multiple regressions for sulfate and sulfur retention are given in Tables 8-71 and 8-72.

8.10.4.1 Northeast

The coefficients of determination, or R^2 values, range from 0.45 to 0.83 for sulfate and from 0.34 to 0.82 for sulfur retention in the NE. In general, watershed attributes that had higher bivariate correlations with water chemistry were selected as explanatory variables in the stepwise regressions. For the northeastern region as a whole, the strongest association is between lake sulfate concentration and long-term total sulfate deposition. Precipitation amount and runoff are also highly associated, with a negative sign, which probably indicates a dilution effect. The sulfate isotherm half-saturation concentration is the most highly associated soil chemistry variable, consistent with the regression results using only soil chemistry variables (Table 8-61). Watersheds having greater areas of poorly drained foot and toe slopes and lowlands generally have lower lake sulfate concentrations; these may be areas of sulfate reduction. Watersheds with shallow bedrock or shallow impermeable soil layers have higher lake sulfate concentrations. Open dry vegetation is correlated with high lake sulfate; open wet vegetation is correlated with lower lake sulfate. Sandy soils are associated with higher lake sulfate. There are some differences in the variables selected in the regressions for the subregions, but most are correlated with those selected for the region as a whole.

These results are consistent with those discussed elsewhere in Section 8. Lake sulfate concentration is largely dependent on atmospheric deposition of sulfate as modified by amount of runoff, sulfate adsorption-desorption characteristics of the soil, and soil depth and texture. Sulfate reduction in wetlands and/or flooded soils can also reduce sulfur concentrations and therefore affect budgets in some northeastern watersheds. Sulfate retention or release resulting from wetting and drying of soils during seasonal cycles or over longer periods of wet or drought years can substantially influence watershed sulfur status based on measurements made at one point in time. The extent to which these processes and thus sulfur budgets are in equilibrium with atmospheric deposition or are acting as long-term sinks cannot be determined with certainty from these analyses; observed relationships suggest reduction may provide long-term watershed sulfur sinks (See also Section 7).

8.10.4.2 Southern Blue Ridge Province

The first variables selected by the stepwise regressions for the SBRP are identical to those selected for the soil properties alone (Tables 8-61 and 8-62). These are exchangeable magnesium, water-extractable sulfate, and adsorption capacity (negative) for stream sulfate, and exchangeable magnesium (negative), base saturation, and adsorption capacity for sulfur retention. For stream sulfate, additional watershed attributes selected are runoff and soil permeability (both negative), and slope, generally consistent with relationships seen in the NE. No additional variables were selected for sulfur retention.

The bivariate correlations also show relationships between stream sulfate and precipitation (negative), shallow soils, and foot and toe slope soils. The latter is the opposite of that seen in the NE; these areas in the SBRP are much better drained than comparable areas of northeastern watersheds, and may be retaining less sulfur through sulfate reduction. They also have high exchangeable magnesium and calcium, and may be adsorbing less sulfate. In the SBRP, sulfate deposition data are not related to stream sulfate data, as discussed in Section 8.2.

8.10.5 Ca plus Mg (SOBC), ANC, and pH

Results of stepwise multiple regressions for Ca plus Mg, ANC, and pH are given in Tables 8-73 through 8-75. This section summarizes the results and discusses potential cause-effect controls on surface water chemistry. As discussed in Section 8.9.6, these water chemistry variables are highly correlated with each other and often show similar relationships with explanatory variables in the multiple regressions and in the bivariate correlations (Tables 8-69 and 8-70).

8.10.5.1 Northeast

The coefficients of determination, or R^2 values, for multiple regressions on these water chemistry variables range from 0.50 to 0.91 for the northeastern subregions. Percentage area on the watershed having open dry vegetation is often selected as the first variable in the models. These are areas in pasture, cultivation, urban, and other disturbed land. They generally coincide with high base saturation and deep, relatively flat soils, all of which correlate well with these dependent variables. The open dry areas often are disturbed, exposing fresh weathering surfaces, have been limed or fertilized, or are associated with land uses that contribute base cations to runoff. Precipitation amount is inversely correlated with all three dependent variables, probably a dilution effect. Bedrock weatherability index is related to these dependent variables as seen in several of the regressions and the bivariate correlations. Soil pH, base status, extractable aluminum, and several sulfate isotherm parameters are also related, along with soil texture. These have been discussed in more detail in Section 8.9.6.1. Watershed attributes including soil depth, permeability, and area in low geomorphic position are commonly correlated explanatory variables. Where water can infiltrate rapidly and follow deep flow paths to contact with high base saturation soils or weatherable minerals, base cation supply is high. There does not seem to be any single good index of these characteristics that is common to all subregions, but combinations of several indices in the multiple regressions lead to reasonably good explanatory power for most subregions. This suggests the importance of knowing hydrologic characteristics of a watershed to explain water chemistry.

8.10.5.2 Southern Blue Ridge Province

In the SBRP as in the NE, the variable most strongly associated with these water chemistry variables is area in open dry vegetation. As in the NE, the geologic weatherability index is related to base cation supply. Runoff, Ca+Mg deposition (probably a surrogate for precipitation), permeability, elevation, slope, and relief all have regression estimates or bivariate correlations with negative signs; the more water that passes quickly through the watersheds into the streams, the lower the base cation concentrations and pH. The R^2 for these models ranges from 0.65 to 0.85.

Table 8-69. Non-parametric Correlations Between Lake Chemistry Variables and Selected Watershed Attributes for the NE DDRP Watersheds

Variable	Units	SO416[a]	SO4_NRET	CAMG16	ALKANEW	PHEQ11
Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 143						
Deposition/Climate						
CA_LTD Calcium deposition, long-term	keq/ha	0.41920 0.0001	-0.16242 0.0526		-0.34929 0.0001	-0.34727 0.0001
MG_LTD Magnesium deposition,long-term	keq/ha			-0.29001 0.0004	-0.22988 0.0057	-0.21387 0.0103
NA_LTD Sodium deposition,long-term	keq/ha	-0.24646 0.0030				
K_LTD Potassium deposition,long-term	keq/ha			-0.26888 0.0012	-0.26041 0.0017	-0.24346 0.0034
CM_LTD Calcium+magnesium, long-term	keq/ha	0.17295 0.0389		-0.33078 0.0001	-0.41435 0.0001	-0.40138 0.0001
NH4_LTD Ammonium deposition, long-term	keq/ha	0.49008 0.0001			-0.22532 0.0068	-0.23133 0.0054
H_LTD Hydrogen ion deposition,long-term	keq/ha	0.55209 0.0001	0.21190 0.0111			
SO4_LTD Sulfate deposition, long-term	keq/ha	0.57387 0.0001	0.22209 0.0077		-0.20025 0.0165	-0.20518 0.0140
NO3_LTD Nitrate deposition, long-term	keq/ha	0.53753 0.0001			-0.26048 0.0017	-0.26870 0.0012
CL_LTD Chloride deposition, long-term	keq/ha		0.17202 0.0399			
PREC_L Precipitation, long-term	cm			-0.32169 0.0001	-0.30643 0.0002	-0.30034 0.0003
RNOF_T Runoff, long-term	cm	-0.32362 0.0001	-0.30330 0.0002	-0.24870 0.0027		
TMP_AVG Avg. Temp., long-term	C	0.24862 0.0028	0.29674 0.0003			
COASTD Distance to coast	km	0.21602 0.0096				

[a] SO416 is the lake sulfate concentration, SO4_NRET is watershed sulfur retention, CAMG16 is the lake calcium + magnesium concentration, ALKANEW is the lake acid neutralizing capacity, and PHEQ11 is the air-equilibrated lake pH.

Table 8-69. (Continued)

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 143

Variable	Units	SO416	SO4_NRET	CAMG16	ALKANEW	PHEQ11
Geology						
GEO_SEN Geological weather. index, mean			-0.17501 0.0366	0.22226 0.0076	0.22715 0.0064	0.21625 0.0095
GEO_MAX Geological weather. index, max.		-0.18158 0.0300		0.27023 0.0011	0.31602 0.0001	0.31118 0.0002
GEO_GT4 Geological weather. index > 4	percent	-0.21270 0.0108		0.26025 0.0017	0.30655 0.0002	0.30405 0.0002
Physiography						
EL_AVG Elevation, average	m	0.27059 0.0011				-0.16687 0.0464
MAXREL Relief, maximum	m	-0.22345 0.0075				
SLP Slope, mean	percent			-0.18579 0.0263		
ATNMEAN ln(a/tan β), mean			0.27666 0.0008			
ATKBMEAN ln(a/kbtan β), mean				0.29688 0.0004	0.27479 0.0011	0.26179 0.0019
GMP_FTN Footslope, toeslope, flood plain	percent	-0.27776 0.0008			0.19420 0.0201	0.18822 0.0244
LOW Lowlands	percent					
Hydrology						
HYD_SLW Hydrologic group C or D	percent			0.29712 0.0003	0.24800 0.0028	0.22654 0.0065
DRN_SLW Drainage class<= 3	percent		0.16782 0.0451	0.36531 0.0001	0.34550 0.0001	0.33196 0.0001
PERM Permeability, mean	cm/hr			-0.34268 0.0001	-0.33047 0.0001	-0.31449 0.0001
PRM_SLW Permeability class <= 3	percent			0.32347 0.0001	0.39821 0.0001	0.38357 0.0001

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Table 8-69. (Continued)

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 143

Variable	Units	SO416	SO4_NRET	CAMG16	ALKANEW	PHEQ11
DEPTH Bedrock depth, mean	m	-0.18515 0.0268				
BRD_LT2 Bedrock class <= 2 (100 cm)	percent		-0.18181 0.0298			
BRD_SHL Bedrock <= 50 cm	percent		-0.18022 0.0313			
IPD_SHL Impermeable layer <= 50 cm	percent			0.27970 0.0007	0.21578 0.0096	0.20136 0.0159
AREA_TER Area, terrestrial	ha	-0.17159 0.0404		0.21169 0.0111	0.26421 0.0014	0.26093 0.0016
AREA_H2O Area, water	ha				0.20137 0.0159	0.22224 0.0076
WALA Watershed area/lake area		-0.18537 0.0267				
VOL Lake volume	m^3					0.17854 0.0335
DDENSITY Drainage density			0.18521 0.0273		0.22157 0.0081	0.21157 0.0115
STRORDER Stream order, maximum		-0.37781 0.0001	0.16568 0.0488	0.22011 0.0085	0.35154 0.0001	0.35029 0.0001
Land Use/Vegetation						
FOREST Forested land	percent		-0.23145 0.0056	-0.32069 0.0001	-0.22830 0.0063	-0.20495 0.0144
CULTIV Cultivated land	percent			0.20787 0.0131	0.24694 0.0030	0.24764 0.0030
PASTURE Pasture/grazed land	percent		0.19619 0.0193	0.39902 0.0001	0.44050 0.0001	0.42920 0.0001
DISTURB Disturbed land	percent	0.26987 0.0012		0.33590 0.0001	0.28701 0.0005	0.28373 0.0006
WETLAND Wetland	percent		0.26558 0.0014			
VGT_CNF Vegetation, coniferous	percent	-0.28421 0.0006				
VGT_DCD Vegetation, deciduous	percent	0.33794 0.0001				

Table 8-69. (Continued)

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 143

Variable	Units	SO416	SO4_NRET	CAMG16	ALKANEW	PHEQ11
VGT_DRY Vegetation, dry open	percent		0.19488 0.0197	0.39888 0.0001	0.43434 0.0001	0.41717 0.0001
VGT_WET Vegetation, wet open	percent	-0.19436 0.0200	0.18205 0.0295			

Table 8-70. Non-parametric Correlations Between Stream Chemistry Variables and Selected Watershed Attributes for the SBRP DDRP Watersheds

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 31

Variable	Units	SO416[a]	SO4_NRET	SOBC	ALKA11	PHEQ11
Deposition/Climate						
CA_LTD Calcium deposition, long-term	keq/ha					
MG_LTD Magnesium deposition, long-term	keq/ha					
NA_LTD Sodium deposition, long-term	keq/ha					
K_LTD Potassium deposition, long-term	keq/ha					
CM_LTD Calcium + magnesium deposition	keq/ha					
NH4_LTD Ammonium deposition, long-term	keq/ha	-0.47863 0.0065				
H_LTD Hydrogen ion deposition, long-term	keq/ha				0.40484 0.0239	
SO4_LTD Sulfate deposition, long-term	keq/ha					
NO3_LTD Nitrate deposition, long-term	keq/ha	-0.38306 0.0334				
CL_LTD Chloride deposition, long-term	keq/ha	-0.36371 0.0443				
PREC_L Precipitation, long-term	cm	-0.44960 0.0112				
RNOF_T Runoff, long-term	cm	-0.46914 0.0078				
TMP_AVG Avg. Temp., long-term	C					

[a] SO416 is the stream sulfate concentration, SO4_NRET is watershed sulfur retention, SOBC is the stream sum of base cation concentration, ALKA11 is the stream acid neutralizing capacity, and PHEQ11 is the air-equilibrated stream pH.

Table 8-70. (Continued)

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 31

Variable	Units	SO416	SO4_NRET	SOBC	ALKA11	PHEQ11
Geology						
GEO_SEN Geological weather. index, mean						
GEO_MAX Geological weather. index, max.						
GEO_GT4 Geological weather. index > 4	percent					
Physiography						
EL_AVG Elevation, average	m			-0.38149 0.0342	-0.36072 0.0462	
EL_MAX Elevation, maximum	m			-0.40040 0.0256	-0.40484 0.0239	
MAXREL Maximum relief	m			-0.36411 0.0440	-0.39194 0.0292	
SLP Slope, mean	percent			-0.40282 0.0247	-0.43185 0.0153	-0.34798 0.0551
ATNMEAN ln (a/tan β), mean						
GMP_FTN Footslope, toeslope, flood plain	percent	0.51896 0.0028	-0.43147 0.0154	0.40300 0.0246		0.49028 0.0051
LOW Lowlands	percent			0.50570 0.0037	0.47039 0.0076	0.53204 0.0021
Hydrology						
HYD_SLW Hydrologic group C or D	percent					
DRN_SLW Drainage class <= 3	percent			0.36819 0.0416	0.37350 0.0385	0.41309 0.0209
PERM Permeability, mean	cm/hr			-0.40524 0.0237	-0.45887 0.0094	-0.36089 0.0461
PRM_SLW Permeability class <= 3	percent			0.46569 0.0083	0.48854 0.0053	0.56103 0.0010

Table 8-70. (Continued)

Spearman Correlation Coefficients Significant at 0.05 / Significance Level / N = 31

Variable	Units	SO416	SO4_NRET	SOBC	ALKA11	PHEQ11
DEPTH Bedrock depth, mean	m					
BRD_LT2 Bedrock class <= 2 (100 cm)	percent	0.37192 0.0394				
BRD_SHL Bedrock <= 50 cm	percent	0.37383 0.0383	-0.38794 0.0310			
IPD_SHL Impermeable layer <= 50 cm	percent					
AREA_TER Area, terrestrial	ha					
AREA_H2O Area, water	ha					
DENSITY2 Drainage density, NSS					0.35286 0.0515	
STRORDER Stream order, maximum						

Land Use/Vegetation						
FOREST Forested land	percent			-0.62067 0.0002	-0.65401 0.0001	-0.60673 0.0003
CULTIV Cultivated land	percent			0.42443 0.0173	0.49383 0.0048	0.53198 0.0021
PASTURE Pasture/grazed land	percent			0.54318 0.0016	0.56287 0.0010	0.49295 0.0048
DISTURB Disturbed land	percent					
WETLAND Wetlands	ha					
VGT_CNF Vegetation, coniferous	percent					
VGT_DCD Vegetation, deciduous	percent					
VGT_DRY Vegetation, dry open	percent			0.60522 0.0003	0.61150 0.0003	0.55585 0.0012
VGT_WET Vegetation, wet open	percent					

	Variable[b]	Subregion[a]					Region	
		1A[c]	1B	1C	1D	1E	NE	SBRP
Soil Physical Properties	SAND		2	3			8	
	CLAY		3	4				
	FRAG		1(-)			5(-)		
	THKA						7(-)	
	SOILDEN							
Soil Chemical Properties	CA_CL							
	MG_CL							1
	SBC_CL		4(-)		4(-)			
	BS_CL							
	CEC_CL							
	AC_BACL							
	PH_01M							
	AL_AO				3	4		
	AL_CD			1				
	AL_PYP							
	C_TOT							
	SO4_H2O							3
	SO4_PO4	2	•					
	SO4_EMX							2(-)
	SO4_B2						3	
	SO4_XIN							
Deposition/ Climate	CM_LTD							
	NH4_LTD							
	H_LTD							
	SO4_LTD						1	
	PREC_L						2(-)	
	RNOF_T					2(-)		4(-)
	TMP_AVG							
	COASTD	1		5				
Geology Physiography	GEO_MAX				2(-)			
	EL_AVG			2				
	MAXREL						6(-)	
	SLP							6
	ATNMEAN						4(-)	
	ATKBMEAN							
	GMP_FTN						9(-)	
Hydrology	PERM							5(-)
	DEPTH							
	BRD_SHL							
	IPD_SHL	4	5					
	AREA_TER	3(-)						
	AREA_H2O				5			
	WALA							
	DDENSITY							
Vegetation	VGT_CNF							
	VGT_DRY				1	3	5	
	VGT_WET					1(-)		
	R^2	0.45	0.76	0.83	0.78	0.64	0.64	0.73

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-69.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

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Table 8-72. Results of Stepwise Multiple Regressions for DDRP Watershed Sulfur Retention (SO4_NRET) Versus Watershed Attributes

	Variable[b]	Subregion[a] 1A[c]	1B	1C	1D	1E	Region NE	SBRP
Soil Physical Properties	SAND			5(-)				
	CLAY							
	FRAG							
	THKA						4	
	SOILDEN							
Soil Chemical Properties	CA_CL							
	MG_CL							2(-)
	SBC_CL		4		2			
	BS_CL							3
	CEC_CL							
	AC_BACL							
	PH_01M							
	AL_AO							
	AL_CD			2(-)				
	AL_PYP		1(-)			5(-)		
	C_TOT							
	SO4_H2O							
	SO4_PO4	5(-)	2					
	SO4_EMX		5			4		1
	SO4_B2						1(-)	
	SO4_XIN							
Deposition/ Climate	CM_LTD							
	NH4_LTD							
	H_LTD							
	SO4_LTD	3						
	PREC_L	4(-)					3	
	RNOF_T				3(-)		2(-)	
	TMP_AVG			1				
	COASTD	2(-)						
Geology Physiography	GEO_MAX		3(-)	4(-)	1			
	EL_AVG	1(-)		3(-)				
	MAXREL							
	SLP							
	ATNMEAN				5			
	ATKBMEAN							
	GMP_FTN							
Hydrology	PERM							
	DEPTH							
	BRD_SHL							
	IPD_SHL					2(-)		
	AREA_TER							
	AREA_H2O							
	WALA							
	DDENSITY							
Vegetation	VGT_CNF							
	VGT_DRY					3(-)		
	VGT_WET				4(-)	1		
	R²	0.64	0.76	0.82	0.76	0.69	0.34	0.44

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-69.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

Table 8-73. Results of Stepwise Multiple Regressions for DDRP Lake Calcium Plus Magnesium Concentrations (CAMG16) and Stream Sum of Base Cations (SOBC) Versus Watershed Attributes

	Variable[b]	Subregion[a]					Region	
		1A[c]	1B	1C	1D	1E	NE	SBRP
Soil Physical Properties	SAND					4(-)		
	CLAY							
	FRAG							
	THKA			3(-)			5(-)	
	SOILDEN							
Soil Chemical Properties	CA_CL							
	MG_CL							2
	SBC_CL							
	BS_CL							
	CEC_CL							
	AC_BACL							
	PH_01M				5		3	
	AL_AO				2		11(-)	
	AL_CD							
	AL_PYP				3(-)			
	C_TOT							
	SO4_H2O			4				
	SO4_PO4							
	SO4_EMX			5(-)				3(-)
	SO4_B2							
	SO4_XIN	3	2(-)				4	
Deposition/ Climate	CM_LTD							4(-)
	NH4_LTD							
	H_LTD							
	SO4_LTD							
	PREC_L					1(-)	2(-)	
	RNOF_T					5(-)		
	TMP_AVG	4(-)		1(-)				
	COASTD						6	
Geology Physiography	GEO_MAX	1					12	
	EL_AVG	2(-)					10(-)	
	MAXREL							
	SLP							
	ATNMEAN							
	ATKBMEAN							
	GMP_FTN							
Hydrology	PERM					3(-)	9(-)	5(-)
	DEPTH	5					8	
	BRD_SHL							
	IPD_SHL			2			7	
	AREA_TER							
	AREA_H2O		3(-)		4			
	WALA							
	DDENSITY							
Vegetation	VGT_CNF		5					
	VGT_DRY		1		1	2	1	1
	VGT_WET		4					
	R²	0.88	0.91	0.83	0.81	0.83	0.68	0.85

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8-69.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

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Table 8-74. Results of Stepwise Multiple Regressions for DDRP Lake and Stream ANC (ALKA11, ALKANEW) Versus Watershed Attributes

	Variable[b]	Subregion[a] 1A[c]	1B	1C	1D	1E	Region NE	SBRP
Soil Physical Properties	SAND						3(-)	4(-)
	CLAY							
	FRAG			4				
	THKA						5(-)	
	SOILDEN							
Soil Chemical Properties	CA_CL				3		7	
	MG_CL							
	SBC_CL							
	BS_CL							2
	CEC_CL							
	AC_BACL							
	PH_01M	4		3			4	
	AL_AO						6(-)	
	AL_CD				5(-)			
	AL_PYP							
	C_TOT							
	SO4_H2O							
	SO4_PO4						8(-)	
	SO4_EMX							
	SO4_B2							
	SO4_XIN	2	2(-)					
Deposition/ Climate	CM_LTD							
	NH4_LTD							
	H_LTD							
	SO4_LTD				2			
	PREC_L				4(-)	2(-)	2(-)	
	RNOF_T							
	TMP_AVG	5(-)		1(-)				
	COASTD							
Geology	GEO_MAX	1				5		3
Physiography	EL_AVG	3(-)						
	MAXREL			5				
	SLP							
	ATNMEAN							
	ATKBMEAN							
	GMP_FTN							
Hydrology	PERM							
	DEPTH							
	BRD_SHL							
	IPD_SHL			2				
	AREA_TER							
	AREA_H2O		4(-)					
	WALA							
	DDENSITY		5(-)					
Vegetation	VGT_CNF		3			1(-)		
	VGT_DRY		1		1	3	1	1
	VGT_WET					4		
	R²	0.85	0.84	0.76	0.87	0.78	0.61	0.82

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England and 1E is Maine.
[b] Variable labels and units are found in Table 8.9.5-1.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

Table 8-75. Results of Stepwise Multiple Regressions for DDRP Lake and Stream Air Equilibrated pH (PHEQ11) Versus Watershed Attributes

	Variable[b]	Subregion[a] 1A[c]	1B	1C	1D	1E	Region NE	SBRP
Soil Physical Properties	SAND						8(-)	
	CLAY							
	FRAG							
	THKA							
	SOILDEN							
Soil Chemical Properties	CA_CL							
	MG_CL				4			
	SBC_CL							
	BS_CL							
	CEC_CL							
	AC_BACL							
	PH_01M		1		3	4	1	2
	AL_AO			2		3(-)		
	AL_CD	4						
	AL_PYP				2(-)			
	C_TOT							
	SO4_H2O			1(-)				
	SO4_PO4							
	SO4_EMX		2(-)			2(-)		
	SO4_B2							
	SO4_XIN		4(-)					
Deposition/ Climate	CM_LTD							
	NH4_LTD							
	H_LTD							
	SO4_LTD							
	PREC_L	2(-)					4(-)	
	RNOF_T							4(-)
	TMP_AVG			4(-)	1(-)			
	COASTD							
Geology	GEO_MAX	1						5
Physiography	EL_AVG			5(-)			5(-)	
	MAXREL						6	
	SLP		3					
	ATNMEAN							
	ATKBMEAN							
	GMP_FTN		5(-)					3
Hydrology	PERM							
	DEPTH							
	BRD_SHL						7(-)	
	IPD_SHL						2	
	AREA_TER	3				5		
	AREA_H2O							
	WALA							
	DDENSITY							
Vegetation	VGT_CNF					1(-)		
	VGT_DRY			3			3	1
	VGT_WET							
	R^2	0.65	0.87	0.77	0.56	0.85	0.50	0.65

[a] 1A is the Adirondacks, 1B is the Poconos/Catskills, 1C is Central New England, 1D is Southern New England, and 1E is Maine.
[b] Variable labels and units are found in Table 8.9.5-1.
[c] Numbers indicate order of entry into stepwise model. (-) indicates a negative parameter estimate.

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8.10.6 Summary and Conclusions

8.10.6.1 Sulfate and Sulfur Retention

In the NE, sulfate deposition, precipitation amount, and watershed hydrologic characteristics have the strongest associations with surface water sulfate concentration and watershed sulfur retention. In the SBRP, soil chemical variables (sulfate adsorption capacity, exchangeable magnesium, base saturation, and water-extractable sulfate) have the strongest associations with stream sulfate concentration and watershed sulfur retention. For stream sulfate concentration, watershed hydrologic variables also entered the regressions in the SBRP. Since soils in the NE are near steady-state with respect to sulfur adsorption, current sulfate deposition is a associated with lake sulfate as discussed in Section 8.2.3. Soils in the SBRP appear to be actively adsorbing sulfate, and the stream sulfate is controlled by soil chemistry (see Section 9.2).

8.10.6.2 Ca plus Mg (SOBC), ANC, and pH

For the base cation-related water chemistry variables in both the NE and the SBRP, the percent of land with open, dry vegetation consistently is among the first variables selected in the regressions. These are areas in pasture, cultivation, urban, and other disturbed-land uses. This variable is notably absent in the regression for the Adirondack Subregion, which contains almost no land with open, dry vegetation and also has the lowest mean lake ANC values. Conversely, the Poconos/Catskills Subregion, with the highest proportion of open, dry vegetation, has the highest mean lake alkalinity. Area of open, dry vegetation is the most strongly associated variable in the ANC models for the Poconos/Catskills and Southern New England Subregions.

Areas of open, dry vegetation have usually been disturbed by the activities of man in some way. The strong relationship between these areas and surface water base cations may result from the disturbances (plowing, fertilization, liming, excavation leading to faster bedrock weathering, waste disposal) or from characteristics that predispose the areas to disturbance (low slopes, fertile soils, etc.). Generally these areas coincide with high base saturation, and deep relatively flat soils, all of which correlate well with the dependent variables. The dependent variables are also correlated with bedrock weatherability and surface water sulfate concentrations overall between the NE and SBRP. Such correlations within each region, however, are weak or do not occur.

8.10.7 Summary Conclusions

- A significant proportion of the variability in surface water chemistry can be explained by watershed and soil characteristics.

- Deposition alone does not explain the large variability seen in surface water chemistry. Sulfate deposition is an important explanatory variable for surface water sulfate concentrations in the NE, but not in the SBRP. Additional information on watershed attributes is essential for explaining index water chemistry.

- Variables found to be associated with surface water sulfate and watershed sulfur retention include: sulfur deposition and soil solution sulfate concentration (in the NE); soil adsorption

capacity and base status (in the SBRP); watershed disturbances such as pits and quarries; amounts of precipitation and runoff; extent of wetlands and flooded soils; and soil depth and particle-size distributions.

- Variables found to be associated with surface water ANC, pH, and Ca plus Mg (sum of base cations) include: bedrock type; watershed disturbances such as area of agriculture or pits and quarries; levels of precipitation and runoff; soil base saturation and pH; soil sulfate concentration; atmospheric deposition; and soil characteristics involving particle-size distribution, permeability, and depth.

- Surface water chemistry may be significantly influenced by watershed disturbances or the extent of sulfate-reducing and acidic organic soils. The Level II and III models do not deal explicitly with these variables. One model assumption is that no land use change occurs during the period being modelled; the available data and model structures do not permit assessment of potential watershed changes that may occur as disturbed lands revert to natural conditions as is happening today in many areas of the eastern United States. The extent of sulfate-reducing wet soils is handled implicitly in model calibration as in-lake reduction of sulfate, and the extent of acidic organic soils is handled by the aggregation of soil chemistry through sampling classes.

- In general, the relationships found in the regressions are the postulated relationships that are incorporated in the Level II and III models. Given the caveats discussed in this document, the Level II and III models incorporate the variables that are most strongly associated with surface water chemistry.

SECTION 9

LEVEL II ANALYSES - SINGLE FACTOR RESPONSE TIME ESTIMATES

9.1 INTRODUCTION

Although a number of watershed processes are recognized as influencing surface water chemistry (Sections 2 and 3), only a few are believed to represent the major controls on short- and long-term changes in watershed response to acidic deposition. The NAS Panel on Processes of Lake Acidification (NAS, 1984) focused on sulfate adsorption and base cation exchange by soils as critical time-varying processes that might contribute to a delayed response to acidic deposition. The NAS Panel recognized scientific uncertainties in the present and potential long-term role of these two processes. Mineral weathering, cation uptake by vegetation, etc., are rate-limited processes, the magnitudes of which are not likely to change substantially over the period of the DDRP projections (50 years). Sulfate adsorption and cation exchange, on the other hand, are capacity-limited processes. As adsorption sites become occupied or as exchangeable cations are leached from the soil, the buffering capacity of watershed soils decreases, resulting in increased probability of acidification. The projected time frame of such changes is believed to vary widely and is thought to be a function of soil physical and chemical properties. In watersheds with thin or very coarse-textured soils, buffering of acidic deposition by adsorption or exchange would be very limited and some systems would respond almost immediately. Alternatively, watersheds with deep soils and high adsorption capacities and/or large exchangeable base cation pools might experience significant changes in soil leachate chemistry only after decades to centuries of high acidic deposition loadings.

This section presents results of Level II Analyses, which involve simulations of the temporal response of individual watershed processes considered in isolation. Sulfate adsorption and cation exchange are examined as mechanisms contributing to delays in surface water acidification for watersheds in the Northeast (NE) and Southern Blue Ridge Province (SBRP). The analyses are based on models that consider only adsorption or exchange within the upper regolith ($\leq$ 1.5 m in the NE, $\leq$ 2 m in the SBRP). These analyses assess the influence of adsorption and exchange on present soil and/or surface water chemistry and project probable future changes in adsorption and exchange. Soil chemistry data collected during the DDRP Soil Surveys and models are used to project future (1) changes in sulfate mobility controlled by sulfate adsorption and (2) changes in base cation leaching, soil pH, and cation exchange pools controlled by base cation exchange. By considering base cation exchange but not resupply (i.e., through mineral weathering), the models presumably overestimate the potential rate of base cation leaching from the soil; this overestimate results in underestimates of response times for future changes in soil and solution chemistry.

Because these analyses only consider temporal response of single processes to acidic deposition in a portion of the watershed (i.e., the upper 1.5 - 2.0 m of watershed soils), model results should not be interpreted as integrated projections of watershed response time. Rather, they represent a set of bounding estimates of the relative importance, now and in the future, of the role of adsorption and exchange within soils as delay mechanisms. The results of model simulations in some cases, however, allow inferences about other processes not considered in the Level II Analyses (e.g., contributions of mineral weathering to watersheds with ANC > 100 μeq L^{-1}). Section 7 provides a partial assessment

of the role of processes other than adsorption in mediating sulfate mobility in watersheds of the NE and SBRP. Level III modelling (Section 10) provides projections of changes in surface water chemistry based on integration of adsorption and exchange with other processes.

9.2 EFFECTS OF SULFATE ADSORPTION ON WATERSHED SULFUR RESPONSE TIME

9.2.1 Introduction

As discussed in Sections 2 and 3, the DDRP has focused on sulfate as the principal anion in acidic deposition and as the major mobile anion affecting chronic surface water acidification at sites in the eastern United States. The extent and duration of sulfate retention within watersheds varies widely within and among regions, depending on deposition history and physical and chemical properties of soils. Sulfate retention, therefore, has been identified as one of the most important variables influencing the rate of watershed chemical response (i.e., changes in ANC) to acidic deposition (Johnson and Cole, 1980; Galloway et al., 1983a; NAS, 1984).

At the start of the DDRP, soils in the glaciated northern areas of North America were generally believed to have low sulfate adsorption capacity, resulting in negligible sulfate retention by soils and watershed sulfate budgets at or near steady state. In contrast, watersheds in the southeastern United States were believed to be characterized by high net sulfur retention, attributable to the moderate to high sulfate adsorption capacities of deep, highly weathered soils (NAS, 1984). Site-specific and regional analyses of watershed sulfur budgets (Rochelle et al., 1987; Rochelle and Church, 1987; discussed in Section 7) have confirmed differences in regional sulfur budgets. These studies did not, however, evaluate causal mechanisms, nor did they project a time frame for changes in the Southeast.

Studies of sulfur retention processes in watersheds, summarized by Church and Turner (1986) and discussed in Section 3.3, suggest that adsorption is the most important net retention mechanism in typical terrestrial systems in the NE and SBRP. Process studies have consistently identified iron/aluminum hydrous oxide content and soil texture (clay content or surface area) as variables that are positively correlated with adsorption, and pH and organic content as variables that are negatively correlated with adsorption. These findings, coupled with the observed differences in these soil variables between the two regions, are consistent with (and have contributed significantly to the development of) the paradigm that northeastern soils have low retention capacity and are near sulfur steady state, whereas southeastern soils have high adsorption capacity and high watershed sulfur retention.

Previous regional soil comparisons (e.g., Johnson et al., 1980; Johnson and Todd, 1983) documented regional differences in sulfate pools and adsorption and correlated them with differences in soil pH, hydrous oxide and organic content of soils. These comparisons provided no direct basis, however, for assessing sulfate dynamics in soils of a region and no means of forecasting response to continued or altered loadings of sulfate. Within the DDRP, assessments of sulfur budgets (Section 7), summary descriptions of soil chemistry data, and empirical linkages of soil chemical variables with surface water chemistry (Section 8) provide important incremental results and an improved understanding of processes controlling sulfate in these watersheds. These results are generally consistent with the hypothesis that the mobility in watersheds of sulfate derived from acidic deposition is controlled by adsorption. The principal DDRP objectives, however, lie not just in identifying processes but in predicting

the dynamics of sulfate in study regions, specifically in projecting future changes in surface water sulfate response to continued sulfur deposition at current or altered deposition levels. Level II Analyses are designed to project response of individual watershed processes; this section describes the procedures for and results of projecting sulfur dynamics in soils of the NE and the SBRP.

9.2.2 Section Objectives

Analyses in this section are limited to consideration of changes in sulfate mobility in DDRP watersheds and regions attributable to sulfate adsorption (and desorption) by soils. Controls on sulfate by other processes (Section 3.3 and Section 7) are of relatively minor importance in most DDRP watersheds and in the regions as a whole. The goal of Level II Analyses of sulfate is to assess the importance of sulfate adsorption in influencing delays in surface water acidification in the NE and SBRP. Specific objectives of Level II Analyses are to:

- characterize and compare sulfate pools and sulfate adsorption capacity of soils in the NE and SBRP;

- estimate the response time of soils in DDRP watersheds to changes in sulfur deposition using an adsorption-based model;

- estimate time to steady state under current deposition loadings and project response time to future increases (SBRP) or decreases (NE) in deposition for systems not presently at steady state, but for which sorption is regarded as an important control mechanism. Extrapolate results to obtain regional projections; and to

- summarize the contributions of sulfate adsorption to delays in surface water acidification resulting from historic or future projected changes in deposition.

The results related to the fourth objective also provide data for evaluating and comparing the relative importance of sorption and other processes considered by DDRP models (e.g., cation exchange). Such comparisons, however, are not made in this section.

It is important to recognize that procedures and models used for this analysis treat sorption processes in isolation. Processes affecting watershed chemistry other than those directly involving sulfate sorption are not considered, and except for sulfur deposition, watershed conditions (e.g., soil mass, soil pH) and fluxes are assumed to be static over the duration of the projections. It is equally important to recognize that the projections and estimates of time to steady state made here apply only to sulfate. Although change in sulfate mobility is one of the principal factors driving changes in base cations and ANC, non-sulfur processes also play critical roles in such changes. Rates of change in ANC, and particularly projected times to reach zero ANC (i.e., become acidic), are not necessarily coincident with times to sulfur steady state. Systems can reach an acidic state prior to, concurrently with, or after sulfur steady-state conditions are reached. The relationship between changes in sulfate and changes in ANC is characterized as part of Level III Analyses and discussed in Section 10.

9.2.3 Approach

Level II sulfate analyses are based on model-based projections of future sulfate dynamics in soils of watersheds in the DDRP NE and SBRP Regions. Projections were made using soil chemistry data generated by the DDRP Soil Surveys (Section 5.5). The principal soil variables used for these analyses are sulfate adsorption isotherms generated for individual soils collected in the surveys and aggregated to the watershed level. Projections were made using a modified version of the sulfate subroutine in the Model of Acidification of Groundwater in Catchments (MAGIC) (Cosby et al., 1985a, 1986b).

9.2.3.1 Model Description

A critical early decision in this analysis was the selection of one or more models to describe sulfate retention in watersheds. The DDRP was conceived and developed as a relatively short-term assessment project. Consequently, project design dictated use of existing models rather than development of new sulfur cycling models. This constraint restricted options for model selection; for instance, no model available in 1985 effectively described sulfur cycling or net retention in soil organic sulfur pools, and only very fragmentary data existed on transformation rates for organic pools. Furthermore, many integrated watershed models were developed for systems with negligible sulfur retention. For these models, terrestrial sulfur retention was set to zero (e.g., the Trickle Down Model, Schnoor et al., 1984, 1986b), or was described by empirical relationships that served principally to fit seasonal or hydrologically-driven variability in dissolved sulfate, without linkage to specific processes (e.g., the Birkenes model, Christophersen and Wright, 1981). After consideration of available models that had adsorption routines, the sulfate subroutine of the MAGIC was viewed as the most straightforward and least data-intensive alternative, and was selected for use.

The model uses a deterministic, mass-balance approach that considers only adsorption as a sulfur retention process by soils (Cosby et al., 1985b,c; 1986b). Sulfate partitioning between dissolved and sorbed phases is defined by an hyperbolic (Langmuir) isotherm. The original MAGIC subroutine has been modified to accommodate multiple soil horizons (up to 10, although either 2 or 3 were used for this study). Soil horizons are treated as a series of continuously stirred tank reactors (CSTRs); all inputs of precipitation and sulfur (wet and dry) deposition are to the top mineral soil horizon (organic horizons are not considered in the model, because sorption is negligible in the O horizon). Evapotranspiration implicitly occurs in the top soil horizon. All flow is then routed sequentially through each soil horizon. Data are input to the model using annual time steps. The projected surface water sulfate concentration is defined by (set equal to) the equilibrated solution sulfate concentration in the lowest soil horizon. Because sorption is essentially an instantaneous process, reaction kinetics are not considered and equilibrium between solution and sorbed phases is assumed to occur in all cases.

For these analyses, model simulations were run starting 140 years prior to the base year (1984 for NE lakes, 1985 for SBRP streams). Soil and streamwater surface water sulfate concentrations were initialized at the start of simulations by assuming both to be at steady state with respect to deposition. Simulations were run either 140 years (NE) or 300 years (SBRP) into the future, allowing projected sulfate concentrations to reach steady state for all watersheds. Data sources for model simulations are described below (Section 9.2.3.2).

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9.2.3.2 Data Sources

Input requirements for the sulfur model include current sulfur inputs and outputs (precipitation, runoff, total sulfur deposition, and sulfate concentration in runoff), scenarios of historic and future sulfur deposition, and soil variables to describe sulfate partitioning and adsorption capacity (adsorption isotherms, soil mass). Data sources are identified in Section 9.2.3.3; procedures for generation of adsorption isotherms and for aggregation of soil chemistry data are described in Section 9.2.3.4.

Procedures used to estimate precipitation and sulfur deposition are described in Sections 5.6.3; both typical year (TY, annual values) and long-term average (LTA) estimates of total sulfur deposition were used for NE and SBRP watersheds. Runoff estimates, based on interpolation of 30-year average USGS runoff maps, were generated as described in Section 5.7.1. Current lake sulfate concentrations were from the EPA's Eastern Lake Survey (Linthurst et al., 1986a) and the Pilot Stream Survey (Messer et al., 1986a) (Section 5.3).

Initial sulfate inputs (year 140) were set to 5 percent of current deposition; estimated sulfur deposition between initial and base years (i.e., 1844 to 1984 in the NE and 1845 to 1985 in the SBRP) was based on emission estimates of Gschwandtner et al. (1985). Estimates of historic deposition for the NE and SBRP are based on emission estimates for Federal Regions I and II (CT, MA, ME, NH, NJ, NY, RI, VT) and Region IV (GA, NC, SC, TN), respectively; linear interpolation between the initial simulation year and 1900 was used. The historic emission pattern was used as a scaling factor for each watershed, which was a procedure that assumed that the relationship between regional emissions and site-specific deposition over the last 140 years was constant.

Two scenarios of future sulfur deposition were used for each region as characterized in Section 5.6.1. The first scenario for each region was constant deposition through the entire simulation period. For the NE, the alternative scenario is constant deposition for 10 years, followed by a linear decrease in deposition for 15 years (by 2 percent per year), then constant deposition at 70 percent of current deposition for the remainder of the simulation period. The alternative scenario for the SBRP also begins with constant deposition for 10 years, followed by a linear increase in deposition between years 10 and 25, then constant deposition (at 120 percent of current levels) for the remainder of the simulation period.

Mapping of soils and quantification of the areal extent of various soils on DDRP watersheds are described in Section 5.4 Sampling and chemical/physical analyses of soils are described in Section 5.5. For each mineral soil horizon, sulfate adsorption data were used to compute adsorption isotherms which were then aggregated with soil mass (computed from horizon thickness, bulk density, and coarse fragment content) to obtain sample class and watershed values. Procedures for derivation of adsorption isotherms and for aggregation of adsorption data are described in Section 9.2.3.4.

9.2.3.3 Model Assumptions and Limitations

Several critical assumptions are encompassed by the choice of model and by methods of data collection. These in turn impose limitations on the scope of model projections. Key model assumptions and their implications for data interpretation include:

- Sorption is the only watershed process affecting sulfate mobility and watershed response time. As noted previously, this decision was intentional and is believed to provide the most effective means of assessing the significance of adsorption by soils as a process delaying surface water acidification. To the extent that other terrestrial processes sequester or generate sulfate on a net basis, model projections will under- or overestimate the time and/or magnitude of the projected response. As noted earlier, the net role of other processes in most DDRP watersheds is believed to be small. (The importance and influence of in-lake processes on sulfur budgets and response time in northeastern lakes is addressed in Sections 7.2 and 10.)

- The analytical approach used to define sulfate partitioning in the soil (hyperbolic isotherms defined by batch equilibrium methods using air-dried soils) adequately describes sulfate partitioning by soils under field conditions. Recent findings (Hayden, 1987) support the use of hyperbolic isotherms and batch equilibrium methods. A preliminary evaluation of effects of soil drying suggested small, non-systematic effects on adsorption; however, subsequent study (Hayden, 1987) suggests that the measured adsorption capacity of soils increases upon drying. This issue is currently being thoroughly assessed by a separate EPA project.

- Soil and watershed conditions influencing adsorption (e.g., soil pH, Fe, Al, and organic content) are static over the life of model projections. Potentially, pH is the most important of these variables since adsorption is strongly pH dependent. If soil pH were to change significantly, the projections of adsorption could be substantially altered. However, soil pH is strongly buffered at low values in most of the NE and SBRP soils considered by DDRP, and substantive changes in soil pH are not expected.

- Hydrologic routing is simple, representing the soil as a series of CSTRs; all flow is routed sequentially through each horizon. The "perfect" hydrologic contact represented by a simplified flowpath such as that used here does not realistically reflect how lateral flow, macropore flow, etc., occur in the soil. However, data to objectively define alternate flowpaths are lacking. (The effect of flow bypassing upper or lower soil horizons under natural conditions would result in projections of higher initial sulfate leaching (part of the input signal would not be attenuated by sorption on the soil), but a more gradual (in terms of change in concentration with time) subsequent sulfate response.) The responses projected here represent an upper bound on initial response time assuming complete contact between the soil and flow through the soil, and a lower bound on time to steady state.

- Because the model runs on an annual time step and uses identical precipitation and runoff data from year to year, projections do not reflect the variability of natural systems. The lack of "realistic" variability in the projections is recognized, but should have little effect on the primary objective of projecting long-term changes attributable to chronic sulfur deposition. If there were any long-term trends in precipitation or runoff, they would not, of course, be represented by model projections.

9.2.3.4 Adsorption Data

Data describing sulfate partitioning by soils, which are used to develop partitioning functions (isotherms) of sulfate adsorption capacity of soils, were generated as part of the DDRP soil survey (Section 5.5). Adsorption isotherms were developed for each soil, as were soil thickness, bulk density, and coarse fragment adjustments. Adsorption isotherms were then aggregated from data for individual soils to watershed values using a mass-weighting procedure. Determination of isotherm coefficients and aggregation of data from individual soils to watershed values are described below.

In the design of the DDRP, emphasis was placed on projecting dynamics of sulfate and other ions at regional scales, rather than on a watershed-by-watershed basis. The design mandated that procedures for sampling and aggregating soils data were targeted at describing soils for the region. Using the sample classes described in Sections 5 and 8, soils for each sample class were sampled approximately eight times across their area of occurrence, which in many cases included several states and covered substantial sulfur deposition gradients. Aggregated sample class chemistry provides a representative value for that sample class across the region, but probably does not optimally estimate soil characteristics at the individual watershed level, and thus does not enable optimal projections for individual watersheds. As an example, sulfate in northeastern lake systems is roughly at steady state across the region; observed lake sulfate concentrations are proportional to sulfur deposition and decrease by over 50 percent from ELS Subregion 1B (Poconos/Catskills) to 1E (Maine) (Linthurst et al., 1986a). Aggregated soil chemistry for sulfur variables in a sample class that extends from New York to Maine are the same for all soils in the class, however, and thus presumably would underestimate concentrations in New York while overestimating them for Maine.

An alternative approach for sampling and data aggregation would have been to focus sampling to enable characterizations of individual watersheds. This watershed focus would generate more intensive sampling of points likely to be representative of each sampled watershed, but would have allowed sampling of fewer catchments in the region, with the risk of describing less of the soil variability across the region. A watershed focus also would have resulted in fewer sites for extrapolation of results to obtain regional population projections. The watershed approach thus is regarded as less effective than the regional sample class approach for describing most soils that occur on watersheds in each region and for generating regional projections. While the sample class approach describes the central tendency and most of the range of watersheds, it does not, however, provide precise watershed-level projections, especially for extreme watershed values in the population. Soils data were mapped and sampled on specific watersheds and aggregated to watershed values in order to allow explicit linkage between soil characteristics and surface water chemistry. To deal with uncertainties in projections, uncertainty estimates for major input variables for Level II models (soil mass and isotherm coefficients for Level II sulfate analyses) were generated, and Monte Carlo analyses were used to describe uncertainty in model projections for a subset of watersheds.

Adsorption isotherms were generated from data for soil-water slurries equilibrated with six different amounts of sulfate (0, 2, 4, 8, 16, and 32 mg S L^{-1}) described as SO4_0, SO4_2, etc., in Section

5.5.4.2.1. For each of the six samples, net sulfate adsorbed by the soil was computed from the change in dissolved sulfate. For example, for the 8 mg L^{-1} sample:

$$SO4\_8n = (SO4\_8_i - SO4\_8_f) * \frac{L}{S} \qquad \text{(Equation 9-1)}$$

where: $SO4\_8_i$ = dissolved sulfate concentration prior to equilibration ($\mu eq\ L^{-1}$)
$SO4\_8_f$ = final dissolved sulfate concentration after equilibration ($\mu eq\ L^{-1}$)
L = volume of liquid (~ 0.050 L)
S = mass of volume of soil (~ 0.010 kg)

An extended Langmuir isotherm ("extended" by addition of a third variable to describe the non-zero Y-intercept) was then fit to the six data points for each soil (final dissolved sulfate and net adsorbed sulfate) (Figure 9-1) (Hayden, 1987). The equation used to model sulfate partitioning has the form:

$$E_c = \frac{B_1 * C}{B_2 + C} + B_3 \qquad \text{(Equation 9-2)}$$

where: B_1 = maximum sulfate adsorption (meq kg^{-1})
B_2 = half saturation constant ($\mu eq\ L^{-1}$)
B_3 = Y-intercept (meq kg^{-1})
C = dissolved sulfate ($\mu eq\ L^{-1}$)
E_c = net adsorbed sulfate at $[SO_4^{2-}] = C$ (meq kg^{-1})

The parameters B_1, B_2, and B_3 were estimated using non-linear least squares, using the Fletcher-Powell (1963) method to minimize the sum of squares function. The Fletcher-Powell method uses a second order algorithm that iteratively constructs an estimate of the inverse Hessian matrix. This matrix, in conjunction with the residual sum of squares, provides an estimate of the covariance matrix for the estimated parameters.

Several approaches were evaluated for aggregating data from individual soils, including weighted averaging of isotherm coefficients or alternatively fitting a single isotherm to all data points for all soils in an aggregation group (e.g., all individual soils in a pedon/master horizon or sample class/horizon). Both approaches were rejected because they provided a poor description of the average partitioning coefficient (isotherm slope) along the isotherm. As an alternative, after fitting isotherms for individual soils, values of net adsorbed sulfate corresponding to several concentrations of dissolved sulfate (0, 10, 25, 40, 75, 125, 200, 500, 1000, 2000 $\mu eq\ L^{-1}$) were computed for each soil. For each value of dissolved sulfate, the mass-weighted average of the corresponding concentrations of adsorbed sulfate was generated for all soils in an aggregation group (typically all soils with the same master horizon designation in a sample class). Finally, a new isotherm was fitted to the set of weighted averages. This isotherm was defined as the aggregate isotherm and was used to describe sulfate partitioning for that group of soils.

This approach provides a very good estimator of the weighted average soil partitioning coefficient (isotherm slope) over the range of dissolved sulfate of interest to this project (0 - 200 $\mu eq\ L^{-1}$), even for groups of soils in which coefficients for individual soils are highly variable. Aggregation was conducted in three steps, with any missing data assigned the aggregate average for other soils in its pedon/horizon: (1) individual soil (sub)horizons to master horizon within a pedon (mass weighting); (2) pedon/horizon

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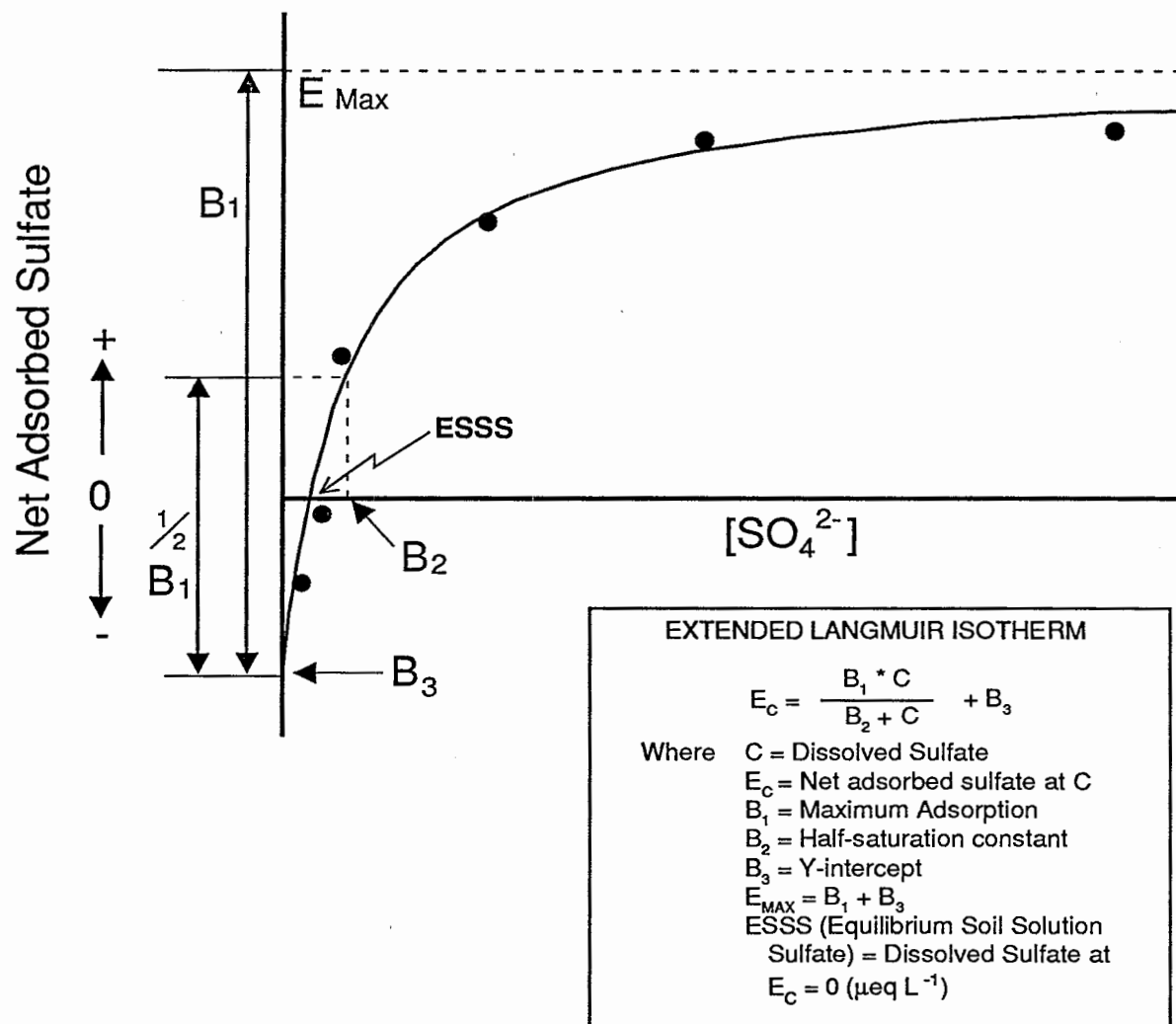
Figure 9-1. Schematic diagram of extended Langmuir isotherm fitted to data points from laboratory soil analysis.

to sample class/horizon (mass weighting); and (3) sample class/horizon to watershed/ horizon (mass and area weighting of each sample class occurring on each watershed). For routine uses, data for soil master horizons were used directly in the model and were not aggregated. For certain model applications, data were aggregated to 1 or 2 horizons per pedon using a comparable mass-weighting approach.

Because the aggregation approach was not conducive to direct computation of parameter uncertainty, uncertainties for the original isotherm fits were retained; a Monte Carlo procedure was used during each step of aggregation to generate estimates of uncertainty in aggregated coefficients at the sample class and watershed level. The uncertainty in the sulfate isotherms was propagated through the aggregation procedure using the Monte Carlo technique described in general in Section 6.3. Application of the procedure to sulfate isotherm aggregation proceeded through steps similar to those used for aggregation of other variables. The aggregation from individual subhorizons to sample class master horizon was repeated 100 times, each time selecting a randomly perturbed set of coefficients for each subhorizon isotherm. The perturbation of B_1 was selected first from a normal distribution with a standard deviation obtained from the residual sum of squares and the inverse Hessian matrix from the nonlinear least squares. The perturbed value of B_1, along with the correlation of B_1 and B_2 from the inverse Hessian matrix, were used to estimate the conditional expectation of B_2 given B_1. This conditional value was then perturbed by a value drawn from a normal distribution with the conditional standard deviation of B_2 given B_1. A similar procedure was used to perturb B_3, except that the mean and variance were adjusted for both B_1 and B_2. The mean values, standard deviations, and correlation matrix of the coefficients were summarized at the sample class level. These values were then passed to the watershed level aggregation algorithm. The uncertainty calculation was conducted as above, except that the correlations were derived from the sample class Monte Carlo study rather than from an inverse Hessian matrix.

The rationale for the mass-weighting aggregation approach described above is consistent with the common aggregation approach discussed in Johnson et al. (1988b). Several alternative approaches to aggregation of soil chemical data were discussed in that document, including weighting schemes that would represent watershed factors such as hydrologic flowpaths, landscape position, etc. Ultimately, alternative aggregations for capacity variables, including sulfate adsorption capacity were rejected. This decision was based principally on the lack of objective criteria for setting weighting coefficients to describe hydrologic routing or other watershed factors (including unsuccessful attempts to empirically determine statistically significant coefficients). The mass weighting approach used here provides unbiased estimates of the pools and/or capacities (e.g., sulfate adsorption capacity, exchangeable base cation pool) for capacity variables in soils of the DDRP watersheds. Hydrologic routing, incomplete soil contact, landscape position, etc., influence the degree of interaction between acidic deposition and the soil, and might alter the rate at which soil pools or capacities are affected. In the absence of quantitative estimates of routing coefficients, however, the unbiased pool estimates generated by the mass-weighting approach provides the best description of soil pools and capacities for the Level II models used here.

9.2.3.5 Evaluation of Aggregated Data and Model Outputs

Several approaches were used to evaluate aggregated soil sulfate data and model outputs. An initial assessment of isotherm data and aggregation procedures was made by comparing the equilibrium

soil solution sulfate of isotherms aggregated to the watershed level (B horizons) to measured surface water sulfate concentrations in the NE and SBRP. If adsorption by the soil were the sole process influencing sulfate mobility and if aggregation procedures were perfect, a 1:1 correlation between soil and lake/stream sulfate concentrations would be obtained. Realistically (due to contributions of factors such as hydrologic routing, heterogeneity of natural soils, uncertainties introduced by soil sampling and analysis, and effects of regionally focused aggregation), a high correlation between soil solution and surface water sulfate was not expected. The purpose of this comparison was to evaluate whether the two sets of values were comparable and whether major biases existed that would invalidate the entire approach.

Results of this comparison (Figure 9-2), show that for the most part agreement between computed soil solution and surface water sulfate concentrations is good. Although the data have considerable scatter, points for NE Subregions A, C, and E and for the SBRP generally plot near the 1:1 line. The effects of aggregating data collected along a deposition gradient (noted in Section 9.2.3.4) are clearly apparent for NE Subregions A, C, and E. Although the lake sulfate concentrations range from roughly 50 to 150 μeq L^{-1}, aggregate soil solution concentrations are clustered near 100 μeq L^{-1}. For watersheds in NE Subregions B and D, computed soil solution sulfate concentrations are consistently biased high. The difference between these watersheds and other systems in the NE and SBRP is believed to be related to differences in soil type rather than geographic location. The difference might be an artifact of soil handling (air-drying) procedures. This bias, although substantial, occurs in only a subset of the data and, in any case, is not sufficiently large to invalidate the data or the aggregation approach. It is also important to note that equilibrium soil solution sulfate is not used directly in the Level II models. Related isotherm variables that affect model projections (reflected by isotherm slope) appear to be much less sensitive to effects of air-drying.

In addition to the evaluation of aggregated data described above, several approaches were taken to evaluate model outputs. Model projections were compared to observed surface water chemistry in several ways. Model simulations start 140 years in the past and run through the present, allowing projections for the base year to be compared to observed lake or stream chemistry, and means and distributions of the two datasets to be compared for biases. Preliminary evaluation of model results for soils on northeastern watersheds indicated very rapid time to sulfate steady state and showed that model inputs (isotherm coefficients) in many cases could be varied by almost an order of magnitude without significantly changing the projected sulfate concentration for the base year. Evaluation of model projections also was done for the SBRP. Using both mean values and sample distributions for the SBRP target population, modelled and measured sulfate concentrations were compared, as well as modelled vs. observed percent sulfate retention. Projected rates of increase in dissolved sulfate for DDRP watersheds also were compared to available data on measured rates of increase for sulfate in southeastern watersheds.

9.2.3.6 Target Populations for Model Projections

For both the NE and SBRP, projected changes in sulfate are presented for lake (NE) and stream (SBRP) populations at regional scales. Model runs were made using data for the DDRP watersheds in the respective regions, then extrapolated to regional target population projections, using weights defined by the National Surface Water Survey (Linthurst et al., 1986a; Messer et al., 1986a). In the NE, model
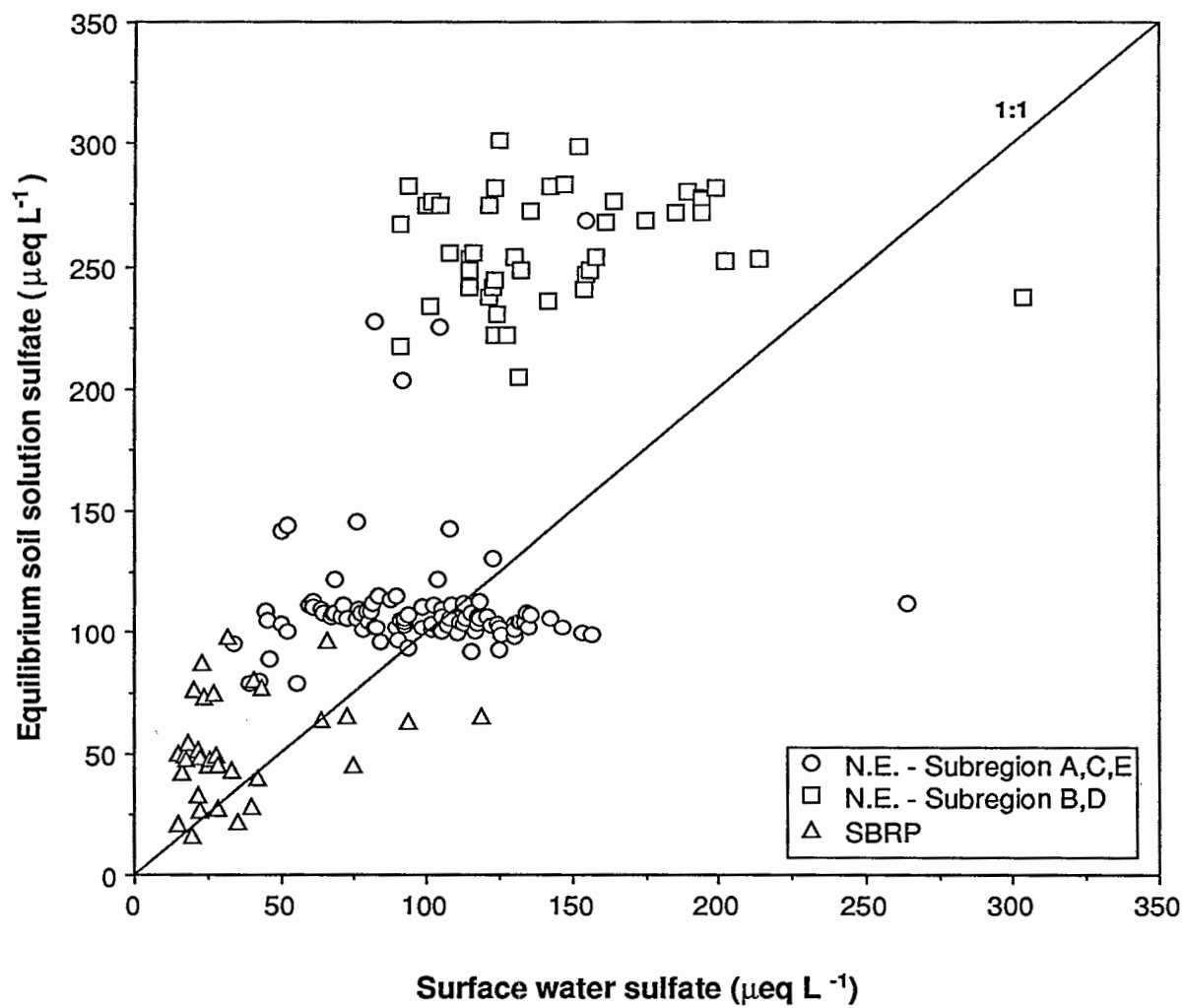
Figure 9-2. Comparison of measured lake (NE) or stream (SBRP) sulfate concentration with computed soil solution concentration.

input data were prepared for all watersheds, and the model run for all watersheds in Priority Classes A through G, i.e., lakes in classes H (seepage lakes) and I (significant internal sulfur sources) were deleted from the analyses. (Priority classes are described in Section 10.4.) After initial assignment of priority classes, the lake type of one northeastern lake (1D2-036) was changed from closed to impoundment, and four additional northeastern watersheds (1C2-068, 1E1-025, 1E1-040, and 1E3-040) were identified as having probable significant internal sulfur sources. Data for lake 1D2-036 were then included in the analyses, and the four lakes with putative internal sulfur sources were deleted. The final dataset used for generating watershed sulfur projections included 131 NE watersheds, representing a regional target lake population of 3,314 lakes.

In the SBRP, all of the 35 DDRP stream watersheds were included in the analysis, except a single watershed in Priority Class E (2A08808), which had significant internal sulfur sources. Using weights defined during the Pilot Stream Survey, results for the SBRP watersheds were extrapolated to describe a regional target population of 1,492 stream reaches.

9.2.4 Results

9.2.4.1 Comparison of Northeast and Southern Blue Ridge Province Isotherm Variables

Before presenting and discussing model projections generated as part of the Level II Analyses for sulfate, a comparison of data used as model inputs is useful, including adsorption isotherm data for soils of the two regions and secondary data derived from the isotherms. Table 9-1 summarizes isotherm data by soil horizon and soil order for the NE and by soil horizon for the SBRP. In addition to isotherm coefficients, data in the table include several derived variables that provide a more convenient basis for comparing the potential for sulfate adsorption by soils in the 2 regions. Derived parameters were computed using a dissolved sulfate concentration of 100 μeq L^{-1} to facilitate comparison. The derived parameters include isotherm slope (soil-water partitioning coefficient), adsorbed sulfate (change in adsorbed sulfate per kg soil as sulfate concentration increases from 0 to 100 μeq L^{-1}), and adsorbed sulfate for soil horizons, which couples adsorption with soil mass to describe potential sorption by the pedon.

Examination of the isotherm data reveals differences in adsorption capacities of soils within the NE and very pronounced differences between soils in the NE and SBRP. Within the Northeast, Entisols have the lowest adsorption capacity, whereas potential sorption capacity of Inceptisols and Spodosols is roughly equal. For all three northeastern soil orders, adsorption capacity and isotherm partitioning coefficients are lowest in the poorly developed C horizon soils. Comparison of NE and SBRP data consistently suggests higher adsorption by SBRP soils; maximum adsorption capacities are higher for each SBRP horizon than for any of the northeastern soils, and the partitioning coefficient (slope) is two- to tenfold higher for SBRP soils than for the same horizon in northeastern soils. These differences are reflected in adsorbed sulfate pools; on a unit mass basis, sulfate pools at 100 μeq L^{-1} are typically three- to tenfold higher for SBRP soils than for those in the NE. When the greater mass of SBRP soils (especially in the B horizon) is considered, the 100 μeq L^{-1} adsorbed sulfate pool in SBRP soils is about 10 times as large as those for northeastern Inceptisols and Spodosols and 30 times that for northeastern Entisols.

Table 9-1. Comparison of Summary Data for Sulfate Adsorption Isotherm Data for Soils in the Northeastern United States and Southern Blue Ridge Province

Region/ Order	Soil Horizon	Isotherm Coef[a] B_1 (meq kg⁻¹)	Halfsat'n (μeq L⁻¹)	Slope@ 100 μeq L⁻¹	Adsorbed Sulfate Pool @ 100 μeq L⁻¹[b] (meq kg⁻¹)	(keq ha⁻¹)
Northeast						
Entisols						
	A/E	2.37	1641	1.08	0.114	0.09
	B	1.05	997	1.21	0.133	0.27
	C	0.76	994	0.63	0.088	<u>0.54</u>
						0.90
Inceptisols						
	A/E	3.15	1560	1.58	0.214	0.17
	B	3.68	1017	2.59	0.308	1.73
	C	1.63	1007	0.96	0.172	<u>0.99</u>
						2.89
Spodosols						
	A/E	2.72	1117	1.28	0.279	0.15
	B	5.13	893	4.33	0.483	1.66
	C	1.19	970	0.98	0.154	<u>0.83</u>
						2.64
Southern Blue Ridge Province						
All						
	A/E	5.89	1199	3.39	0.541	0.98
	B	7.13	322	12.18	2.657	20.9
	C	4.80	361	6.45	1.837	<u>5.86</u>
						27.74

[a] Coefficients for Langmuir isotherm of the form:

$$\text{Adsorbed } SO_4^{2-} = \frac{B_1 * C}{\text{halfsat'n} + C}$$

where c = dissolved sulfate concentration

[b] Computed pools of adsorbed sulfate using the equation listed in footnote a.

The observed differences in adsorption characteristics of northeastern and SBRP soils are generally as expected. Retention capacity of soils in the SBRP, expressed as adsorbed sulfate for the pedon, is much higher than for soils in the NE. Two principal reasons for this difference are apparent. The first is related to differences in sulfate adsorption capacity of A and B soil horizons in the two regions. Comparison of soil chemistry characteristics for the two regions suggests that differences are not, as has been suggested (e.g., NAS, 1984), attributable solely to differences in soil age and degree of weathering. Although upper horizons of northeastern soils have lower clay content than SBRP soils, the northeastern soils do have substantial concentrations of extractable iron and aluminum. Extractable aluminum is often higher in northeastern soils than in those of the SBRP. Northeastern soils, however, also have much higher organic content than SBRP soils, and organic blocking is likely to reduce anion adsorption capacity of northeastern soils substantially and to account for much of the regional difference in adsorption capacity of upper soil horizons (Chao et al., 1964a; Johnson and Todd, 1983). The second factor affecting total pedon adsorption capacity is explicitly tied to soil age and extent of weathering. Soils in the NE have typically undergone significant weathering only to a depth of 30-50 cm; subsoils are minimally weathered and have few clays or hydrous oxides and thus little effective substrate for sorption. In the SBRP, by contrast, most soils are extensively weathered to a depth of well over a meter, and subsoils have abundant clays and hydrous oxides and very low organic content, resulting in high anion adsorption capacity. SBRP soils thus not only have higher adsorption capacity per unit soil mass than soils in the NE, but also have a much greater mass of those soils with high adsorption capacity. This results in potential sulfate retention capacities for SBRP soils that are 10- to 30-fold higher than for typical northeastern soils and leads to differences in projected response times to sulfur deposition for the two regions.

9.2.4.2 Model Results - Northeastern United States

Based on model projections using long-term average deposition data, sulfur response times for soils in northeastern watersheds are very rapid in all cases. For typical systems in the NE, the projected lag between changes in deposition and surface water response is on the order of a decade. For some watersheds the delay is as short as five years, and the longest projected lags are less than 15 years. For all of the 131 northeastern watersheds modelled as part of the Level II Analyses for sulfate, response times are sufficiently short that, during periods of higher deposition prior to 1975, sulfate concentrations exceeded steady state with 1984 levels of deposition. Concentrations are projected to be declining currently in response to reduced deposition over the past decade (Figure 9-3).

Based on the results shown in Figure 9-3, it is apparent that the sulfate model used for this analysis predicts very short lags in sulfate response time and thus significant deviation from sulfur steady state for soils in northeastern watersheds only during periods when sulfur inputs are changing rapidly. When deposition inputs are decreased, projected surface water sulfate concentrations are also projected to decrease rapidly; during the period of re-equilibration to the lower deposition level, soils release (desorb) sulfate and the watershed has negative sulfur retention (i.e., watershed output exceeds input; Figure 9-4). Conversely, as Figure 9-4 also shows, during the lag phase when deposition is increased, soils adsorb sulfate and there is positive retention by the watershed. As used in this section, steady state for sulfur

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Northeast Lakes
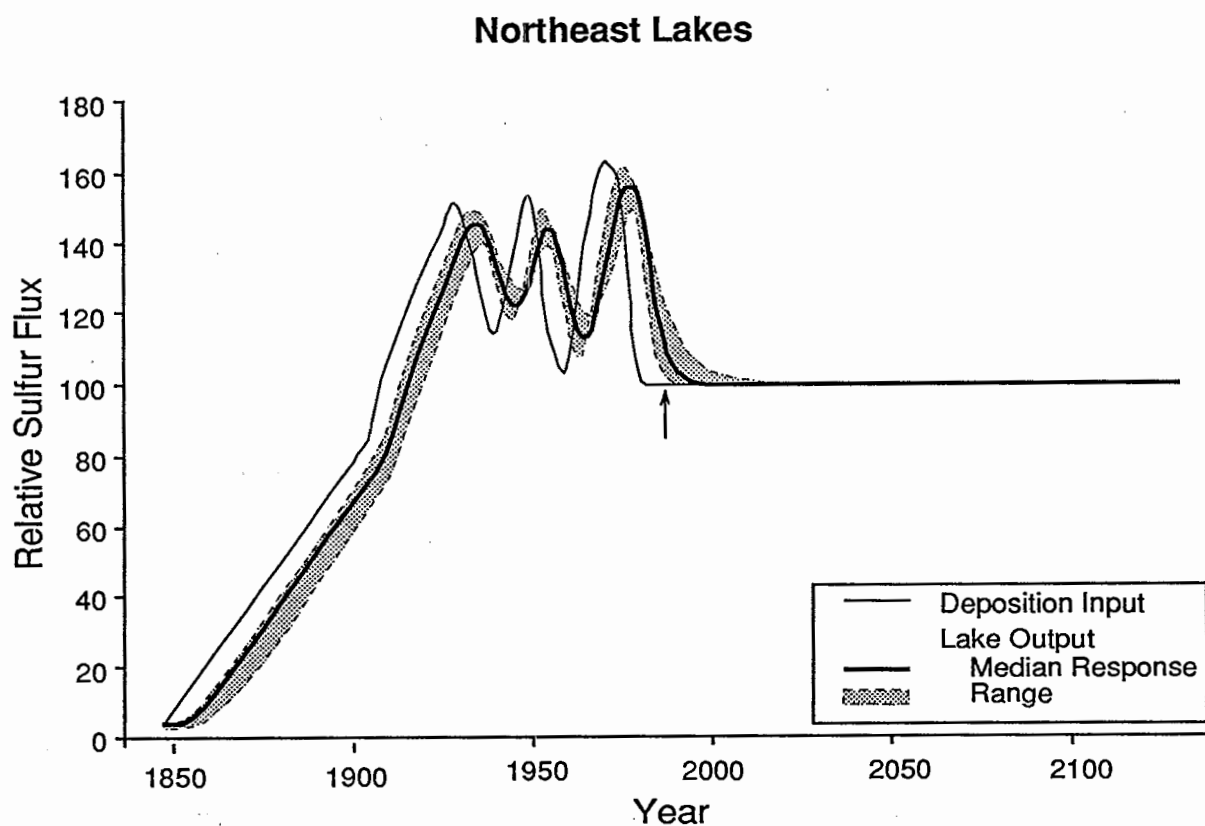
Figure 9-3. Historic deposition inputs and modelled output for soils in a representative watershed in the northeastern United States. The historic deposition pattern is based on emission estimates of Gschwandtner et al. (1985). Sulfur flux is expressed on a relative scale, 1984 deposition flux = 100. The base year (1984) is indicated by the arrow. Note that because precipitation and runoff are constant throughout the simulation period, changes in flux correspond to proportional changes in projected lake sulfate concentration.

SULFATE CONCENTRATION

PERCENT SULFUR RETENTION
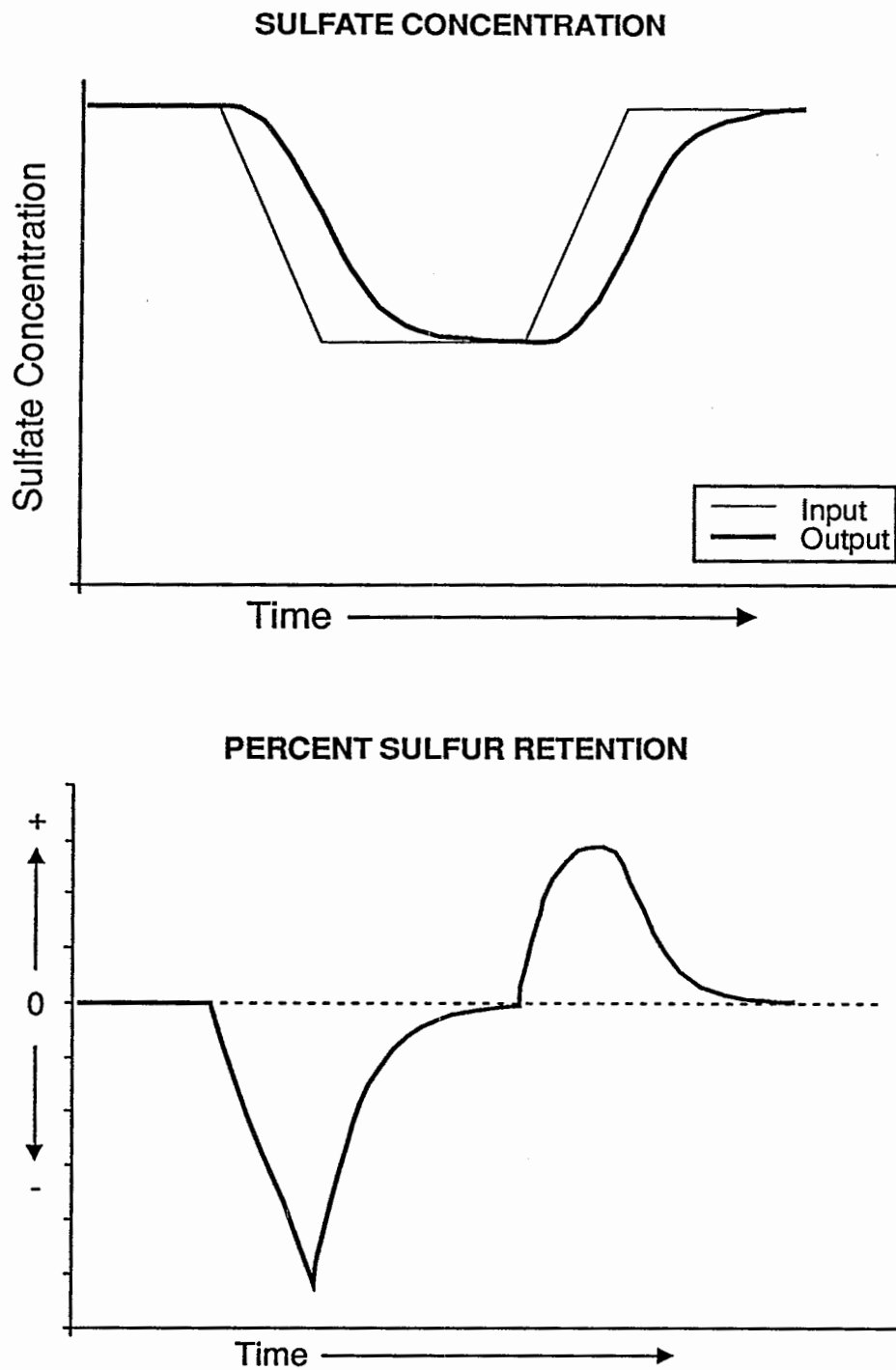
Figure 9-4. Schematic of surface water response to changes in sulfur inputs. When deposition decreases, sulfur concentration decreases to a new steady state and percent sulfur retention is negative. Conversely, when deposition is increased, sulfate retention is positive during the period in which sulfate output is increasing to the new steady-state concentration.

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refers solely to sulfur input/output budget status; no inference is intended regarding stasis of the biogeochemical sulfur cycles within the watersheds. Percent sulfur steady state is computed as

$$\text{Percent Sulfur Steady State} = (\frac{S_{output}}{S_{input}}) \, 100 \qquad \text{(Equation 9-3)}$$

and is related to percent sulfur retention by

$$\text{Percent Sulfur Retention} = (\frac{S_{input} - S_{output}}{S_{input}}) \, 100 \qquad \text{(Equation 9-4)}$$

$$= 100 - \text{Percent Sulfur Steady State}$$

9.2.4.2.1 Evaluation of base year data, calibration of model inputs -

Sulfur input-output budgets, calculated for DDRP lakes using ELS sulfate concentration data and long-term average deposition data, were computed as described in Section 7.3. Percent sulfur retention ranges widely among northeastern lakes, from -60 to +70 percent, with a mean of -2.5 percent (Table 9-2). In contrast to the computed percent retention, the range of model projections for 1984 is much narrower due to the short response times for northeastern watersheds. The short response times, coupled with decreases in deposition since 1975, result in model forecasts for the 1984 base year (when northeastern lakes were sampled for the ELS) of slight to moderate negative retention for all northeastern lakes (Tables 9-2 and 9-3, Figure 9-5). For long-term average (LTA) deposition data, modelled retention in 1984 varied from -19.3 to -1.3 percent, with a population median of -7.1 percent. Estimates using typical year (TY) deposition data were almost identical, ranging from -18.9 to -0.1 percent retention, with a median of -6.8 percent (Table 9-3).

Although computed and modelled percent sulfur retention differ considerably, the range and distribution of measured and modelled sulfate concentrations for 1984 are very similar, and are comparable to steady-state sulfate concentrations (Figure 9-5). As indicated by percent retention data, modelled concentrations slightly exceed steady-state concentrations for all systems, whereas (on a watershed-by-watershed basis) measured sulfate often deviates substantially and unsystematically from steady-state concentrations. Because DDRP objectives are focused at the regional population level, the close overlap of measured and steady-state sulfate concentrations is reassuring, in that it suggests the sulfur data used for model projections provide a good representation of the regional population of lake sulfate concentrations.

Results discussed in the preceding paragraphs are based on use of soils data without adjustment or model calibration. Projections of sulfate concentration and percent sulfur retention are essentially unbiased, but the range of percent sulfur retention projected by the models is much smaller than the range of measured percent sulfur retention. Sensitivity analyses indicate that, because of the rapid response times of northeastern systems, projected lake sulfate concentrations for 1984 remain near steady state even if the principal model inputs (isotherm coefficients and/or soil mass) are adjusted by a factor of 2. Model projections of base year sulfate concentrations and percent sulfur retention remained

Table 9-2. Summary Statistics for Modelled Changes in Sulfate Concentration, Percent Sulfur Retention, and Delta Sulfate for Northeast Watersheds Using Long-Term Average Deposition Data

Sulfate Concentration

Scenario Year	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Lake SO_4	110.0	39.5	33.8	81.7	105.4	130.7	213.8
Constant Depn.							
0	120.3	46.7	54.7	83.7	114.3	142.7	249.3
10	111.6	41.0	51.1	77.9	106.2	126.0	218.8
20	110.7	39.9	50.8	77.5	106.0	126.0	211.7
50	110.5	39.7	50.8	77.5	106.0	125.5	209.6
100	110.5	39.7	50.8	77.5	106.0	125.5	209.6
Steady State	110.5	39.7	50.8	77.5	106.0	125.5	209.6
Decreased Depn.							
20	103.8	38.4	47.8	72.6	99.1	118.0	204.1
50	77.5	28.0	35.6	54.3	74.2	87.9	148.6
100	77.4	27.8	35.6	54.2	74.2	87.8	146.7
Steady State	77.4	27.8	35.6	54.2	74.2	87.8	146.7

Percent Sulfur Retention

Scenario Year	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Lake SO_4	-2.5	24.9	-60.0	-20.9	-3.1	15.6	61.1
Constant Depn.							
0	-7.9	4.0	-19.3	-10.0	-7.1	-5.2	-1.3
10	-0.7	1.0	-4.7	-0.8	-0.3	-0.1	0.0
20	-0.1	0.2	-1.1	-0.1	>-0.1	>1.0	0.0
50	0.0	<0.1	>-0.1	0.0	0.0	0.0	0.0
100	0.0	0.0	>-0.1	0.0	0.0	0.0	0.0
Decreased Depn.							
20	-17.0	1.7	-21.9	-20.9	-19.4	-15.2	-13.1
50	-0.1	0.3	-1.4	-0.8	>-0.1	>-0.1	0.0
100	0.0	<0.1	>-0.1	>-0.1	0.0	0.0	0.0

Delta Sulfate (Change from Year 0 to n)

Scenario	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Constant Depn.							
0-10	-8.7	6.5	-30.6	-11.1	-6.4	-4.1	-0.7
0-20	-9.6	7.8	-37.6	-12.0	-6.8	-4.2	-0.7
0-50	-9.7	8.2	-39.7	-12.1	-6.8	-4.2	-0.7
0-100	-9.7	8.2	-39.7	-12.1	-6.8	-4.2	-0.7
Decreased Depn.							
0-20	-16.5	8.7	-45.2	-19.0	-14.1	-10.6	-5.8
0-50	-42.8	19.0	-100.7	-52.5	-39.1	-29.4	-16.9
0-100	-42.9	19.3	-102.6	-52.5	-39.1	-29.5	-16.9

Table 9-3. Summary Statistics for Modelled Changes in Sulfate Concentration, Percent Sulfur Retention, and Delta Sulfate for Northeast Watersheds Using Typical Year Deposition Data

Sulfate Concentration

Scenario Year	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Lake SO_4	110.0	39.5	33.8	81.7	105.4	130.7	213.8
Constant Depn.							
0	127.8	54.7	52.4	79.6	118.2	157.6	281.3
10	118.7	48.3	50.2	75.7	111.6	146.6	247.6
20	117.7	47.2	50.1	75.7	111.2	146.0	240.3
50	117.6	46.9	50.1	75.7	111.2	146.0	238.8
100	117.6	46.9	50.1	75.7	111.2	146.0	238.8
Steady State	117.6	46.9	50.1	75.7	111.2	146.0	238.8
Decreased Depn.							
20	110.6	45.0	47.3	71.1	103.7	137.0	231.3
50	82.7	32.8	36.2	54.2	77.8	102.2	168.7
100	2.6	32.6	36.2	54.2	77.8	102.2	167.2
Steady State	82.3	32.9	35.1	53.0	77.8	102.2	167.2

Percent Sulfur Retention

Scenario Year	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Lake SO_4	4.2	19.9	-53.6	-4.6	0.0	17.0	68.6
Constant Depn.							
0	-7.7	3.8	-18.9	-9.5	-6.8	-5.1	-0.1
10	-0.7	0.9	-4.4	-0.7	-0.4	-0.2	0.0
20	>-0.1	0.2	-1.0	>-0.1	>-0.1	0.0	0.0
50	-0.1	<0.1	>-0.1	0.0	0.0	0.0	0.0
100	0.0	<0.1	>-0.1	0.0	0.0	0.0	0.0
Decreased Depn.							
20	-17.4	1.6	-21.7	-18.5	-17.4	-16.1	-13.3
50	-0.7	1.1	-3.2	-0.9	-0.1	>-0.1	0.0
100	-0.6	1.1	-3.2	>-0.1	>-0.1	0.0	0.0

Delta Sulfate (Change from Year 0 to n)

Scenario	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Constant Depn.							
0-10	-9.1	7.1	-33.7	-12.0	-6.6	-4.1	-0.1
0-20	-10.0	8.6	-41.1	-12.8	-7.0	-4.3	-0.1
0-50	-10.2	8.9	-43.0	-12.9	-7.0	-4.3	-0.1
0-100	-10.2	8.9	-43.1	-12.9	-7.0	-4.3	-0.1
Decreased Depn.							
0-20	-17.6	10.1	-50.1	-20.2	-14.5	-10.4	-3.3
0-50	-45.1	22.1	-112.7	-55.2	-40.4	-27.7	-15.4
0-100	-45.2	22.4	-114.5	-55.3	-40.4	-27.7	-15.4

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Northeast Lakes
Year 0 Sulfur
Deposition = Long Term Average, Constant
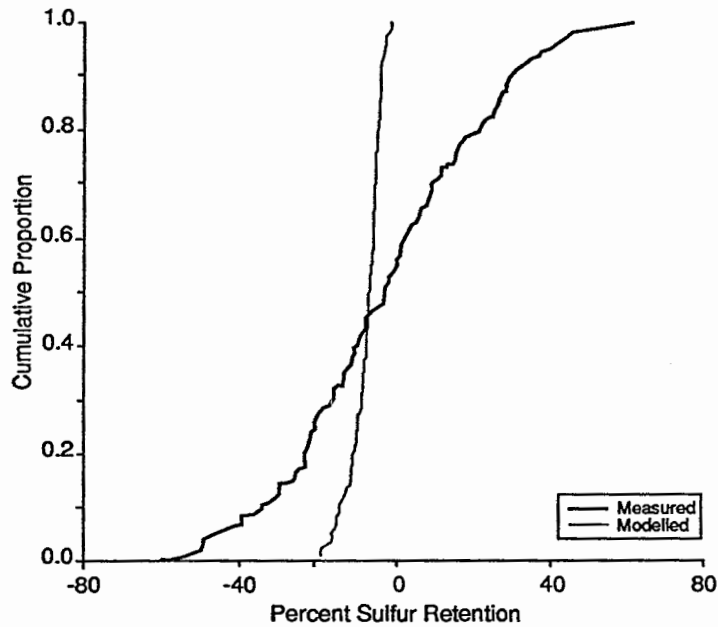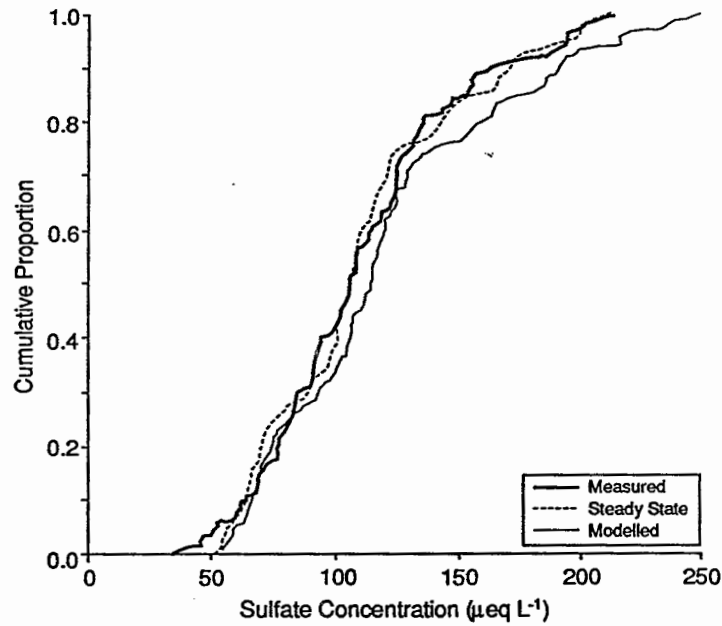
Figure 9-5. Comparison of measured, modelled and steady-state sulfate for Northeast lake systems in 1984.

unbiased, but the distribution of percent retention again was small. Changes made in deposition or rainfall/runoff ratios resulted in changes in the steady-state sulfur concentrations and in modified projections of sulfate concentration, but the range of modelled percent sulfur retention was again virtually unchanged. The net result of changing deposition/hydrologic fluxes was the introduction of bias in projected sulfate concentrations, without an expansion in the range of projected percent sulfur retention to match observed distributions. Systematic changes in soils or deposition data that increased the ranges of sulfate response (percent retention in the base year) could not be identified without introducing bias in projected average sulfate concentrations or percent sulfur retention.

An alternative calibration approach of adjusting soil chemistry data for individual watersheds was also considered in order to match model projections with measured sulfate concentrations and percent retention. The success of this approach, attempted for a subset of northeastern watersheds, was marginal. For watersheds with sulfur retention less than about -25 percent (output $\geq$ 125 percent of input), no combination of adsorption parameters could match observed retention, unless historic deposition sequences were altered. For watersheds with positive computed retention, matching modelled to measured sulfate concentrations required increases in adsorption capacity (isotherm E_{max} and/or soil mass) by a factor of 14 to 24. Concurrent sensitivity analyses for SBRP watersheds (Section 9.2.4.3.1) indicated that no adjustment of isotherm parameters was necessary or appropriate. It was concluded that model inputs should not be calibrated, based on these results, that is (1) the lack of bias in average projections for the NE, (2) substantial adjustments to isotherm data required for matching mean values and ranges of projected sulfate concentrations and percent retention with measured distributions, and (3) absence of similar needs for such adjustments for the SBRP, suggesting that there were no systematic biases. This conclusion, in turn, led to the conclusion that, to the extent that significant deviations from steady state are currently observed for sulfur in the NE (especially positive retention), they should be attributed to uncertainties in sulfur input/output budgets or to other retention processes such as in-lake retention or sulfate reduction in wetlands.

9.2.4.2.2 Projections of future sulfate concentrations -

Projections of future sulfate concentrations and percent sulfur retention in soils of northeastern watersheds, for periods ranging from 10 to 100 years, are presented in Figures 9-6, 9-7, and 9-8, and in Tables 9-2 and 9-3. As previously noted, the reliability of model projection decreases with longer projection periods. Model projections for periods longer than 50 years are included principally to provide bounds on potential change after the 50-year period that is the focus of DDRP. Results using both LTA and TY deposition scenarios, and for both the constant and ramped future deposition sequences, are included. Projected sulfate concentrations and percent retention based on the LTA and TY deposition datasets are very similar; in order to avoid redundancy, therefore, discussion is limited to results based on the LTA deposition dataset, except to note differences between the two sets of projections.

As expected on the basis of discussion in the preceding section, projected changes for sulfate in the NE are rapid and times to steady state are short. If current levels of deposition are maintained, the only projected changes are small declines in sulfate concentrations as watersheds come to steady state. Within 10 years, sulfate is projected to decrease from a median of 107.9 to 100.7 percent of steady-state concentration, and maximum concentration is projected to decrease from 119.3 to 104.7 percent of steady-state concentration. The corresponding median and maximum declines in sulfate concentrations

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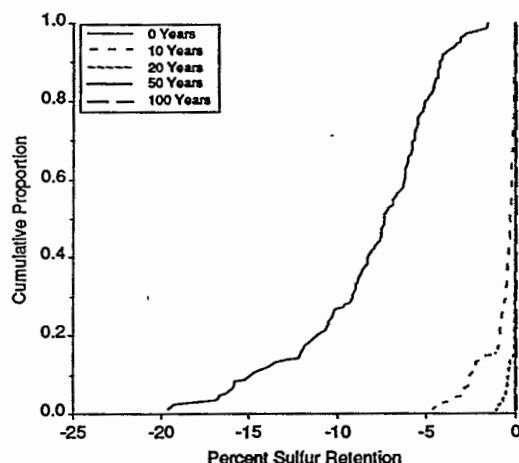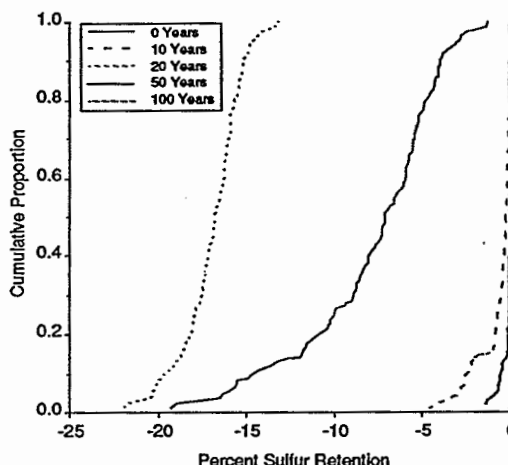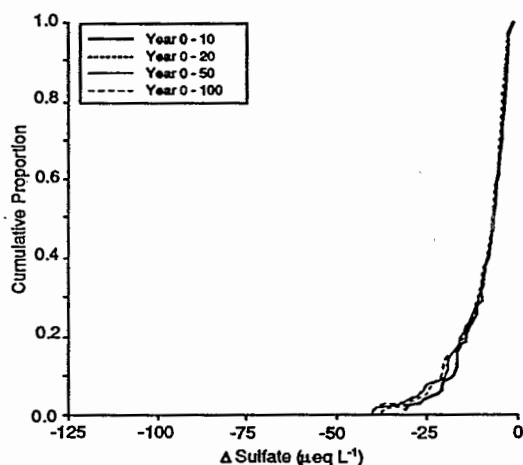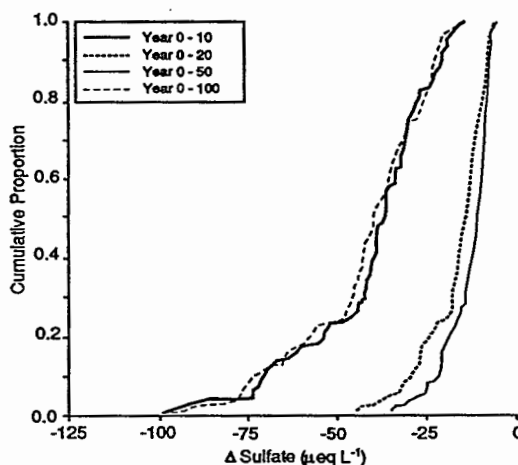
Figure 9-6. Projected changes in percent sulfur retention and sulfate concentration for soils in northeastern lake systems at 10, 20, 50 and 100 years. Data are shown for long-term average deposition for constant and decreased inputs.

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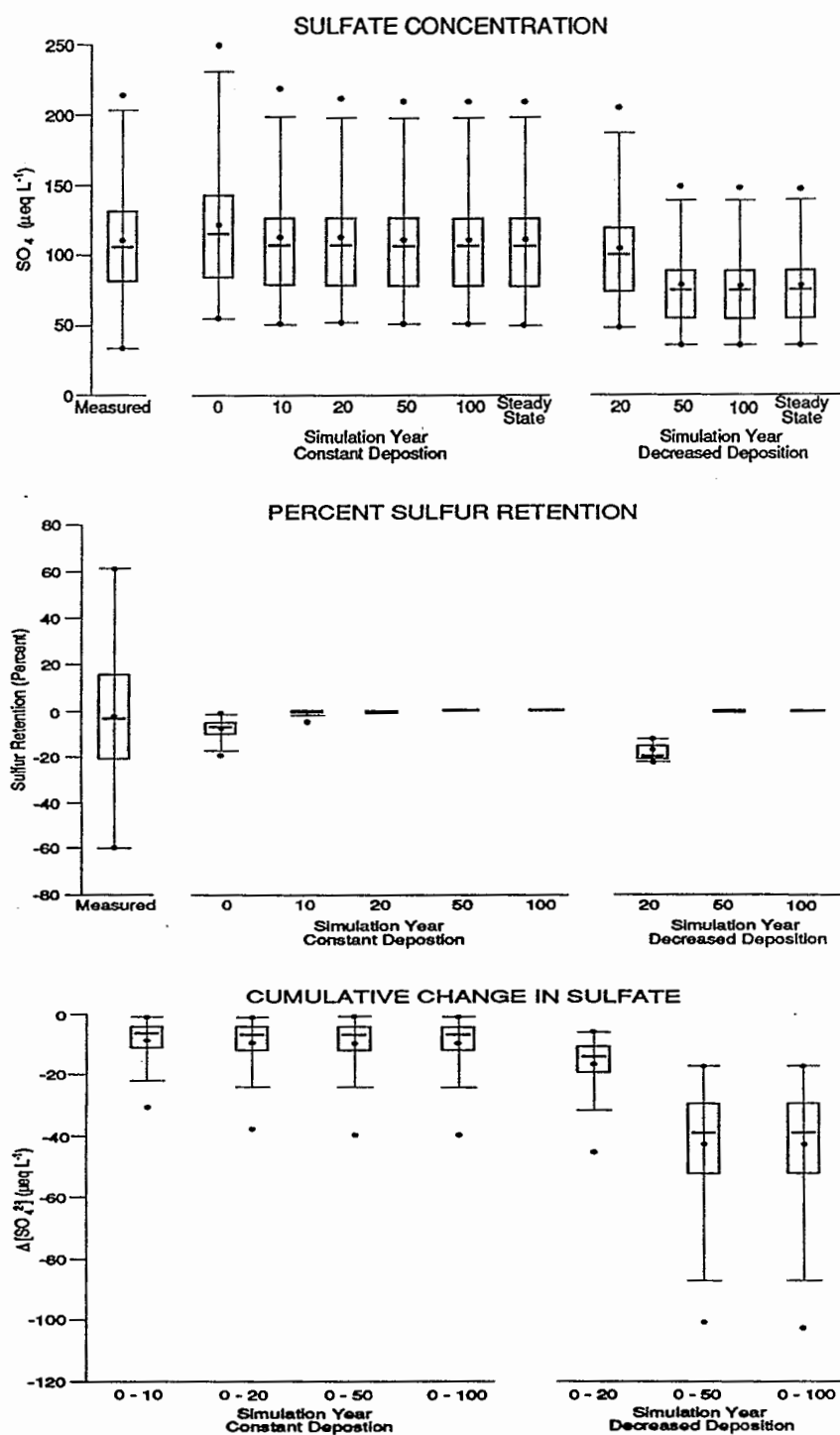
Figure 9-7. Box-and-whisker plots showing changes in sulfate concentration, percent sulfur retention, and change in sulfate concentration for soils in northeastern lake watersheds, using long-term average deposition data.
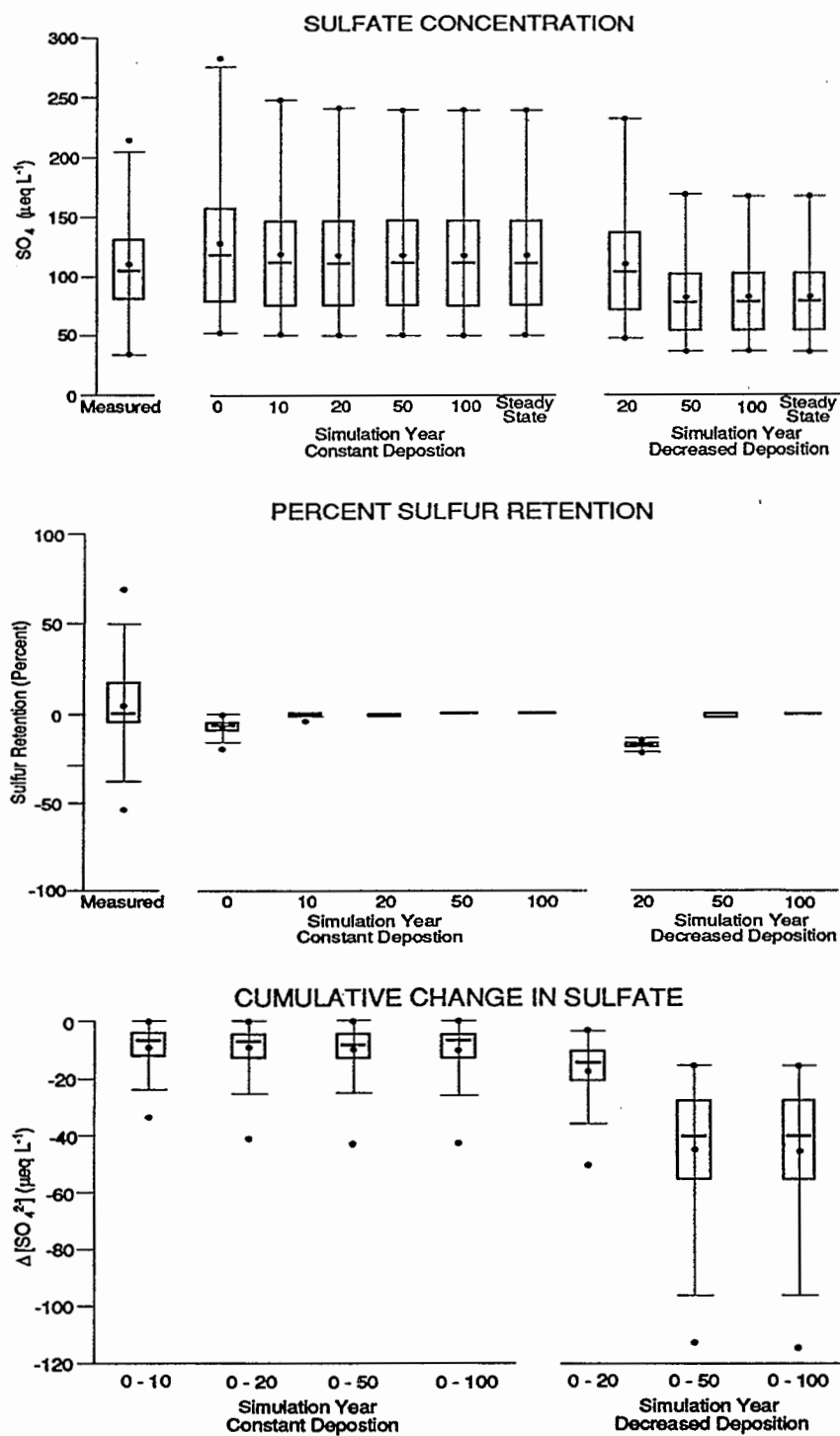
Figure 9-8. Box-and-whisker plots showing changes in sulfate concentration, percent sulfur retention, and change in sulfate concentration for soils in northeastern lake watersheds, using TY deposition data.

are 8.7 μeq L^{-1} (from 114.3 to 106.2 μeq L^{-1}) and 30.6 μeq L^{-1} (249.3 to 218.8 μeq L^{-1}), respectively. Within 20 years, at constant deposition, sulfate in all northeastern systems is projected to be within 2 μeq L^{-1}, or 1 percent, of steady state.

For the scenarios of a ramped 30 percent decrease in sulfur deposition, similarly short response times are projected. Most watersheds are projected to have virtually reached steady state with current deposition by year 10; they begin to respond almost immediately to the reductions in deposition. As inputs decrease, watersheds begin to re-equilibrate by desorbing sulfate, and projected percent retention becomes negative. In year 20, during the period of decreased deposition, projected watershed sulfur outputs are roughly 15-20 percent above inputs. At year 25, when the decrease in inputs ends, however, systems again quickly re-equilibrate, and at 50 years, projections of watershed sulfur retention are within 1 percent (and 2 μeq L^{-1}) of the new, lower steady-state concentration for all northeastern watersheds.

At year 50, projected changes in sulfate concentration in the ramped deposition scenario are considerably larger than for the constant deposition scenario. The projected decrease in median sulfate is 39.1 μeq L^{-1}, with a range of 16.9 to 100.7 μeq L^{-1}. Projected changes for model runs using the TY deposition dataset occur over time frames comparable to those for LTA deposition and are slightly larger (median and maximum of 40 and 114 μeq L^{-1}, respectively) due to the slightly higher sulfur inputs defined for most watersheds by the TY dataset. These results indicate that if deposition were reduced, a rapid and proportional decrease in sulfate leaching in soils and reduced sulfate flux to surface waters would occur in the NE. Because projected changes in sulfate concentration would result in equivalent increases in ANC and/or decreases in base cation leaching from watersheds, decreased deposition would result in substantial increases in ANC or deceleration of base cation removal.

Projected sulfate concentrations and percent retention approach steady state asymptotically, and thus the response times discussed here (although short) are overestimates. The projected annual changes in sulfate concentration and percent retention decrease exponentially as the systems come to steady state, and rates of change become increasingly small for the last few years. Given the uncertainties in hydrologic and sulfate measurements and the annual variability in watershed sulfate fluxes, 95 or 105 percent of steady state is regarded as indistinguishable from steady state. Time to reach 95 or 105 percent of steady-state concentration is a useful means of describing and comparing watershed response to altered sulfur deposition. For the current period, in which sulfate concentrations are declining in response to reduced deposition, 48 percent of the systems are projected to be within 5 percent of steady state at the end of the base year, 75 percent within 2 years, and 100 percent within 9 years (Figure 9-9). Following the decrease in deposition in the ramp scenario, the most rapidly responding systems are projected to have sulfate concentrations within 5 percent of steady state only 3 years after the end of the reductions; projected median and maximum times are only 6 and 15 years, respectively, after the end of the decrease in deposition.

9.2.4.2.3 Summary of results for the Northeast -

Model projections for the northeastern United States, using two deposition datasets and two scenarios of future deposition, uniformly indicate rapid soil response to past and potential future changes in sulfur deposition to watersheds. At present, watershed sulfur concentrations are projected to be slightly higher than steady-state concentrations and are decreasing due to recent decreases in deposition. About

**Northeast Lakes
Time To Sulfur Steady-State**
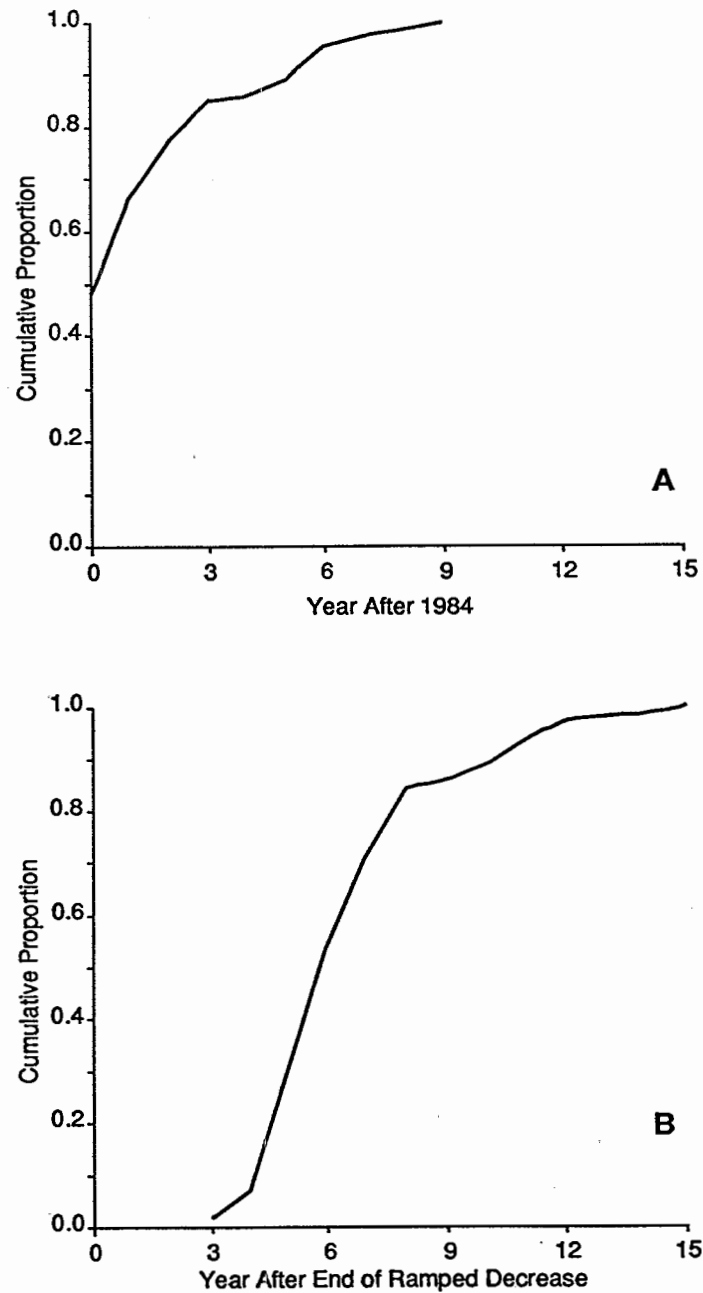
Figure 9-9. Projected time to steady-state concentration for sulfate in northeastern lakes (A) at current deposition and (B) after end of decreasing input in ramp scenario. Results for long-term average deposition are shown.

half of the watersheds in the NE are estimated to have soils within 5 percent of steady state in the 1984 base year, and all are projected to be within 5 percent of steady state within 9 years of the base year. For a hypothesized future decrease in deposition, median time to reach steady state (within ± 5%) was projected to be only 6 years following the end of the decrease in deposition, and maximum projected response time was only 15 years. These projections lead to the following conclusions:

- To the extent that watershed sulfur budgets in the NE deviate significantly from steady state (particularly if they are retaining sulfate), the deviations are probably not the result of sorption reactions in soils, but should be attributed to uncertainties in sulfur input/output budgets, non-sorption sulfur sources (e.g., sulfide mineral weathering), or alternative retention processes (e.g., reduction in lakes or wetlands). It is emphasized that this Level II Analysis has considered sorption by soils as the only process regulating sulfur mobility in watersheds. Other processes are recognized as having the potential to influence sulfur budgets significantly in at least a small proportion of watersheds, but their consideration is beyond the scope of this analysis.

- Watersheds in the NE should be regarded as direct response systems in terms of sulfate dynamics. Soils have low sorption capacities and therefore can buffer changes in sulfur inputs for only a very few years. If deposition is reduced, watersheds are expected to respond with a rapid and proportional decrease in sulfur output.

9.2.4.3 Model Results - Southern Blue Ridge Province

9.2.4.3.1 Evaluation of base year data, model calibration -

In contrast to sulfate chemistry and dynamics in northeastern soils of watersheds, stream systems in the SBRP are characterized by a wide range of sulfate concentrations and wide variability in percent sulfur retention. Figure 9-10 shows the deposition sequence used for SBRP watershed modelling, the sulfate response of a typical SBRP watershed, and the range in projected sulfate responses for stream systems in the region. The historic deposition sequence used for the SBRP differs considerably from that used for the NE. Significant increases in sulfur input began relatively recently in the SBRP, and deposition reached 50 percent of current levels only about 25 years ago. Unlike the historic deposition scenario for the NE, historic sulfur inputs have never significantly exceeded current levels of deposition. The lower cumulative deposition to SBRP watersheds and the high sulfate adsorption capacity of many soils in the region are the most important factors affecting the current sulfur budget status of watersheds in the region. Typical watersheds in the SBRP presently retain over 50 percent of sulfur inputs, but as shown in Figure 9-10, sulfate concentrations in SBRP watersheds are now projected to be increasing at a substantial rate (proportional to changes in sulfate flux from the watershed). Measured increases in sulfate concentration, at rates comparable to those projected for SBRP watersheds in this analysis, have been reported for several stream systems in the region and have been summarized by Church et al. (in review). The range of watershed response rates is much broader than that for the NE: a few watersheds are projected to be already close to steady state, while sulfate concentrations in others are just beginning to increase and are not likely to reach steady state during the 140-year period.

SBRP Streams
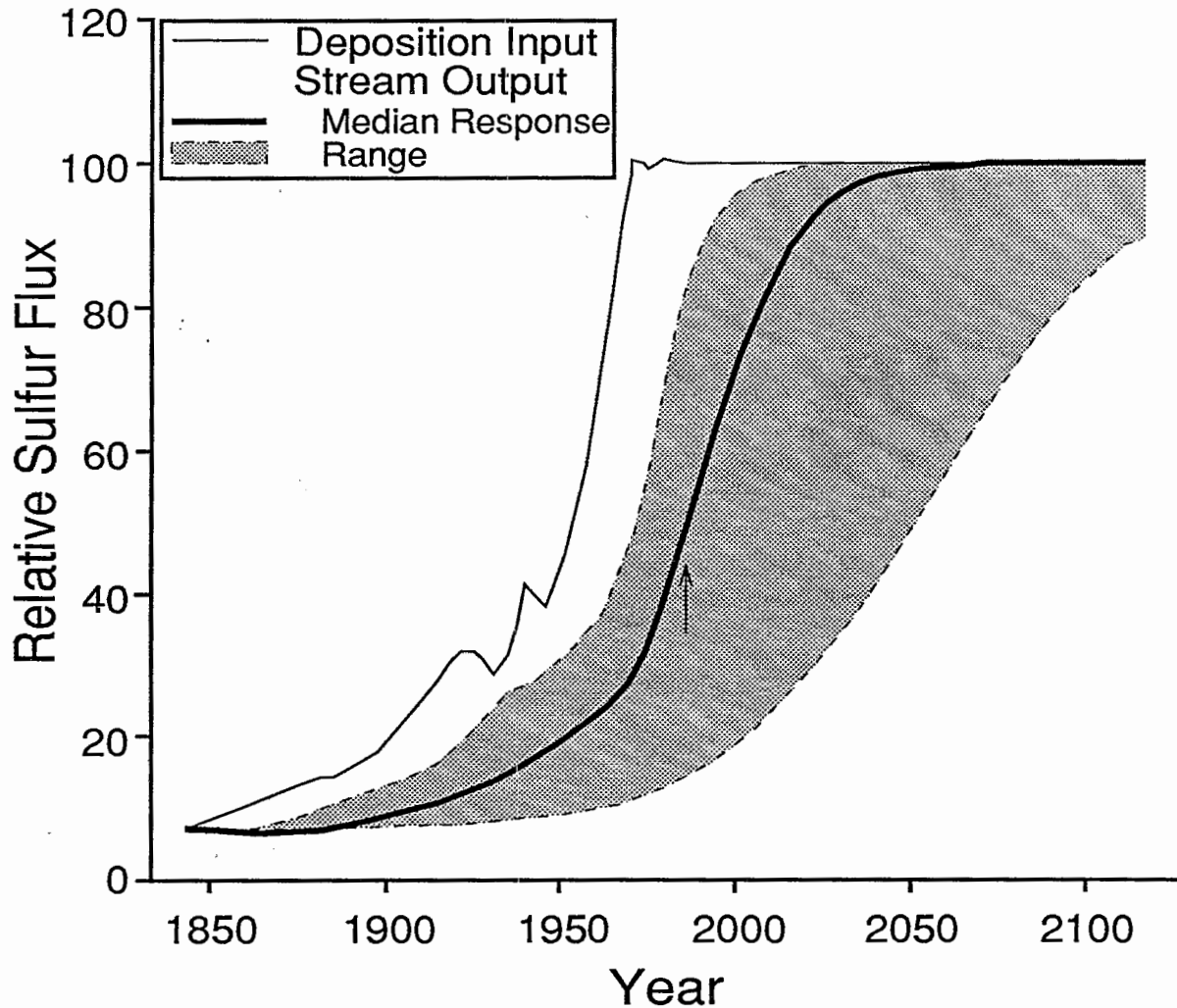
Figure 9-10. Historic deposition inputs and modelled output for soils in stream systems in the Southern Blue Ridge Province. Note the much slower response compared to systems in the Northeast, shown in Figure 9-3. Historic deposition input is based on emission estimates of Gschwandtner et al. (1985). Sulfur flux is expressed on a relative scale, 1985 deposition flux = 100. The base year for projections (1985) is indicated by the arrow. Note that because annual precipitation and runoff are constant throughout the simulation period, changes in flux correspond to proportional changes in projected stream sulfate concentration.

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An early issue in evaluating SBRP model projections was calibration of the model and data for the region. Because both the response times projected for watersheds and the range of base year projections are much wider in the SBRP than in the NE, the need for and effects of calibrating input data are much more obvious for SBRP systems. As for the NE, the model runs were begun at -140 years, continued through the base year (1985, when SBRP streams were sampled in the Pilot Stream Survey), and then for 300 years into the future. Starting with uncalibrated isotherm data, measured and modelled sulfate concentrations and percent sulfur retention were compared to evaluate bias and their distribution. The measured and modelled data were in close agreement for both sulfate concentration and percent sulfur retention (Table 9-4 and Figure 9-11). Model projections essentially are unbiased for both parameters with the average modelled concentration differing by only 2 μeq L^{-1} from the average for measured data (39.0 vs 36.8 μeq L^{-1}) and average retention differing by only 3 percent. Ranges and standard deviations of model projections also closely approximate those of measured data. Modelled sulfate concentrations are slightly higher than measured concentrations over most of the observed range, although modelled concentrations are slightly lower at the high and low ends of the distribution. Corresponding relationships for percent sulfur retention indicate lower modelled retention over most of the range. Overall, the two sets of data are very similar, and a small systematic adjustment could be made to one of the isotherm coefficients to completely eliminate bias. Using LTA deposition data, differences between measured and modelled base year sulfate concentration and percent sulfur retention are very small and are comparable to differences in projections of base year sulfate concentrations and percent retention using different deposition datasets (LTA, TY). There is thus no compelling rationale for adjusting either the data or the model. For all subsequent projections, therefore, isotherm data were used without adjustment.

Comparison of modelled rates of increase in sulfate concentration (for base year 1985) in the DDRP watersheds to measured rates of increase for watersheds in the region (Table 9-5) indicates generally good agreement. The range of rates generated by the model for DDRP watersheds encompasses all of the measured rates; observed rates (except those for watersheds 2 and 18 at Coweeta) are between the 25th and 75th percentiles of the 34 DDRP sample watersheds. The close agreement between observed and modelled rates of increase provides additional support for the use of isotherm data without extensive calibration and provides a useful check on the model projections generated from those data.

Concurrent with assessments of the need for data adjustments during model calibration, differences in model projections resulting from use of different deposition datasets were evaluated. Comparison of projections based on LTA and TY deposition data (Figure 9-12) reveals systematic but very small differences. For year zero data (expressed as percent sulfur retention) retention is marginally higher for the LTA data, whereas projected concentrations are 5 to 10 μeq L^{-1} higher for the TY data; times to steady state for the two sets of projections are very similar. Time to sulfur steady state is typically 3-4 years shorter for projections based on TY than for LTA deposition data. Given these small differences, the balance of this discussion will focus only on the long-term results, except to note differences between the two sets of projections.

9.2.4.3.2 Projections of future sulfate dynamics -

Projections of future sulfur dynamics for the SBRP differ in almost every respect from those for the NE. Projected sulfate concentrations for the NE are slightly above steady state, and the projected

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Table 9-4. Comparison of Measured and Modelled Base Year (1985) Sulfate Data for SBRP Watersheds, Using Long-Term Average Deposition Data. Values Represent Population-Weighted Mean ± 1 Standard Deviation

Parameter	Measured Value	Modelled Value
Sulfate concentration (μeq L^{-1})	36.8 ± 25.7	39.0 ± 21.0
Percent sulfur retention	68.3 ± 16.0	64.8 ± 17.5

SBRP Streams
Year 0 Sulfur
Deposition = Long Term Average, Constant
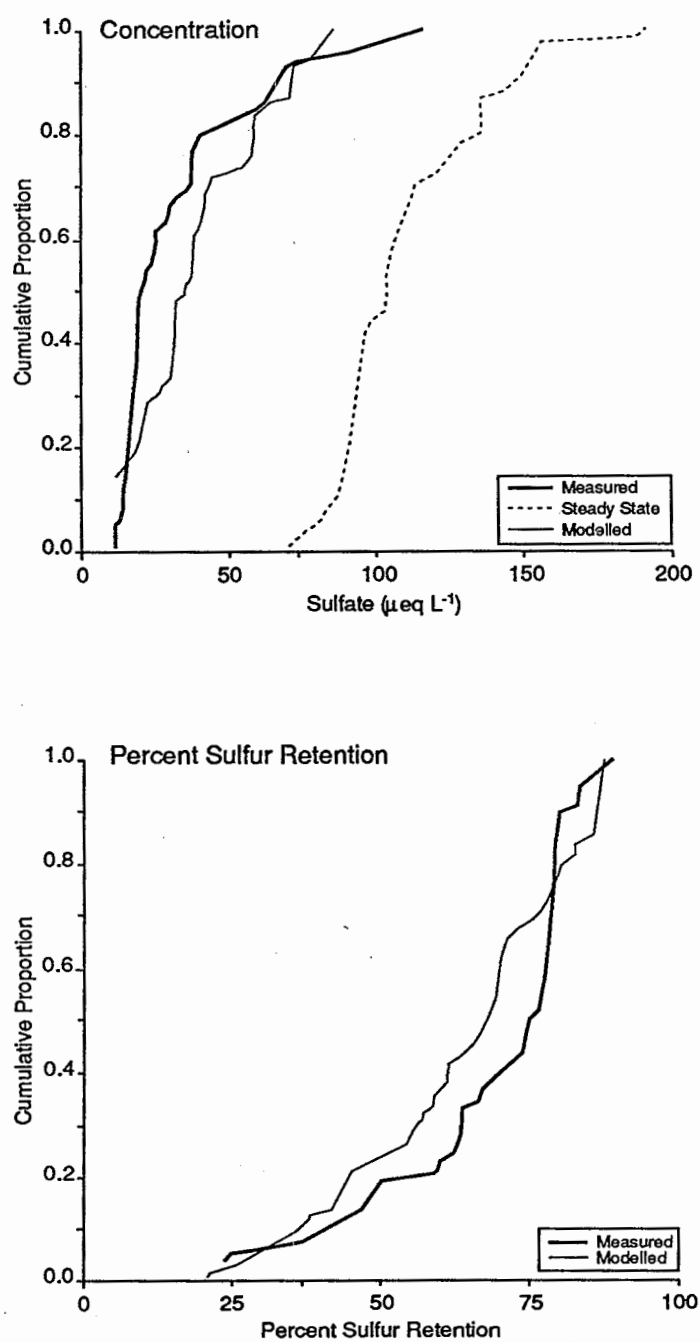
Figure 9-11. Comparison of measured, modelled, and steady-state sulfate for stream systems in the Southern Blue Ridge Province in 1985.

Table 9-5. Comparison of Modelled Rates of Increase for [SO$_4^{2-}$] in DDRP Watersheds in the SBRP with Measured Rates of Increase in Watersheds in the Blue Ridge and Adjoining Appalachians

Site	Period of Record	[SO$_4^{2-}$] (μeq L^{-1})	Rate of [SO$_4^{2-}$] Increase (μeq L^{-1} yr^{-1})	References[a]
DDRP watersheds	model-based estimates	15-119 Q_1 = 0.80 Q_3 = 1.90	median = 1.21 range 0.2-2.9	this study
Cataloochee Cr., NC	1968-1981	26	1.0	a
Coweeta, NC				
WS 2	1974-1983	13	0.7	b
WS 18	"	13	0.6	
WS 27	"	29	0.8	
WS 36	"	24	0.8	
Deep Run, VA	1980-1986	100	1.7	c
Madison Run, VA	1968,1982	70	1.3	d
Fernow, WV				
WS 4	1970-1985	85-90	1.0	e

[a]   References: (a) Smith and Alexander, 1986; (b) Swank and Waide, 1988; J. Waide, personal communication; (c) P. Ryan, Univ. of VA, personal communication; (d) USGS, 1969, 1970; Lynch and Dise, 1985; (e) D. Helvey, personal communication.

SBRP Streams
(DDRP watersheds only)
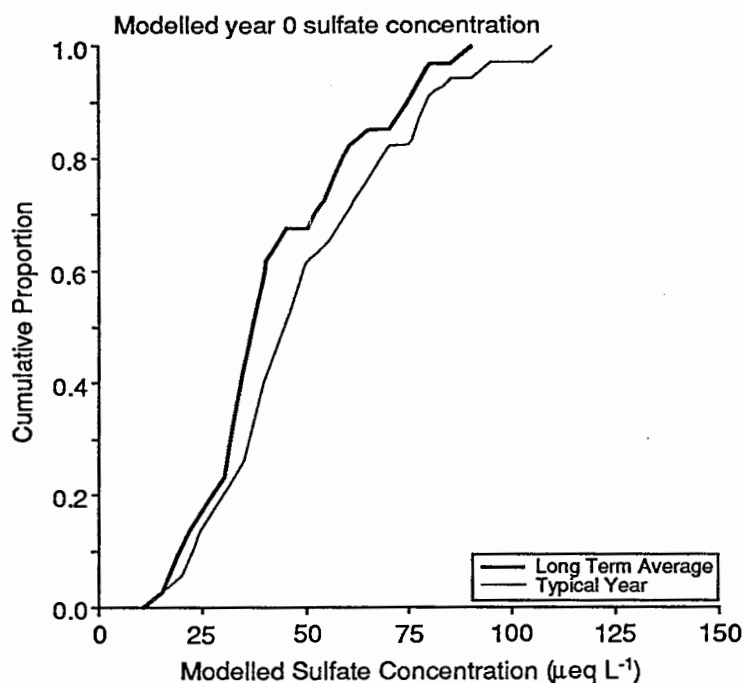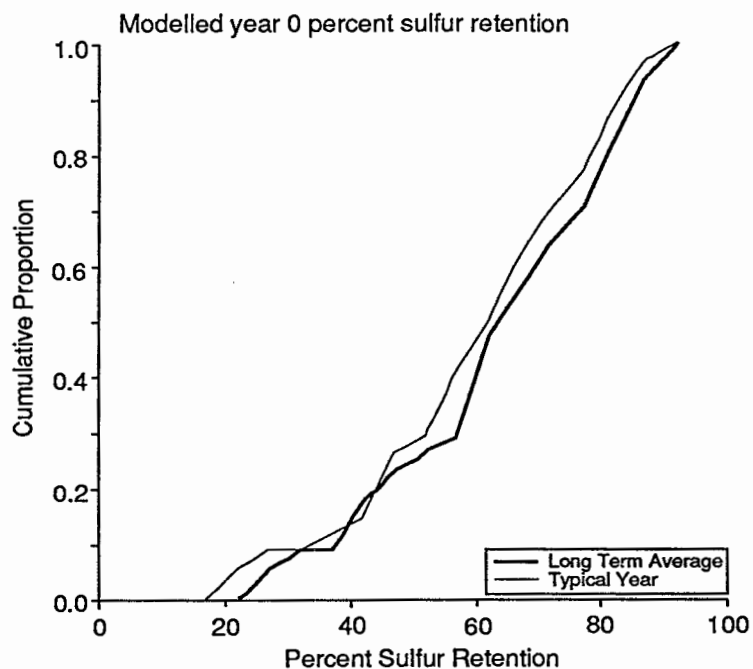
Figure 9-12. Comparison of forecasts based on two sulfur deposition datasets for soils in SBRP watersheds. Modelled-sulfate concentration and percent sulfur retention for the 1985 base year are shown for long-term average and TY data.

response is small decreases in sulfate concentration as systems move toward steady state over the next decade. In contrast, most SBRP watersheds are presently far below steady-state concentrations; however, moderate to large increases in sulfate concentrations are projected over time frames of several decades to over a century. As previously noted, the reliability of model projections decreases with the duration of the projections. The time interval of primary interest to DDRP is 0 to 50 years; projections for longer periods (≥100 years) are included principally to characterize the magnitude of potential change following the 50-year projection period. Results using LTA and TY deposition data (Figure 9-13, Tables 9-6 and 9-7), indicate significant increases in sulfate concentration and corresponding decreases in percent sulfur retention for most SBRP watersheds within 20 years. At current deposition, the projected increase in median sulfate concentration at year 20 is 24 μeq L^{-1}, with an additional increase of 25 μeq L^{-1} by year 50. The range of the increase is 5 to 48 μeq L^{-1} at 20 years and 15 to 93 μeq L^{-1} at year 50. By year 100, when the average projected total increase for stream sulfate is 66 μeq L^{-1}, most watershed sulfur budgets are projected to be near steady state; increases after year 100 will be restricted to a small subset of systems with very long projected response times.

Between years 0 and 20, percent sulfur retention decreases by about 20 percent for soils in most watersheds, and only a few watersheds approach zero percent retention. Decreases during this period appear to be controlled by deposition/sorption capacity relationships. After year 20, however, a substantial number of watersheds are at or very close to steady state, and by year 50 over half of the SBRP watersheds have less than 10 percent sulfur retention. By year 100, over 75 percent of the watersheds are within 5 percent of steady state, and most have projected retention of 1 percent or less. Only a few systems, with very long response times, remain below steady-state concentration by year 140.

Box and whisker diagrams (Figures 9-14 and 9-15) summarize changes in sulfate concentration, percent sulfur retention, and delta sulfate between 0 and 140 years. These diagrams illustrate not only the trends for these parameters, but also the relationships among them. In particular, sharp increases in sulfate concentration and in delta sulfate are shown at 20 and 50 years. The increases slow by year 100 as percent sulfur retention approaches zero, constraining further changes in sulfate concentration.

Using the ramped deposition sequence, no differences in status at year 0 are projected, and differences in sulfate concentration between constant and ramped scenarios at year 20 are insignificant (1 μeq L^{-1} or less). Because increases in sulfur input are not matched by enhanced sulfur output at year 20, percent sulfur retention for year 20 is higher for the increased deposition scenario than for constant deposition. Major effects of the increased deposition are seen in year 50 projections. Projected sulfate concentrations for year 50 are typically 12 - 15 μeq L^{-1} higher for the scenario with increased deposition than with constant deposition, whereas percent sulfur retention is only slightly higher for the projections with increased deposition. By year 100, almost all of the increase in deposition can be observed as an increase in projected sulfate concentration; percent sulfur retention is comparable to, and in most cases, actually lower for the increased deposition scenario forecasts than for the constant deposition projections (Tables 9-6 and 9-7).

Figure 9-16 illustrates projected time to sulfur steady state (± 5 percent of steady state) for current and increased deposition scenarios. At current deposition levels, soils in SBRP watersheds are projected to reach steady state in as little as 16 years after the base year, with a roughly linear increase in the
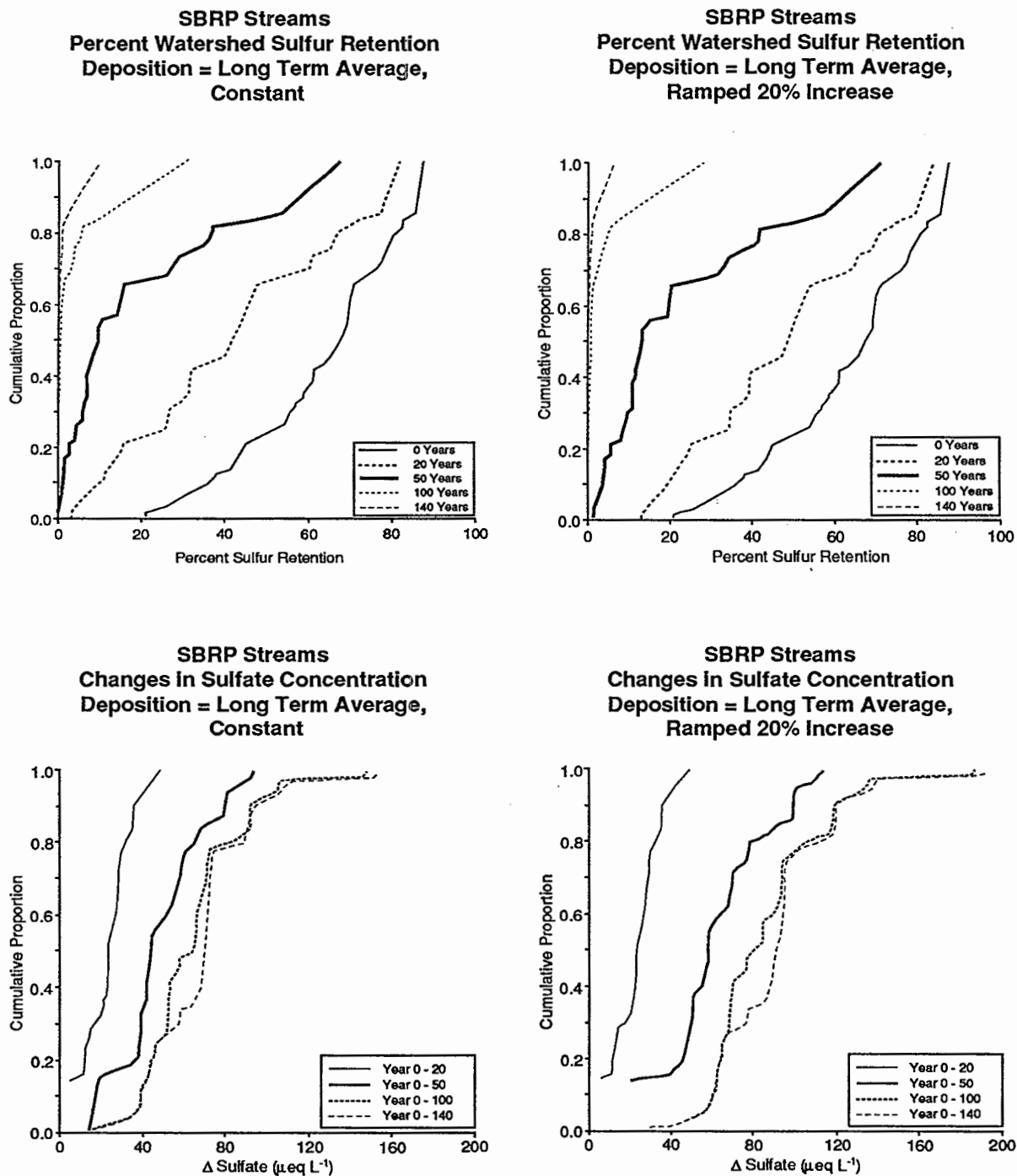
Figure 9-13. Projected changes in percent sulfur retention and in sulfate concentration for stream systems in the Southern Blue Ridge Province at 0, 20, 50, 100 and 140 years. Data for long-term average deposition, at constant and increased deposition, are shown.

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Table 9-6. Summary Statistics for Modelled Changes in Sulfate Concentration, Percent Sulfur Retention, and Delta Sulfate for Watersheds in the Southern Blue Ridge Province, Using Long-Term Average Deposition Data

Scenario Year	Sulfate Concentration						
	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Stream SO$_4$	36.8	25.7	14.7	19.8	23.6	40.8	119.2
Constant							
0	39.0	1.0	12.0	21.7	35.3	57.5	85.5
20	62.7	31.0	17.2	36.7	62.3	86.9	134.0
50	88.2	33.7	31.0	65.4	89.6	111.1	154.0
100	104.8	28.6	65.7	86.2	103.1	127.0	184.4
140	108.9	25.8	69.5	86.7	103.6	127.6	189.8
Steady State	110.5	24.7	69.5	94.9	103.6	127.8	190.4
Increased							
20	63.0	131.3	17.2	36.8	62.4	87.6	135.0
50	100.9	40.1	33.1	72.8	101.4	130.6	179.7
100	126.3	33.8	82.0	103.5	124.2	152.2	222.5
140	131.4	30.4	83.4	106.7	124.3	153.1	228.2
Steady State	132.6	29.7	83.4	113.8	124.3	153.3	228.5

Scenario Year	Percent Sulfur Retention						
	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Stream SO$_4$	68.3	16.0	23.7	65.1	74.9	79.1	85.9
Constant							
0	64.8	17.5	21.0	54.3	69.1	78.9	83.8
20	43.8	24.3	3.2	26.2	42.8	65.0	81.9
50	21.1	22.7	<0.1	4.3	9.6	32.5	67.4
100	5.7	10.6	<0.1	0.2	0.6	3.9	30.8
140	1.6	3.5	<0.1	<0.1	0.1	0.8	10.0
Increased							
20	50.1	21.7	13.0	34.5	49.3	69.0	84.0
50	24.8	23.0	1.2	8.6	13.2	36.9	71.0
100	5.1	9.6	<0.1	0.3	0.6	3.4	28.0
140	1.0	2.2	<0.1	<0.1	0.1	0.6	6.3

Scenario	Delta Sulfate (Change from Year 0 to n)						
	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Constant							
0-20	23.7	11.5	5.2	15.0	23.6	29.4	48.4
0-50	49.2	20.4	14.6	39.0	43.8	60.7	93.2
0-100	65.8	23.6	14.7	48.2	67.0	73.5	149.1
0-140	69.9	24.3	14.7	48.3	71.3	74.4	154.5
Increased							
0-20	24.0	11.7	5.2	15.1	24.0	30.4	49.5
0-50	61.9	25.3	21.1	48.1	58.4	78.5	113.9
0-100	87.5	27.9	28.6	66.4	85.2	101.8	187.2
0-140	92.4	8.1	28.6	66.5	94.8	101.9	192.9

Table 9-7. Summary Statistics for Modelled Changes in Sulfate Concentration, Percent Sulfur Retention, and Delta Sulfate for Watersheds in the Southern Blue Ridge Province, Using Typical Year Deposition Data

Scenario Year	Sulfate Concentration						
	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Stream SO_4	36.8	25.7	14.7	19.8	23.6	40.8	119.2
Constant							
0	43.5	22.7	12.5	25.2	40.8	57.6	106.5
20	71.1	32.5	18.6	45.0	72.4	92.4	134.1
50	99.8	34.3	35.4	81.7	106.5	119.1	171.9
100	116.8	27.0	77.3	93.1	120.2	131.2	199.2
140	120.5	23.9	86.3	97.0	120.2	133.3	203.1
Steady State	121.7	23.0	86.4	104.0	120.2	133.5	203.1
Increased							
20	71.6	32.8	18.6	45.1	72.7	92.9	136.3
50	115.0	41.0	38.1	92.4	123.7	140.3	197.8
100	141.2	31.5	97.8	112.3	144.2	159.0	240.8
140	145.3	28.2	103.6	120.3	144.2	159.6	243.8
Steady State	146.0	27.6	103.7	124.8	144.2	160.2	243.8

Scenario Year	Percent Sulfur Retention						
	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Stream SO_4	70.8	16.7	17.3	66.0	78.2	82.1	87.0
Constant							
0	64.4	17.9	19.6	54.6	68.4	79.6	88.0
20	41.9	24.8	2.6	21.6	38.9	64.2	82.2
50	18.8	22.4	0.3	2.7	7.0	31.1	66.0
100	4.5	8.9	<0.1	<0.1	0.3	3.1	25.7
140	1.1	2.4	<0.1	<0.1	0.1	0.4	6.8
Increased							
20	48.4	22.2	12.3	30.5	45.8	68.4	84.2
50	22.1	22.7	1.0	5.6	10.9	33.4	69.5
100	3.8	7.5	<0.1	0.1	0.3	2.4	21.7
140	0.6	1.3	<0.1	<0.1	0.1	0.3	3.7

Scenario	Delta Sulfate (Change from Year 0 to n)						
	Mean	Std. Dev.	Min.	P_25	Median	P_75	Max.
Constant							
0-20	27.7	12.3	6.1	19.3	30.9	34.8	49.9
0-50	56.4	22.4	16.8	41.3	56.5	74.1	122.5
0-100	73.4	25.4	16.9	61.4	66.9	88.0	164.3
0-140	77.1	26.3	16.9	61.7	80.8	88.4	168.5
Increased							
0-20	28.2	12.6	6.1	19.9	31.1	35.4	50.5
0-50	71.6	27.1	25.7	60.2	69.8	89.8	148.3
0-100	97.7	29.0	34.1	81.7	93.2	113.4	205.9
0-140	101.8	29.5	34.1	81.8	102.1	113.9	209.5
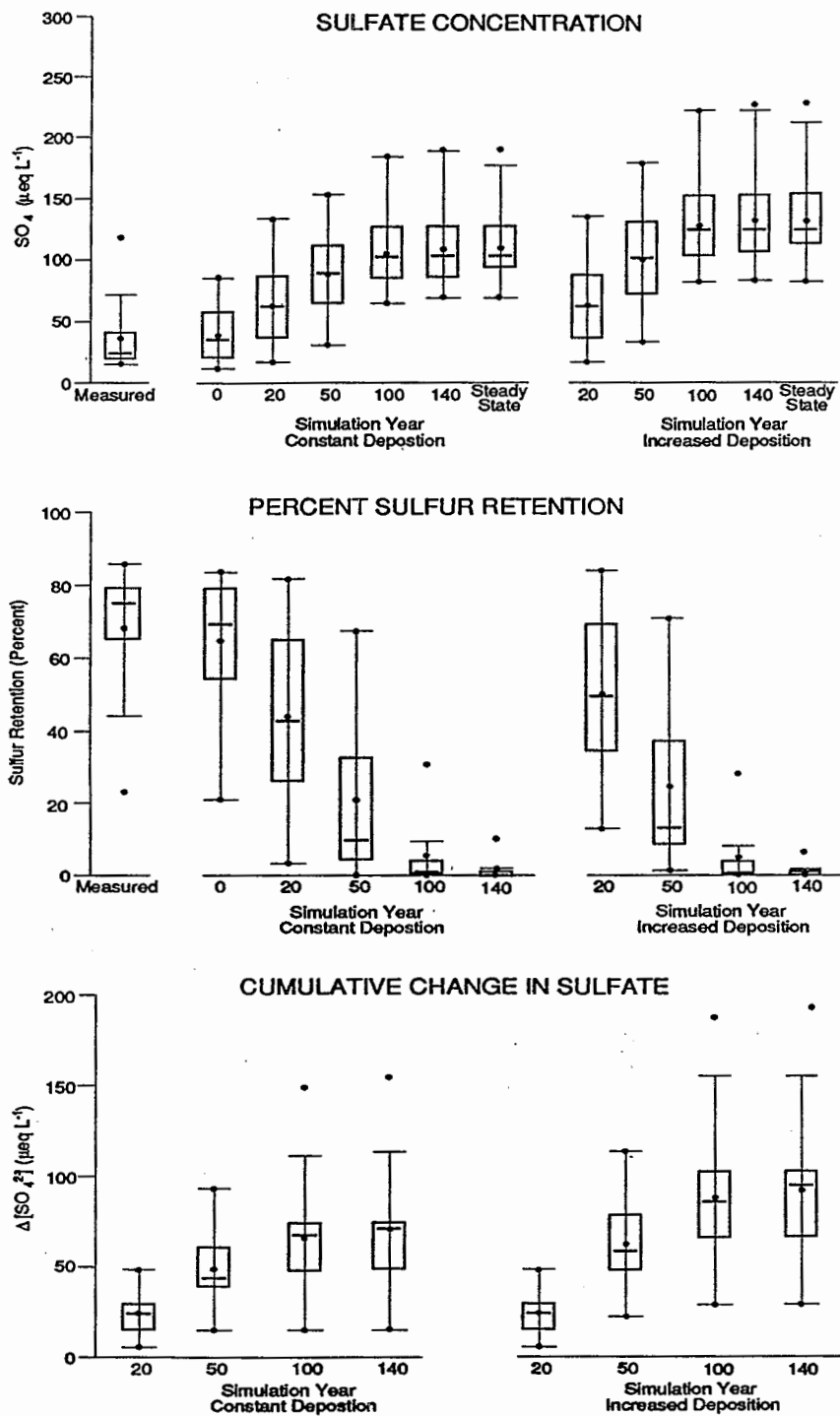
Figure 9-14. Box and whisker plots showing changes in sulfate concentration, percent sulfur retention, and change in sulfate concentration for soils in watersheds of the Southern Blue Ridge Province. Data are shown for long-term average deposition data.
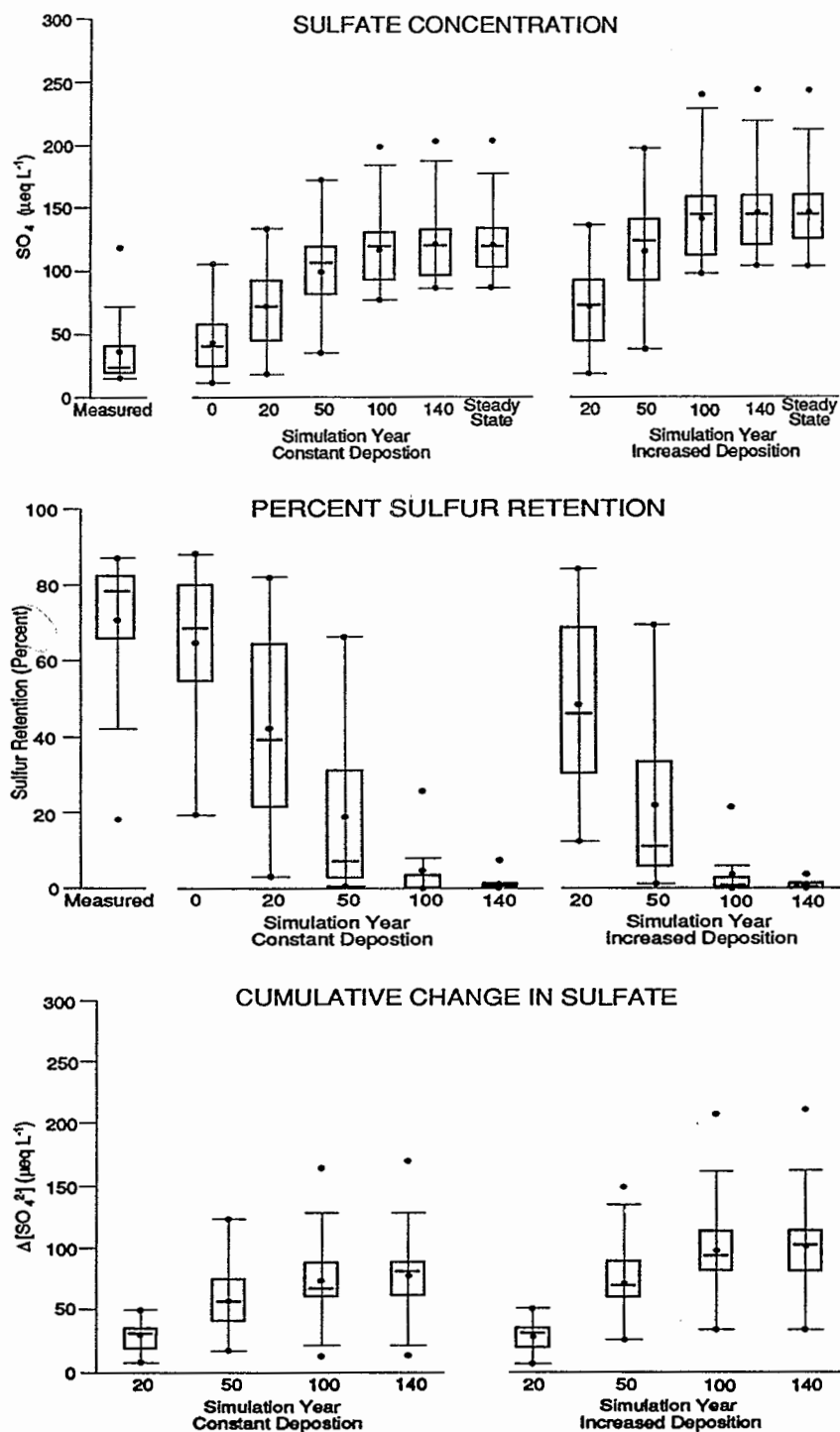
Figure 9-15. Box and whisker plots showing changes in sulfate concentration, percent sulfur retention, and change in sulfate concentration for soils in watersheds of the Southern Blue Ridge Province. Data are shown for TY deposition data.

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SBRP Streams
Time To Steady-State
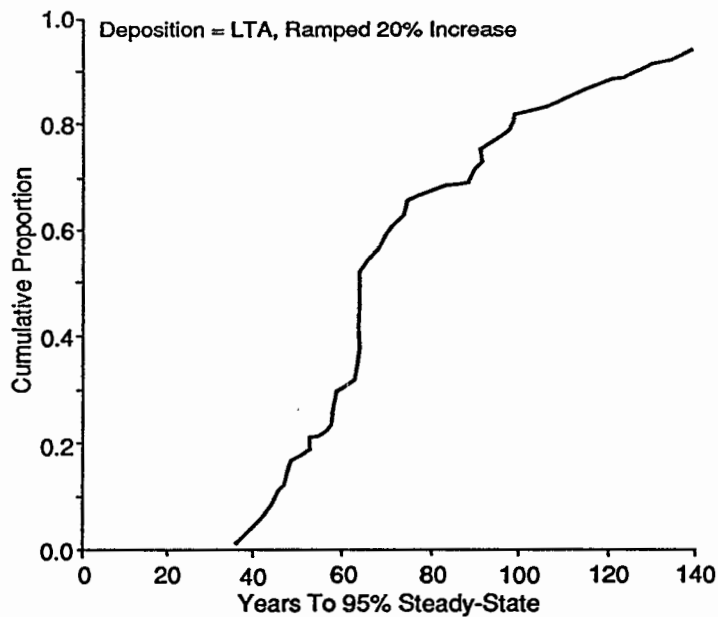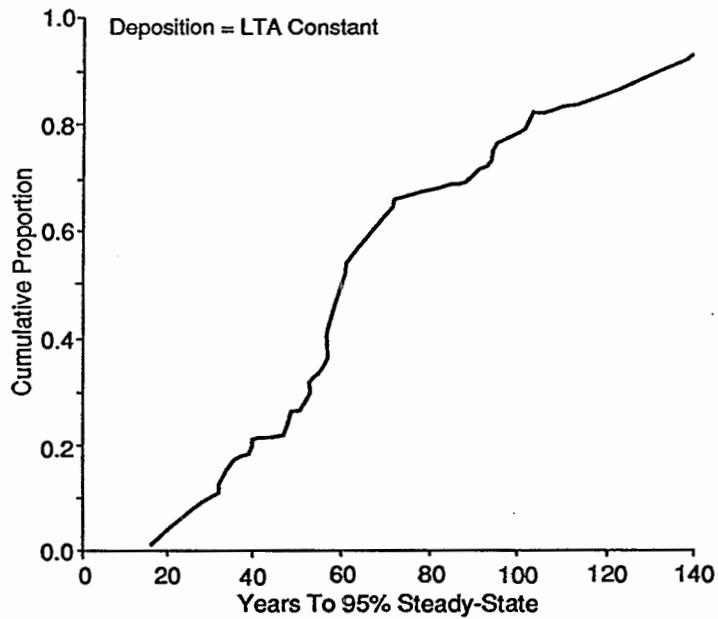
Figure 9-16. Projected time to 95 percent of steady-state sulfur concentration of Southern Blue Ridge Province stream systems. Results for long-term average deposition, for constant and increased deposition scenarios, are shown.

proportion of systems at steady state until year 75, when about 75 percent will be at steady state. Following year 75, the increase in the number of systems at steady state is slower, with about 95 percent of watersheds reaching steady state by the final year of model forecasts, year 140. For the systems that reach steady state in more than about 60 years, increased deposition negligibly changes times to steady state. For those systems projected to reach steady state in less than 60 years, especially those that respond most quickly, increased deposition delays time to steady state. Higher deposition, coupled with modest delays in increased watershed sulfur output, maintain these systems below steady state for as long as two decades. The results for these watersheds do not correspond to lower stream sulfate concentrations. Higher input simply results in a higher input to output ratio; projected stream sulfate concentrations are in all cases the same or higher for the increased deposition scenario than for current deposition.

The magnitude and consequences of the projected changes in sulfate over the next 20 to 100 years on overall stream chemistry in the SBRP are substantial. The projected changes represent 50 to 100 percent increases in sulfate concentration within 20 years and, on average, about a threefold increase in sulfate concentration when systems reach steady state. Increases in sulfate of this magnitude will cause major changes in surface water base cations and/or ANC and will accelerate base cation leaching from soils, as discussed in Sections 9.3 and 10.

9.2.4.4   Uncertainty Analyses and Alternative Aggregation Approaches

9.2.4.4.1 Uncertainty analyses -

As noted in Section 9.2.3.4, partitioning coefficients (isotherm slopes) for sulfate equilibrium between soil and solution phases are nonlinear; because the coefficients of these nonlinear isotherms are highly correlated, generation of weighted averages of isotherm coefficients is not an effective or appropriate means of aggregating isotherm data for soils. The procedures for aggregation of isotherm data described in Section 9.2.3.4 are not conducive to direct estimation of uncertainty for adsorption isotherm coefficients or for derived variables such as isotherm slope. The development of uncertainty estimates for Level II sulfate projections thus required an alternative approach to data aggregation and use in model runs.

Section 9.2.3.4 described a Monte Carlo procedure for generating uncertainty estimates for model projections. The procedure, however, also involved derivation of new isotherm coefficients and model projections for each DDRP watershed that were developed independently of projections that used data aggregated by the original mass-weighting approach. Because the two sets of independent coefficients and the projections generated from them could significantly differ, the initial concern in uncertainty analyses was to assess comparability of the two sets of model outputs. Direct comparison of coefficients was not possible, since the uncertainty analysis generated a new aggregate isotherm for each of the 100 model runs. Moreover, such an analysis would have been inconclusive since two sets of very different isotherm coefficients can describe virtually identical partitioning curves over the range of dissolved sulfate concentrations of interest here (0 to 300 μeq L^{-1}). Instead, the mean and median values (which are virtually identical) from the Monte Carlo simulations for each SBRP watershed were compared to projections generated using the aggregate isotherm from the original mass-weighting aggregation. Comparisons were made for projected sulfate concentration and projections of time to sulfur steady state for several reference years.

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Results indicate very close agreement between the two sets of projections for the base year and time to steady state (Figure 9-17). Results for sulfate concentrations at other time intervals also were similar. For the comparisons of concentration at year 0 and for projected time to steady state, slopes and intercepts of the two lines are virtually equal to 1.0 and 0, respectively, and the coefficients of determination exceed 0.99 in both cases. These results are important for two reasons: (1) they demonstrate no fundamental inconsistencies between the aggregation and uncertainty procedures used to generate the two sets of projections and that the uncertainties developed using the Monte Carlo approach can be used to characterize uncertainty for projections and summaries that use data aggregated by the routine aggregation approach; and (2) they also suggest that the adsorption isotherms and the projections generated from those isotherms are highly constrained, i.e., two different and independent data aggregations generate virtually identical projections.

Mean values and confidence intervals for projected base year sulfate concentrations for stream systems in the SBRP are shown in Figure 9-18. Uncertainties are generally modest in magnitude, and upper and lower confidence intervals are almost symmetrical and are within 10 to 15 μeq L^{-1} of the mean sulfate concentration. Uncertainties increase very little with mean projected sulfate concentration. Only uncertainties in sulfate adsorption capacity (including those in both the original least squares fitting of isotherms to raw data points and data aggregation) and soil mass were considered. Separate analyses of the components of uncertainty for four SBRP watersheds indicate that uncertainty in soil mass is the primary contributor to the total variability in base year projections of sulfate concentration; upper and lower confidence bounds are within 5 percent of the median sulfate concentration for the four sets of Monte Carlo simulations in which soil mass was held constant.

Projections of mean time to sulfate steady state in SBRP watersheds (with 5 and 95 percent confidence intervals) are shown in Figure 9-19. Similar to base year results, confidence intervals are almost symmetrical; but in contrast, uncertainties in response time increase with mean projected concentration. Relative uncertainties are smaller than those observed for the base year concentration, averaging only about 20 percent of the mean time interval. As was the case for the base year evaluation, uncertainty in soil mass is the largest contributor to uncertainty in the projections; confidence intervals for projected time to steady state vary by less than 5 percent of the median value in Monte Carlo analyses for which soil mass was held constant. This result provides additional confirmation that the isotherm fits are highly constrained and also highlights the important influence of uncertainty in soil mass on projections involving changes in capacity variables.

9.2.4.4.2 Alternative aggregation approaches -

Uncertainties in aggregated data associated with the method of aggregation also were considered. Use of the sulfate subroutine in MAGIC requires aggregating data for the entire watershed into one compartment per soil horizon per watershed. Aggregating data for a variety of soils with differing chemistry, vegetation, hydraulic contact times, etc., inevitably introduces errors and uncertainty. Johnson et al. (1988b) discussed the rationale for several aggregation procedures and described the mass weighting approach based on soil sample classes that was used for routine data aggregation for this analysis. They did not address the possibility of adjusting aggregated data to account for differences in soil chemistry at intermediate spatial scales, nor did they address other approaches to describe "watershed effects" on aggregated soil chemistry (Section 8.9). As one means of assessing possible

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SBRP Streams
(DDRP watersheds only)
Deposition = Long Term Average, Constant
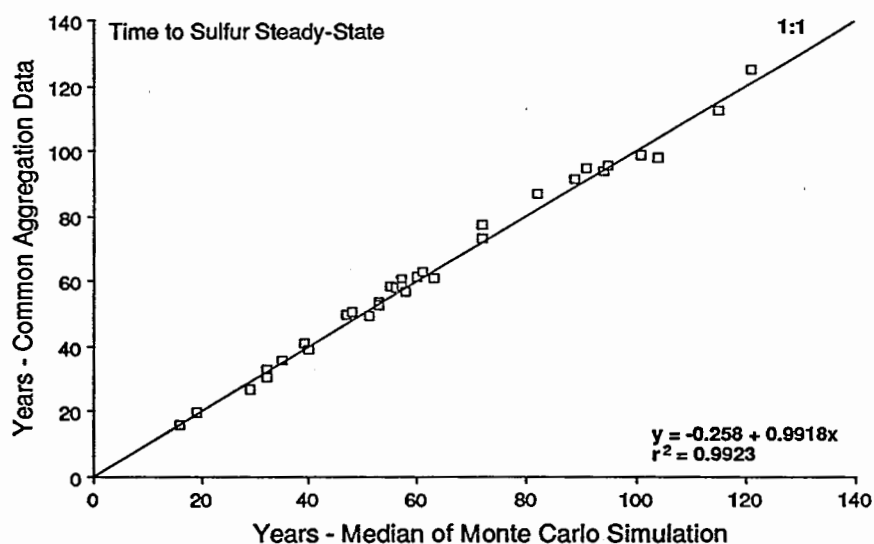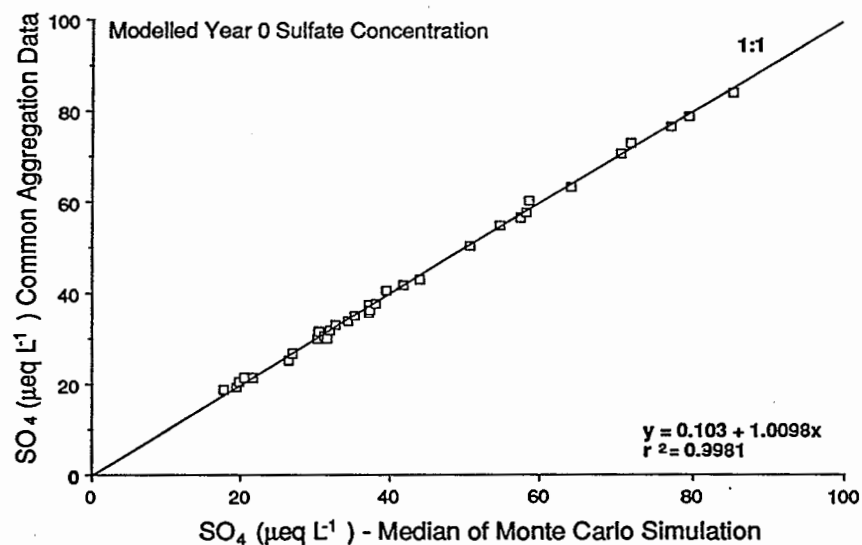
Figure 9-17. Comparison of model simulation results for DDRP Southern Blue Ridge watersheds. Data generated by the mass-weighting common aggregation approach and median projected values from Monte Carlo uncertainty analyses are shown.

SBRP Streams
Year 0 Sulfate
Deposition = Long Term Average, Constant
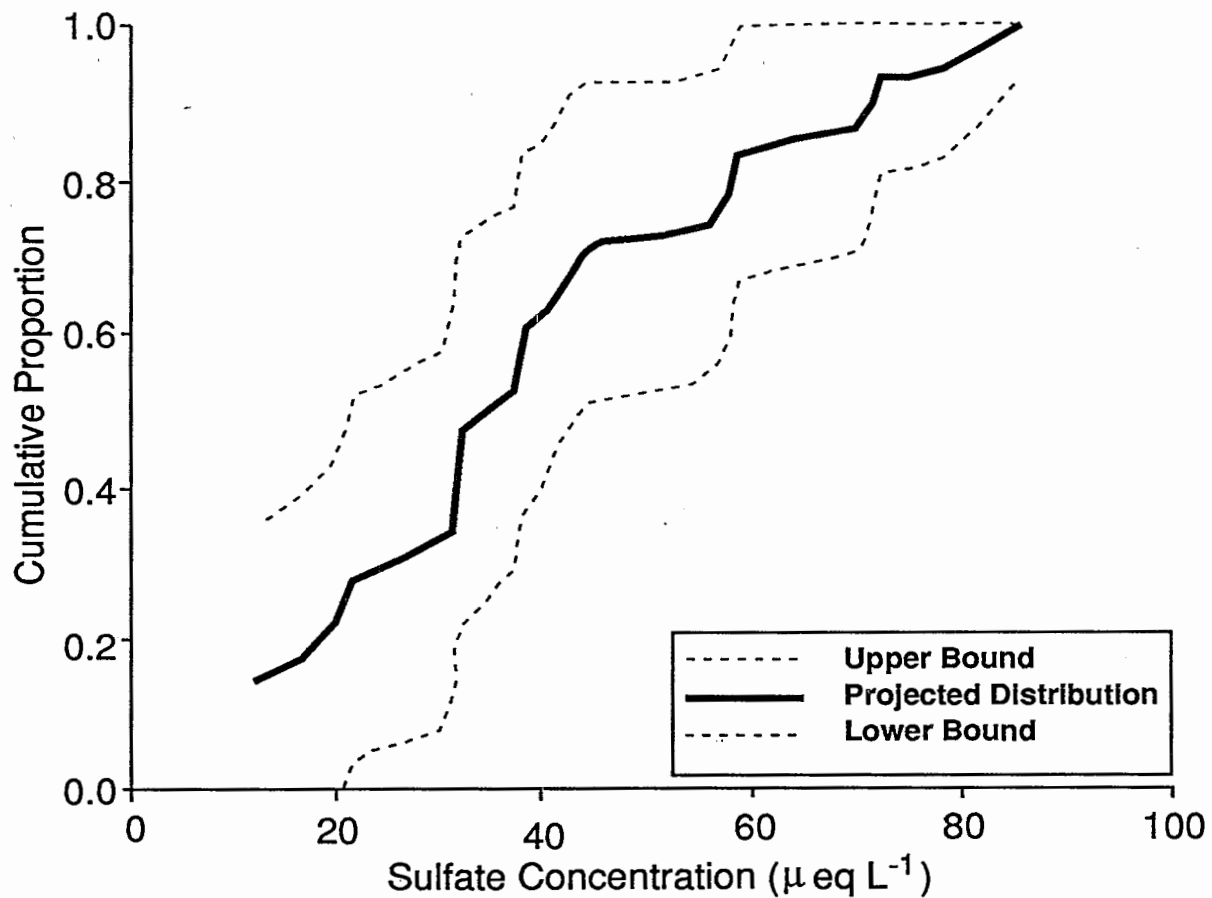
Figure 9-18. Projected base year sulfate concentration with upper and lower bounds for 90 percent confidence intervals for Southern Blue Ridge Province watersheds.

SBRP Streams
Time to Sulfur Steady State
Deposition = Long Term Average, Constant
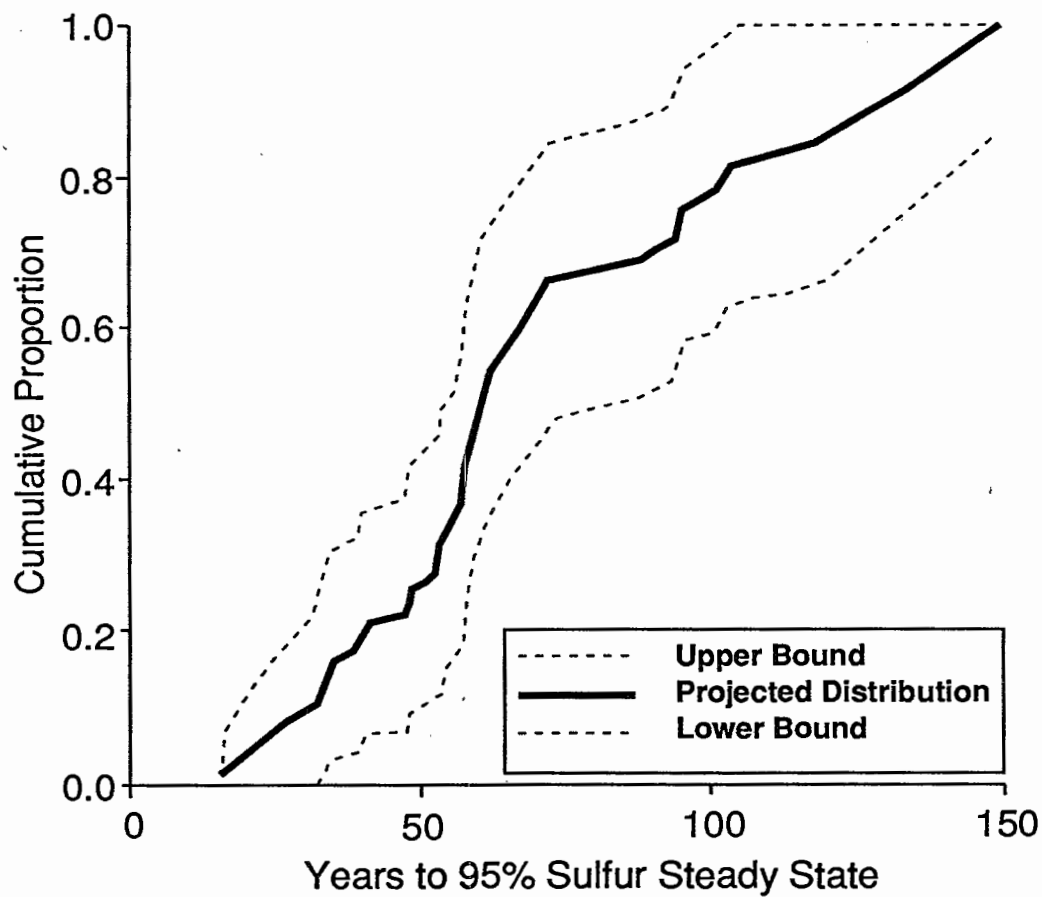
Figure 9-19. Projected time to sulfur steady state with upper and lower bounds for 90 percent confidence Intervals in Southern Blue Ridge Province watersheds.

watershed effects, data for the pedons sampled on individual DDRP watersheds in the SBRP were aggregated and were used with LTA deposition data to make projections. Measured chemistry and projections using the standard aggregation approach described by Johnson et al. (1988b) differed considerably (Figure 9-20). Projections using the pedons-on-the-watershed approach substantially overpredicted year zero sulfate concentration (modelled mean SO_4^{2-} = 67.4 μeq L^{-1} vs. measured mean SO_4^{2-} = 36.0 μeq L^{-1}) and underpredicted percent sulfur retention (median retention of 38 percent vs. 75 percent for measured retention and 69 percent for standard aggregation projections). Projections using the alternative approach also indicated that almost 20 percent of SBRP watersheds are already at sulfate steady state, in contrast to measured watershed sulfur retention, which indicates that more than 20 percent are at steady state. Additionally, model simulations based on the standard aggregation approach project all watersheds to have >20 percent retention in the base year and no watersheds to reach steady state for 16 years.

The overpredictions using the alternate aggregation (pedon-on-the-watershed) result from the soil sampling design in the SBRP. The design called for approximately equal numbers of samples for each soil sampling class, even though the spatial areas covered by the classes are widely variable. As a result, for this aggregation approach, in which data were arithmetically averaged, soils collected from sample classes with below-average areal spatial coverage were assigned artificially high weights. Because sample classes with small areal coverage (e.g., shallow or flooded soils) often have low sulfate adsorption capacity, averaged adsorption capacities are biased low and corresponding projected response times are short. This component of uncertainty is not introduced in projections using the common aggregation approach, because data are area weighted; the alternative aggregation approach, moreover, raised questions about sampling design and the magnitude of uncertainties in parameter estimates. For these reasons, it was dropped from consideration for this analysis. The issue of watershed effects (watershed-to-watershed differences in soil chemistry) is under active investigation, and changes in aggregation procedures for future analyses remain a possibility.

A second question concerns the number of soil horizons used for aggregation. The model formulation treats soils as a series of continuously stirred tank reactors (CSTRs) in which reactions proceed to equilibrium. This treatment results in model projections that are sensitive to the number of CSTRs. At one extreme, for a one-CSTR model, projected output concentrations respond immediately to changes in inputs and responses are sustained over a long period of time. At the other extreme, a model with an infinite number of small CSTRs (having a total soil mass equivalent to that for the 1-compartment model) would act much like a chromatography column: output remains constant until the breakthrough of the front through the soil column, at which time output concentration increases as a square wave (ignoring dispersion) to steady state. The number of horizons, which can be varied for the Level II Analysis, will affect the timing of projected changes as well as the concentration at any point in time (base year in this case). Results of running the model with soil chemistry data aggregated to 1, 2, and 3 horizons (A/E, B, and C) are displayed in Figure 9-21. Few differences between projections for 2- and 3-horizon aggregations are evident, but 1-horizon projections do differ. The close agreement between 2- and 3-horizon projections was not unexpected; the A/E horizon is thin and has relatively low adsorption capacity (i.e., the A/E horizon CSTR has a very short response time), so combining it with B horizon data has little effect on projections. On the other hand, combining all data in one horizon results in a system that responds immediately to altered inputs (thus resulting in projections of higher

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SBRP Streams
(DDRP watersheds only)
Deposition = Long Term Average, Constant
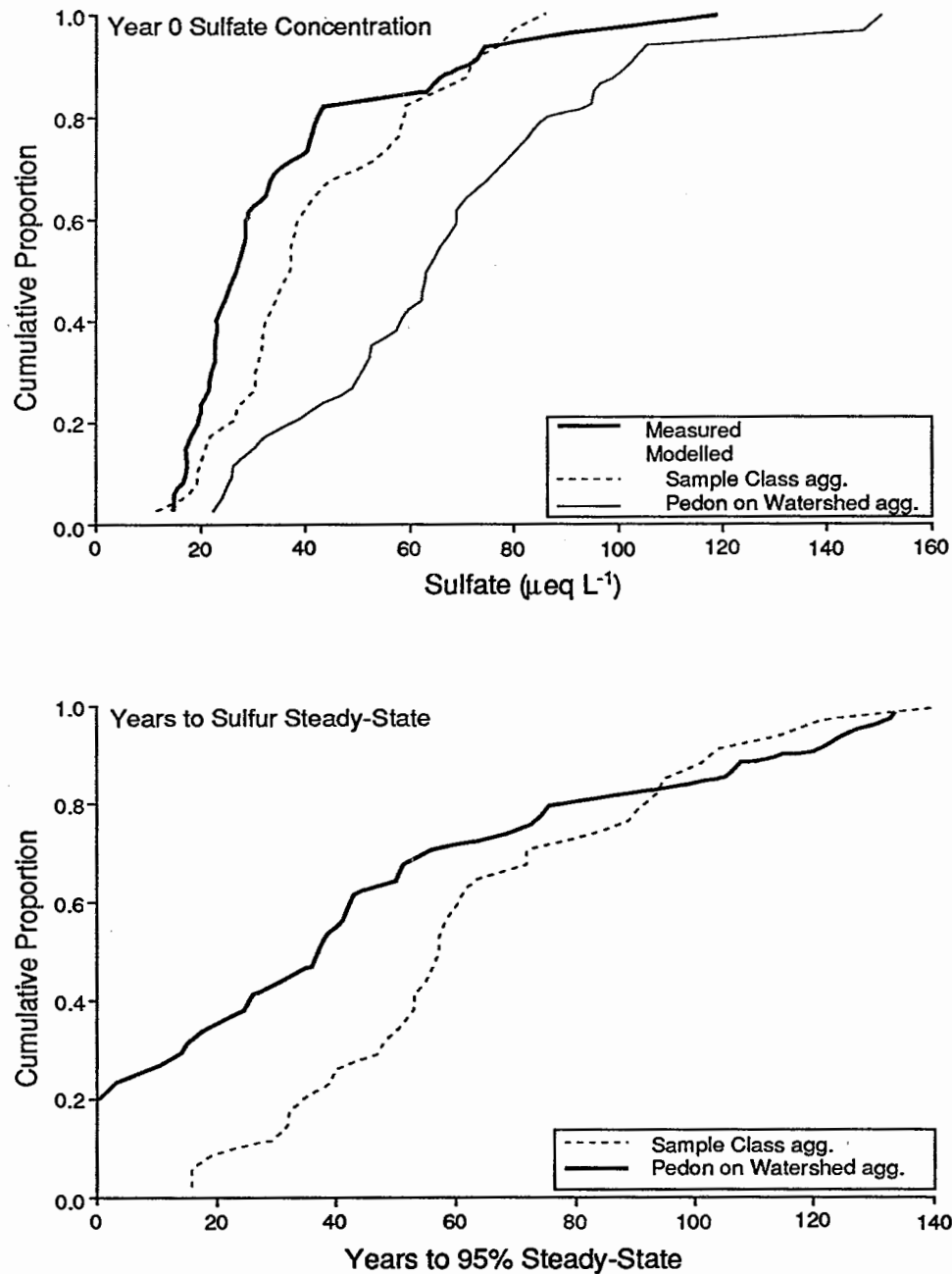
Figure 9-20. Effects of data aggregation on simulated watershed sulfur response for soils in DDRP watersheds of the Southern Blue Ridge Province. Results for the common (sample class) aggregation procedure and for an alternative aggregation using pedons sampled on each watershed are shown.

SBRP Streams
(DDRP watersheds only)
Deposition = Long Term Average, Constant
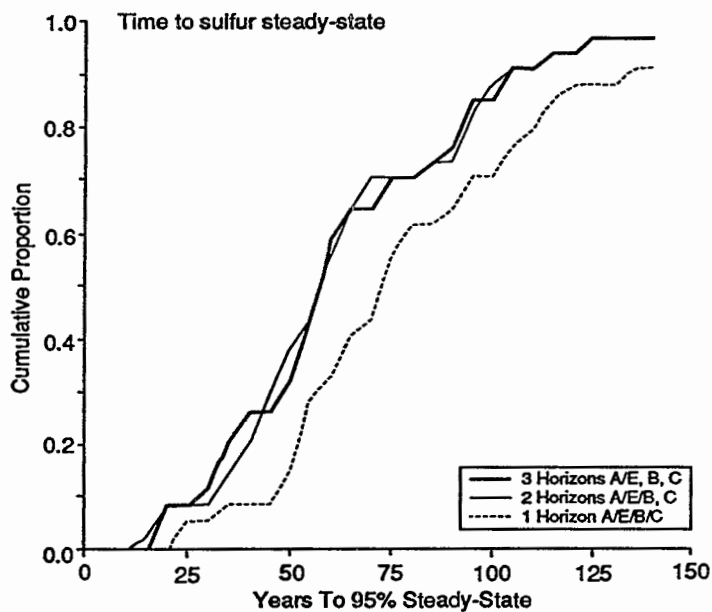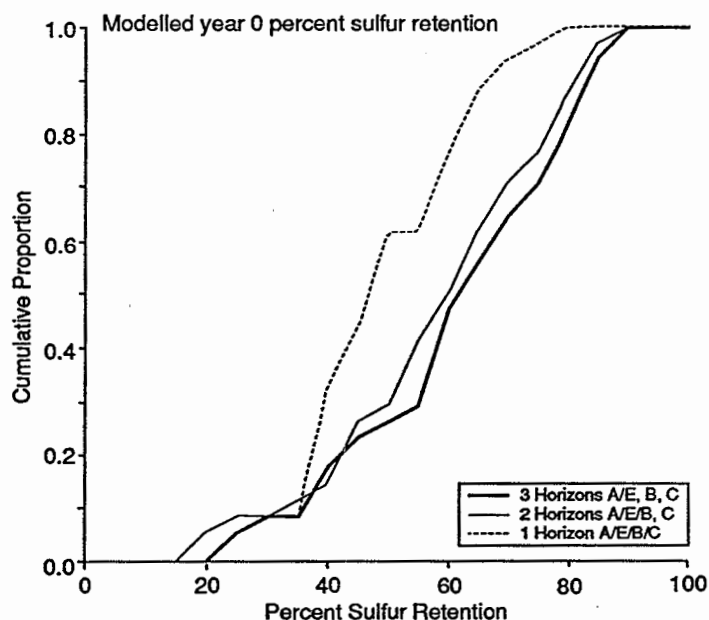
Figure 9-21. Evaluation of alternate soil aggregation procedures for soils in SBRP watersheds. Modelled percent sulfur retention for the 1985 base year and time to 95 percent steady state for soils aggregated to one, two, or three discrete horizons.

base year sulfate concentrations); it also results in a system that responds more gradually than a multiple-horizon model, projecting longer times to steady state. Model data provide no real basis for choosing among 1-, 2-, or 3-horizon models for routine modelling efforts. Based on differences in soil chemistry among A/E, B, and C horizons and on the good fit between measured and modelled projections of base year sulfate concentration and percent sulfur retention using the three-horizon model, the three-horizon model was chosen for routine analysis.

9.2.4.5 Summary of Results from the Southern Blue Ridge Province

The response of soils and surface waters in the SBRP to sulfate deposition represents a "textbook example" of delayed response watersheds. The response to major sulfur deposition increases that have occurred over the last two to three decades has been high watershed sulfur retention, with only modest increases in stream sulfate concentrations for most SBRP watersheds. Measured data summarized by Church et al. (in review) and model projections indicate, however, that the delay is now ending and that surface water sulfate concentrations are increasing at rates projected to accelerate over the next few decades. Major increases in stream sulfate concentration are projected for SBRP streams in the next 20 years, with continued increases for at least 50 years for most watersheds. When SBRP watersheds come to steady state for sulfate (at projected times ranging from 16 to >150 years) sulfate concentrations will be, on average, about three times current concentrations. The projected changes in stream sulfate will result in substantial changes in streamwater chemistry and could substantially accelerate base cation leaching from soils.

The results of these analyses are generally consistent with those of other DDRP analyses. Model projections of base year sulfate in soils of northeastern and SBRP watersheds are consistent with, and provide a mechanistic explanation for, analyses by Rochelle and Church (1987). Their analyses, summarized in Section 7.3, show watersheds in the northeastern United States to be at or near sulfur steady state, whereas SBRP watersheds have high net sulfur retention. The very short sulfate response times projected for the NE are also consistent with results of regression analyses presented in Sections 7 and 8, which indicate that deposition is the principal control on surface water sulfate in the NE and that significant sulfur retention (where observed) is probably attributable to sulfate reduction in lakes and/or wetlands rather than to sorption.

The short sulfur response times projected for northeastern soils in this analysis are comparable to watershed response times projected by integrated models (Section 10). Projected response times for the SBRP are roughly comparable to those generated for SBRP watersheds by MAGIC (Section 10.11), although the projections of time to steady state generated in Level II Analyses for SBRP systems are generally somewhat shorter than the MAGIC forecasts. Two factors are believed to contribute to the differences in projections:

- Hydrologic routing in the two models is different. The Level II projections used a simplified routing in which all water was routed through all soil horizons, while a substantial portion of runoff in MAGIC simulations bypassed either the upper or lower soil compartment.

- Soil depth was treated differently by the two modelling efforts. Level II models considered adsorption within the top 1.5 to 2 meters of the regolith while the Level III models assigned

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the adsorption capacity (and other chemical properties) of the lower soil horizon to all material between the B-C horizon boundary and the estimated depth to bedrock. The MAGIC projections are therefore based on a larger mass of soil, having a larger integrated pedon adsorption capacity, which ultimately results in a slower projected response to changes in sulfur deposition.

Despite the differences between the two modelling approaches (Level II limited to adsorption in the developed soils as compared to Level III models which integrate hydrologic processes with biogeochemical processes in the entire catchment), the magnitude of differences between the two sets of projections was generally small. Results are viewed as mutually supportive, both of the two modelling approaches and of the projections generated by them.

9.2.5 Summary Comments on Level II Sulfate Analyses

At the start of the DDRP, it was widely believed that soils in the northeastern United States had low sulfate adsorption capacity, resulting in rapid sulfate response to changes in sulfur deposition and further resulting in watershed sulfur budgets near steady state. Conversely, observed sulfur retention in southeastern watersheds was attributed to high sulfate adsorption capacity of soils in that region. Measured sulfate data for the two regions and model forecasts summarized in Table 9-8 are consistent with previous soil sulfate data and provide strong support for this paradigm of regional sulfur dynamics. DDRP model projections also suggest fundamental differences in future sulfate dynamics of the two regions. Northeastern watersheds are very close to steady state; assuming constant deposition at current levels for the future, only small changes in sulfate concentration are anticipated as systems reach equilibrium with deposition inputs. If deposition were to change in the future, model projections suggest very rapid response by watersheds in the region, with systems projected to reach steady state with the altered deposition inputs in 5 to 15 years.

In the SBRP, sulfate adsorption by soils has delayed effects of acidic deposition, but model projections indicate that soils and watersheds in the region are now moving into a more dynamic phase, in which relative adsorption by soils will decline and stream sulfate concentrations will increase sharply in the coming decades. Major changes in stream water sulfate are projected for the next 20-50 years. If and when they occur, equivalent changes in surface water base cations or ANC are inevitable, and enhanced leaching of soil base cations is likely to occur.

In a qualitative sense, the differences of the current status and projected future sulfate dynamics for the two regions are unequivocal. Sulfur budget status and soil adsorption isotherm data document clear differences in soil and surface water chemistry for the two regions, and projections of future response times differ by roughly an order of magnitude. In making such comparisons, it is important to recognize that the models embody a variety of assumptions and approximations and that the projections carry significant uncertainty. Given the magnitude of the differences in projected responses for the two regions, however, their responses to sulfur deposition undoubtedly are also very different. Sulfate retention appears to have been a minor contributor to delays in surface water response to acidic deposition in the NE, but has been and continues to be a critical process delaying effects of deposition in the SBRP. In considering the projected responses for sulfur, especially in the SBRP, it is important to recognize that projections presented here apply only to sulfate and are based on the assumption that

Table 9-8. Summary Comparison of Watershed Sulfur Status and Model Forecasts in the Northeastern United States and Southern Blue Ridge Province. Model Projections are Based on Long-Term Average Deposition Data, Assuming Constant Future Deposition

	NE Lakes		SBRP Streams	
	Median	Range	Median	Range
CURRENT STATUS				
Steady State Sulfate	106.0	50.8 - 209.6	103.5	69.5 - 190.4
Lake/Stream Sulfate	105.4	33.8 - 249.3	23.6	14.7 - 119.2
Percent Sulfur Retention	-3.1	-60.0 - 61.1	74.9	23.7 - 85.9
MODEL FORECASTS				
Sulfate Conc. (μeq L^{-1})				
Year 0	114.3	54.7 - 249.3	35.3	12.0 - 85.5
Year 20	106.0	50.8 - 211.7	62.3	17.2 - 134.0
Year 50	106.0	50.8 - 209.6	89.6	31.0 - 153.9
Year 100	106.0	50.8 - 209.6	103.1	65.7 - 184.4
Year 140	------	--------	103.6	69.5 - 189.8
Percent Sulfur Retention				
Year 0	-7.9	-19.3 - -1.3	69.1	21.0 - 83.8
Year 20	-0.1	-1.1 - 0.1	42.8	3.2 - 81.9
Year 50	>-0.1	-0.2 - 0.1	9.6	<0.1 - 67.4
Year 100	>-0.1	>-0.1 - 0.1	0.6	<0.1 - 30.8
Year 140	-----	-----	0.1	<0.1 - 10.0
Delta Sulfate (μeq L^{-1} yr^{-1})				
Year 0-20	-6.8	-37.6 - -0.7	23.6	5.2 - 48.4
Year 0-50	-6.8	-39.7 - -0.7	43.8	14.6 - 93.2
Year 0-100	-6.8	-39.7 - -0.7	67.0	14.7 - 149.1
Year 0-140	----	------ ------	71.3	14.7 - 154.5

adsorption and desorption are the only processes influencing watershed sulfur retention. Finally, readers should be cognizant of the complexity in the relationships among sulfate, base cations, and ANC, which are influenced by several processes. The timing and magnitude of changes in ANC need not be directly correlated with changes in sulfate. In particular, time to steady state for sulfate should not be equated to time to zero (or to any other threshold value) ANC.

9.2.6 Conclusions

Watersheds in the northeastern United States can be characterized as direct response systems in terms of sulfate dynamics mediated by sorption in soils. Northeastern watersheds are near sulfur steady state and are projected to respond quickly to changes in sulfur deposition.

- In the base year (1984), median measured percent sulfur retention was -3.1 percent for LTA deposition, 0 percent for TY deposition data.

- Modelled percent sulfur retention for the base year was slightly negative for both LTA and TY data, -7.1 and -6.8 percent, respectively.

- If deposition continues at current levels, all northeastern watersheds are projected to be within 5 percent of steady state in less than 10 years. Median sulfur concentrations will decrease to within one percent (2 μeq L^{-1}) of steady state in 20 years.

- At current deposition, changes in median sulfate concentration as watersheds reach steady state will be small (7 μeq L^{-1}) with a maximum of 40 μeq L^{-1} (for LTA deposition); for TY deposition, median and maximum projected changes in sulfate are 7 and 43 μeq L^{-1}, respectively. Changes will have little impact on overall water chemistry of most lakes in the region.

- If deposition is decreased 30 percent, the magnitude of changes would be much greater, with a decrease in median sulfate of 39 or 40 μeq L^{-1} (LTA and TY deposition, respectively). Maximum projected decreases are 103 and 115 μeq L^{-1} for the two deposition datasets.

- Projected response of northeastern lake sulfate concentrations to future changes in deposition, such as the ramped deposition decrease, are rapid; model forecasts predict all watersheds to be within 5 percent of steady-state sulfate concentrations within 15 years after the end of the deposition decrease.

- Based on the rapid projected response of northeastern watersheds, sulfate adsorption has played a minor role in the delay of surface water acidification in the NE.

- Large deviations from sulfur steady state observed for a few watersheds in the base year cannot be attributed to sorption. Alternative explanations include uncertainties in sulfate input/output budgets, internal watershed sulfur sources, and watershed retention processes, principally sulfate reduction in wetlands and lakes.

Watersheds in the Southern Blue Ridge Province should be characterized as delayed response systems. Sulfate adsorption by soils has minimized the effects of acidic deposition on surface water chemistry in the region. Sulfate concentrations in SBRP watersheds are projected to increase significantly in the next 20 to 50 years, however, as the adsorption capacity of soils is exhausted.

- Median measured sulfate retention in SBRP watersheds for the 1985 base year was 74.9 percent for LTA deposition, 78.2 percent for TY deposition data. The percent retention varies from 24 to 86 percent for LTA deposition.

- Median modelled retention for the base year is also high: 69.1 and 68.4 percent for LTA and TY deposition datasets, respectively. The range of modelled percent retention for LTA deposition was 21 to 84 percent.

- Time to steady state at current deposition varies from 16 to more than 150 years; median projected time is 61 years. At 20, 50, 100, and 140 years from the base year, projected median percent sulfur retention is 43, 9.6, 0.6, and 0.1 percent. Maximum projected retention for the same periods is 82, 67, 31, and 10 percent.

- As soils in SBRP watersheds reach steady state, average sulfate concentrations in watershed runoff will increase roughly threefold. The median sulfate concentration is projected to increase from 35 μeq L^{-1} to 62, 90, 103, and 104 μeq L^{-1} at 20, 50, 100, and 140 years. Maximum projected increases for sulfate for the same periods are 48, 93, 149, and 155 μeq L^{-1}.

- For the 20 percent increase in deposition in the SBRP, times to steady state increase by up to 20 years for the watersheds with short retention times, but are almost unchanged for most watersheds. The increase in deposition has almost no effect on projected sulfate concentrations at year 20, but results in significant increases in delta sulfate at later years compared to the constant deposition scenario. Projected increases in median sulfate concentration for the increased deposition scenario at years 50, 100, and 140 are 58, 85, and 95 μeq L^{-1}; maximum projected increases are 114, 187, and 193 μeq L^{-1}.

- Model projections indicate that adsorption of sulfate by soils has played a major role in delaying potential adverse effects of sulfur deposition on surface waters in the SBRP. Most SBRP watersheds will not reach sulfate steady state for several decades, but significant increases in sulfate concentration are projected for the next 20 to 50 years.

- The large increases in sulfate concentration projected for the next 20 to 50 years will have major implications for overall surface water chemistry and are likely to accelerate base cation leaching from soils.

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9.3 EFFECT OF CATION EXCHANGE AND WEATHERING ON SYSTEM RESPONSE

9.3.1 Introduction

During the development of the NAS panel report (NAS, 1984), much discussion was devoted to the role of cation exchange and mineral weathering in "protecting" watersheds from acidification. One group of panel members argued that cation exchange in most watersheds has a large capacity to buffer against potential changes caused by acidic deposition. Therefore, they argued, if cation exchange is an important process within a specific watershed, then the future effects of acidic deposition are probably not a concern. Another group of panel members argued that the buffering capacity of soils was finite, and that continued exposure to current levels of acidic deposition would have long-term, adverse effects on water quality in some systems. The conclusion of the committee as a whole was that the role of cation exchange in buffering against the effects of acidic deposition is an area of considerable uncertainty, and that these processes need to be considered when attempting to project future effects of acidic deposition on aquatic ecosystems.

Toward this goal, the Level II base cation studies were designed to determine the role of base cation exchange in controlling future changes in surface water chemical composition. The specific objectives were to

- identify the role that base cation exchange has in determining current surface water composition;

- determine the capacity of base cation exchange processes to buffer against future changes in surface water composition as a result of acidic deposition; and

- make projections regarding the magnitude and extent of changes that could occur in regionally representative soils and surface waters as a result of continued exposure to acidic deposition.

Background information concerning weathering and base cation exchange processes is presented in Section 3.4. Given the objectives stated above and relying on our current understanding of the processes presented in Section 3.4, a number of hypotheses were developed that were used to guide the investigations of the role of cation supply processes in regulating surface water chemistry in representative watersheds in the DDRP study regions.

9.3.1.1 Level II Hypotheses

Five hypotheses guided the investigations in the Level II analyses:

(1)   Cation exchange processes determine surface water composition.

(2)   Soils delay surface water acidification.

(3)   Increased deposition induces net cation leaching.

(4)   Cation resupply rate is slow.

(5)   Soil chemistry is an indicator of soil response to acidic deposition.

It was not possible in all cases to test the hypotheses with the survey data collected for the Project. For example, testing of the fourth hypothesis requires time series data, the collection of which was beyond the scope of the DDRP. As a result, this hypothesis was treated as a "system-level" assumption for the analyses, the implications of which are discussed below.

9.3.1.1.1 Cation exchange processes determine surface water composition -

The first hypothesis, that cation exchange processes regulate observed surface water composition, is designed to identify the primary process or processes that regulate surface water chemistry. In systems that have attained steady state with respect to sulfate deposition (see Sections 7 and 9.2), primary mineral weathering and biological uptake are probably the principal processes that modify the composition of incident deposition. (Under steady-state conditions, the base cation exchange pool should actively reflect the dynamic balance between these two important processes.) Regardless of their relative importance, however, if soils are the media that regulate surface water ANC values, then this should be reflected by the composition and chemical properties of the soil exchange complex.

The hypothesis is tested by comparing surface water composition projected using soil cation exchange models with observed values. A close correspondence between the observed and projected values suggests that soil exchange processes have a major role in regulating surface water chemistry. Major discrepancies between observed and projected values would provide information regarding alternative controlling processes. For example, if the outputs from the soil models suggest that soils are strong hydrogen ion buffers, i.e., if the aggregated model results fall into narrow ranges of pH and ANC, this would suggest that other processes, such as primary mineral weathering, are serving as major sources (or, for cation accretion into biomass, sinks) for base cations in the population of watersheds being studied. Examining this hypothesis, therefore, provides bounds for arguments regarding which processes are primarily involved in regulating observed surface water composition.

9.3.1.1.2 Soils delay surface water acidification -

The second major hypothesis is that soils will delay, but not prevent, the acidification of surface waters. The concept behind this hypothesis is that soils have a finite capacity to buffer against changes in surface water chemistry caused by increased levels of acidic deposition. In essence, the chemical and physical characteristics of a soil reflect a soil's response to some given set of environmental conditions. Therefore, at a given level of deposition, vegetative uptake, mineral weathering, etc., the cation exchange pool reflects a balance of the various sources and sinks for cations in that area. This balance is dynamic, changing seasonally and with the shifting flow of cations among the various reservoirs.

When a perturbation such as acidic deposition is imposed on a system, the system (in this case the soil) evolves toward a new state of balance. The rate at which changes take place depends both on the sizes of the cation reservoirs in the system and on the flux of material between reservoirs. If the transfer rates of material between reservoirs is slow, or if the mass of material in the affected reservoirs

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is large relative to the transfer rates, then rates of evolution toward the new balance point tend to be slow. Conversely, if reservoirs are small relative to the size of the flux between reservoirs, then adjustments to a new system state can occur rapidly.

We contend, with this hypothesis, that the pool of base cations on soil exchange complexes is large relative to the rate of cation loss from the system by leaching. As a result, the rate of adjustment of the exchange complex to the new deposition conditions should require years to decades before a new steady-state, or dynamic balance, condition is attained.

To test the hypothesis, a model approach is used. Measured soil properties serve as inputs to the various models. The Level II models, all of which have a mass balance component, track the loss of base cations from soils at the specified levels of deposition. The models are primarily concerned with exchange processes and do not explicitly include cation supply via weathering. Therefore, the computed mass balances should correspond to the maximum leaching rates that could occur. The rate of change of base cation status of the soils included in the study, then, should be related to the amount of time over which the soils should delay acidification of surface waters.

9.3.1.1.3 Increased deposition induces net cation leaching -

The third major hypothesis is that increased levels of deposition, specifically increased concentrations of sulfate and nitrate in deposition, increase the rate of cation leaching from the soil exchange complex by way of the mobile anion effect (Johnson et al., 1980; Seip, 1980). Two factors are considered when evaluating this hypothesis. First, the average base status of the soil exchange complex represents a balance among the various supply and demand processes in the ecosystem. For example, under steady-state conditions, weathering should supply sufficient base cations to meet the demands of vegetative uptake while maintaining soil solution concentrations in equilibrium with the soil exchange complex. Perturbations to the system, such as changed deposition, will alter this steady-state condition.

Second, charge balance requirements need to be maintained between the soil exchange complex and soil solutions. Maintaining charge balance, coupled with the increased anion loads provided by acidic deposition, requires that total (acid plus base) cation concentrations in soil solutions increase. The ratio of the base to acid cations will not change dramatically, however, at least during the initial stages of leaching. The higher concentrations of base cations in soil solutions lead to a net depletion of base cations from the exchange complex. If this increased leaching is not matched by an increased level of supply (e.g., from weathering), then the overall effect will be a net depletion of the base cations from the exchange complex.

We have tested this hypothesis using a modelling approach. As for the second hypothesis, model runs are conducted that enable the determination of whether the increased anion concentrations in deposition will, indeed, result in an increased rate of leaching of the base cations. The mass balance computations, in combination with the equilibrium mass action descriptions of the system, should permit an unequivocal evaluation of this concept.

9.3.1.1.4 Cation resupply is slow -

The fourth hypothesis, that the rates of cation resupply to the soil exchange complex are slow relative to the rates of base cation stripping, is not being tested directly in this study. Rather, the hypothesis is being subsumed in the models as an assumption, or, more accurately, the assumption is that exchange reactions provide sufficient buffering such that resupply rates are not an issue for the time scales of concern to the study.

One reason for using this approach is that, with current technology, no definitive method exists for distinguishing the different sources of base cations to surface waters. Therefore, by assuming that all base cations are derived from exchange sites, the modelling yields, effectively, "worst case" scenarios for the depletion of the soil buffering capacity. If, under these circumstances, the results suggest an extensive capacity of the soil to buffer against the effects of acidic deposition, then the resupply rate is not an issue of importance in this study.

9.3.1.1.5 Soil chemistry as indicators of soil response to acidic deposition -

The final hypothesis is intended to provide the groundwork to use selected soil properties as qualitative indices of soil "health" and the expected response to acidic deposition. Recently, several attempts have been made to correlate soil properties with their anticipated response to acidic deposition (vanLoon, 1984; Stuanes, 1984; Lau and Mainwaring, 1985). Results from these studies suggest that soil properties are useful indicators of how soils will respond to continued exposure to present or anticipated levels of acidic deposition.

The hypothesis is being tested using two approaches. First, the results from the Level I statistical analyses (see Section 8.8.4) have been presented. These results suggest significant relationships between present day soil properties and observed surface water chemistry. These observations support the contention of the relationship between basic soil properties and the response of the system to acidic deposition. Second, as part of the Level II modelling activities, relationships will be examined between current soil properties and the magnitude of projected changes in soil and surface water composition. While these results will not integrate the roles of multiple processes, e.g., weathering and ion exchange, they should provide some additional evidence for examining the hypothesis.

9.3.1.2 Approach

As previously discussed (see Section 9.1), the approach used for Level II base cation analyses is model-based. The primary processes believed to regulate exchange processes are known, and models have been developed that describe these processes in internally consistent manners. As such, existing model formulations are used extensively in conducting these studies.

Data used in running the models were collected specifically for this study. Section 5 provides details of the type, quantity, and level of information gathered. In collating the data for use in the models, certain decisions were made regarding how data from individual soils and watersheds would be condensed, or aggregated, for use in the models. Because the primary goal of the DDRP is to make regionally representative projections about future changes in surface water chemistry as a direct result

of acidic deposition, a decision was made to aggregate the data, first into groups of soil with similar chemical and physical characteristics and, then, to the watershed level.

Because this aggregation approach was used, projections regarding individual watersheds will not, necessarily, be accurate reflections of the chemistry observed in that watershed. On a population basis, however, the models should provide useful information about the anticipated behavior of the soils in the DDRP study regions. Details regarding the soil aggregation procedures are outlined below (Section 9.3.1.2.2).

Finally, the rationale used to define the time scales over which simulations were executed is presented. Model projections are inherently uncertain. As the durations of simulations increase, the associated overall uncertainty increases. Therefore, there are practical limits to the usefulness of long time frame projections. Section 9.3.1.2.3 provides a brief discussion about the trade-offs between uncertainty and information gained.

9.3.1.2.1 Off-the-shelf models -

In designing the Level II base cation studies, one of the issues considered was the selection of models. As discussed in Section 2, a decision was made during the planning stages of the DDRP to use only published, peer-reviewed, and publicly available models. A primary advantage of this decision was that the data requirements for these models were known, so the field programs could be developed to collect the appropriate data required. A second advantage was that minor modifications or improvements could be incorporated into the model codes in a timely manner. Because of concerns relative to field design issues, and because the report from the NAS (NAS, 1984) indicated that models describing the major soil processes controlling base cation dynamics were available, only published and publicly available models were selected for application in the Level II base cation studies. The selected models are described in Reuss (1983), Reuss and Johnson (1985), and Bloom and Grigal (1985) (see Section 9.3.2).

9.3.1.2.2 Aggregated soil chemistry data -

Having selected models for use in the Level II Analyses, the next major issue was preparation of data for use in the models. Soil physical and chemical data were gathered on a representative sampling of soils in the NE and SBRP (Section 5.5.1). These data were obtained from individual pedons and soil horizons. To transform these data into a form usable by the models, the data were aggregated to produce information that was representative of whole watersheds.

Details of the aggregation procedures were presented by Johnson et al. (1988b). Briefly, the steps taken to produce the aggregated data depend on the structure of the model to be applied. In general, data are first averaged within the master horizons (i.e., O, A/E, B or C horizons) of individual soil sampling classes. Then, if required by the models (e.g., those that describe the soil as a single "box"), results from the master horizons are averaged to yield values of parameters representative of the sampling class as a whole. The procedures used to average soil chemical and physical properties at the horizon and sampling class levels varied slightly in accordance with the model for which the data were being developed. For models that use capacity variables as inputs, e.g., the Bloom-Grigal model, soil properties

were averaged using mass weighting procedures. For models using intensity variables as inputs, an intensity weighting scheme (Johnson et al., 1988b) was developed that preferentially weighted the lowest subhorizon in generating values for master horizons, and then employed straight numerical averages to produce sample class/pedon data.

Finally, data from individual sampling classes were averaged, using areal weighting, to produce soils data representative of the watershed as a whole. The weighting used in this last aggregation step was strictly related to the relative occurrence of the sampling class on a particular watershed. The weighting precludes bias based on the location of the soil on a watershed. For example, although it might be argued that riparian soils have a greater influence on the composition of surface waters than do ridge-crest soils, riparian zone soils and those soils immediately adjacent to the lakes are not preferentially weighted relative to upland soils. The decision to use the uniform weighting approach was based primarily on the difficulty of developing uniform, broadly based algorithms to apply preferential weighting to specific soils based on geomorphic considerations.

9.3.1.2.3 Scale of temporal forecasts -

Another decision to be made in implementing the Level II Analyses was the time scale over which to run the model simulations. In the near term, dramatic, permanent changes to surface water composition are not expected to occur on annual time scales. Acidic deposition is a phenomenon that has probably affected eastern North America for at least several decades. Rapid responses to changing deposition, if they were to occur, have probably already taken place.

For long time scale projections, the major factor determining the duration of simulations to be run is the uncertainty associated with the major parts of the modelling efforts. As soil composition and properties evolve with continued exposure to acidic deposition, the response of these soils is also expected to change. We anticipate that, for longer time scales, projected changes will become more dramatic. However, the larger changes are balanced by the increases in the uncertainty of the analyses for periods exceeding, e.g., 50 years.

Using these procedures as guidelines for bounding the time intervals to be modelled, simulations for 20, 50, and 100 years were selected for the NE Region. For the SBRP, simulations for 20, 50, 100, and 200 years were selected. The 20- and 50-year projections provide information about relatively near-term changes that might be anticipated and are relevant time frames with regard to the implementation of regulatory controls.

The 100- and 200-year projections are included as "worst-case" results. Such projections will allow policymakers to understand the magnitude of changes that could occur. The 200-year simulations are included for the SBRP primarily because major changes to sulfate mobility in soils in this region are expected to occur during the next century (see Section 9.2). By extending the model simulations for an additional 100 years, the full effect of changes in mobile anion concentrations will become evident. Inasmuch as the NE is, essentially, at steady state with regard to sulfur deposition (see Section 7), this additional time is not required.

9.3.2 Descriptions of Models

The model originally selected to conduct the base cation analyses was one developed by Reuss (1983) and Reuss and Johnson (1985). This model uses a mass action approach to modelling soil exchange processes. As such, the model requires a broad range of data as input, which was incorporated into the design of the field program for the Project. An additional factor in the selection of the Reuss model for use in the Level II Analyses was the fact that its data requirements are compatible with those of some of the Level III models to be used in the study.

In addition to the Reuss model, one other model was incorporated into the Level II base cation studies, a model developed by Bloom and Grigal (1985). This model describes soil exchange processes based on observed relationships between the cation exchange pool and soil pH. This model, therefore, not only expands the model base from which the Level II Analyses are conducted, but also provides an alternative approach for describing soil exchange reactions.

9.3.2.1 Reuss Model

9.3.2.1.1 Model description -

The Reuss model was originally developed by Reuss (1983) and coworkers (Reuss and Johnson, 1985; Johnson and Reuss, 1985). The model is an equilibrium-based, mass balance model in which the solubility of a gibbsite-like phase is assumed to control the concentration of aluminum. Subsequently, exchange reactions are used to partition the cations Al^{3+}, Ca^{2+}, Mg^{2+}, Na^+ and K^+ between the solid and solution phases. Figure 9-22 presents schematically the processes considered in the model. The model computes soil pH, soil solution ANC, and base cation and dissolved aluminum concentrations. The model then "re-equilibrates" soil solutions with atmospheric carbon dioxide and computes surface water composition.

Reuss's approach has several advantages for modelling exchange reactions in soil environments over the use of simple exchange reactions. First, the charge balance requirement of the code makes the model responsive to ionic strength. In forested soils, composition of the soil solutions have been shown to depend on ionic strength (Richter et al., 1988). Therefore, this aspect of the model permits a more realistic simulation of natural exchange reactions than do the less involved computations. Second, the model allows the user to specify the partial pressure of carbon dioxide (pCO_2) in the soil gas. Although the pCO_2 in forested soils rarely exceeds about 1 percent (Fernandez and Kosian, 1987; Solomon and Cerling, 1987), these levels can be high enough to significantly affect soil solution composition (Reuss and Johnson, 1985, 1986). Third, by relying on a gibbsite-like phase to regulate aluminum activities, one degree of freedom in the solution composition is effectively constrained. Finally, the mass balance constraints allows the user to track cation depletion from the exchange complex as a function of time, hydrogen ion loading, and the imposed physicochemical environment.

The Reuss model focuses on soil exchange reactions. The model does not consider other cation source/sink processes such as mineral weathering, nitrogen transformations, or afforestation, even though these processes may have equal or greater influence in regulating surface water composition in certain ecological settings. Models have been developed that include these processes, and thus yield an
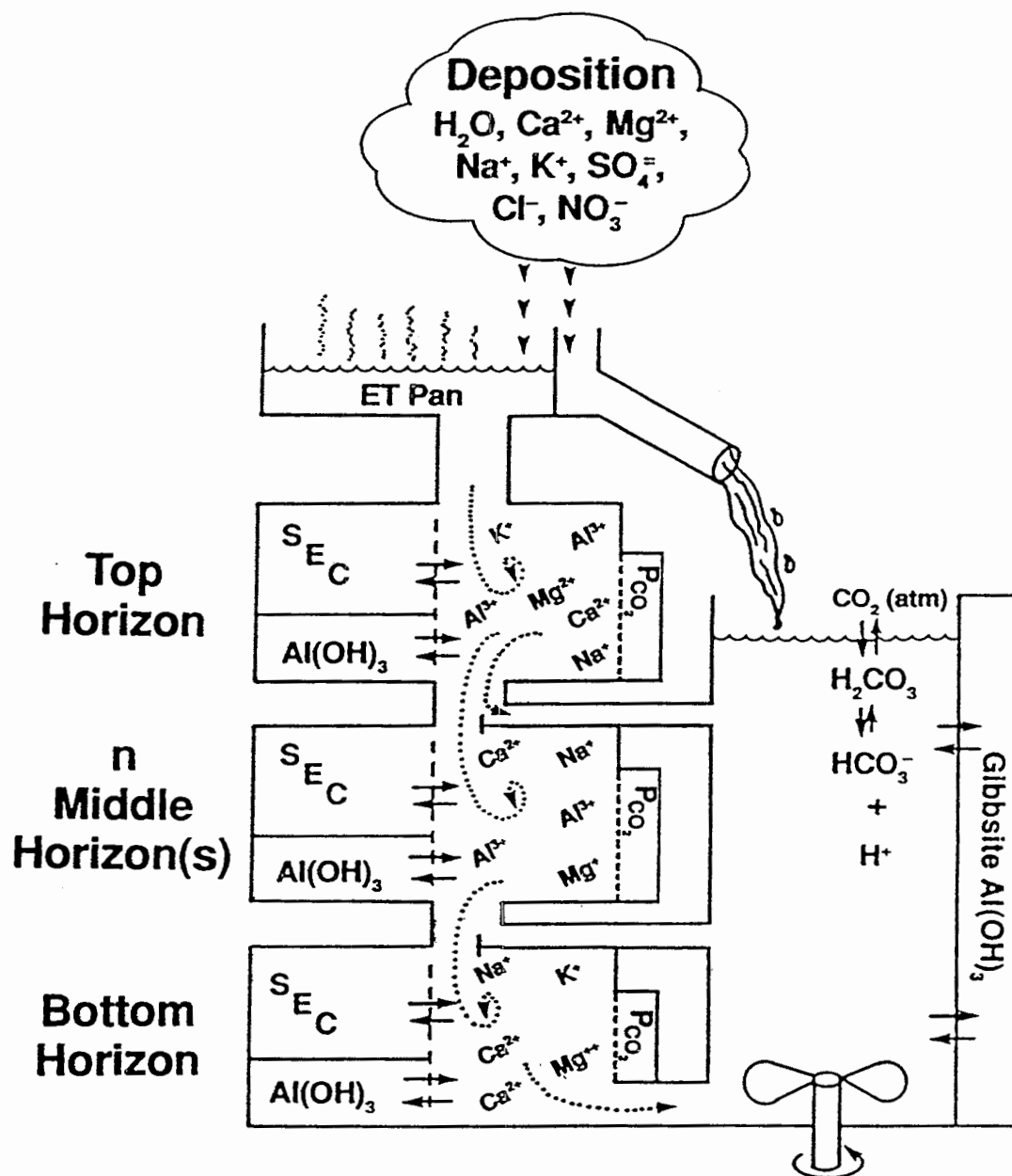
Figure 9-22. Schematic diagram of the principal process involved in the cycling of base cations in surficial environments. Arrows indicate the major pathways through which ions are interchanged among the reservoirs. No attempt is made to distinguish the relative fluxes among the different reservoirs. The heavier lines, however, indicate those processes that serve as the focus of the Level II modelling efforts presented here.

integrated system response (Cosby et al., 1985a,c, 1986a,b; Gherini et al., 1985; Galloway et al., 1983a; Nikolaidis et al., 1988) to the imposed deposition. These integrated models, however, cannot be used effectively to understand the contributions of individual processes, such as soil cation exchange, to the buffering responses of watersheds.

9.3.2.1.2 Model Formulation -

The original versions of Reuss's code were written in BASIC. Table 9-9 lists the chemical species, principal reactions, and related chemical definitions used in developing the computer code. The original versions were written for a one-horizon setting in which the water flux, rather than time increment, was used in scaling the step sizes for time-series simulations. Reuss's codes also ignored ammonium inputs to soils, thus effectively using H^+ as the surrogate for NH_4^+ deposition. In incorporating the Reuss model into the DDRP, a number of modifications were made.

The model was adapted for this study by recoding in FORTRAN, which enabled greater execution speeds and, thus, an ability to handle more simulations. The formats of the input and output datasets were revised to better accommodate the needs of this study. In recoding the model, a number of operational changes were implemented. For example, the data of May et al. (1979) instead of those employed by Reuss and Johnson (1985) were selected to describe aluminum speciation. In addition, the algorithms used to partition ions between solution and the solid-phase exchangers were modified to provide more accurate mass action expressions for thin and low base saturation horizons. Given these changes, rigorous one-to-one comparisons of results obtained from the FORTRAN and BASIC versions of the model have not been possible, as the two models yield slightly different results. A more substantial modification to the code entailed the use of the Vanselow exchange formulation. In the original versions, the Reuss code employed the Gaines-Thomas formulation for cation exchange processes. Comparisons of three exchange formulations (Holdren et al., 1989), including the Gaines-Thomas, Vanselow, and Gapon models, suggested the Vanselow model provided results more representative of field data than the other two models. Differences among the three models, in general, were small, but significant.

The selectivity coefficients for the Vanselow formulation are based on a mass action expression of the form:

$$K_V = \frac{\{ N^{n+} \}^m \cdot [X_M]^n}{\{ M^{m+} \}^n \cdot [X_N]^m} \qquad \text{(Equation 9-5)}$$

where $[X_M]$ and $[X_N]$ are the mole fractions of the solid species indicated, m and n are the appropriate stoichiometric coefficients; the species enclosed in the braces {i} indicate activity of the ith aqueous species. The specific mass action expressions for the exchange reactions considered are listed in Table 9-9.

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Table 9-9. List of the Chemical Species and Reactions Considered Within the Reuss Model Framework

Aqueous Species: H^+, OH^-, Na^+, K^+, NH_4^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_4^-$

Solid Phases:[a] $Al(OH)_3$, Exch-Al, Exch-Ca, Exch-Mg, Exch-Na, and Exch-K

Mass Action Equations:

$$K_W = \{H^+\}\{OH^-\}$$

$$K_C = \{H^+\}\{HCO_3^-\}/(pCO_2)$$

$$K_{sp}(gibb) = \{Al^{3+}\}/\{H^+\}^3$$

$$K_1^{Al} = \{Al(OH)^{2+}\}\{H^+\}/\{Al^{3+}\}$$

$$K_2^{Al} = \{Al(OH)_2^+\}\{H^+\}^2/\{Al^{3+}\}$$

$$K_4^{Al} = \{Al(OH)_4^-\}\{H^+\}^4/\{Al^{3+}\}$$

$$K_{ex}^{c-a} = \{Ca^{2+}\}^3[X-Al]^2/\{Al^{3+}\}^2[X-Ca]^3$$

$$K_{ex}^{c-m} = \{Ca^{2+}\}[X-Mg]/\{Mg^{2+}\}[X-Ca]$$

$$K_{ex}^{c-n} = \{Ca^{2+}\}[E-Na]^2/\{Na^+\}^2[X-Ca]$$

$$K_{ex}^{c-k} = \{Ca^{2+}\}[E-K]^2/\{K^+\}^2[X-Ca]$$

Charge Balance Equation:

$$H^+ + Na^+ + K^+ + NH_4^+ + Al(OH)_2^+ + 2.0*(Ca^{2+} + Mg^{2+} + Al(OH)^{2+}) + 3.0* Al^{3+} =$$

$$OH^- + HCO_3^- + Cl^- + NO_3^- + Al(OH)_4^- + 2.0 * SO_4^{2-}$$

ANC or Alkalinity:

$$ANC = (OH^-) + (HCO_3^-) + (Al(OH)_4^-) - (H^+) - (Al(OH)_2^+) - 2*(Al(OH)^{2+}) - 3*(Al^{3+})$$

or

$$ANC = (Na^+) + (K^+) + (NH_4^+) + 2*[(Ca^{2+}) + (Mg^{2+})] - (Cl^-) - (NO_3^-) - 2*(SO_4^=)$$

---

[a]
   Exch - Al = Exchangeable aluminum
   Exch - Ca = Exchangeable calcium
   Exch - Mg = Exchangeable magnesium
   Exch - Na = Exchangeable sodium
   Exch - K = Exchangeable potassium

Other modifications to the code were also incorporated. The model was expanded to allow inclusion of up to four horizons. With this expansion, a provision was made to allow the user to route soil water from any horizon directly to surface water. This "routed water" is assumed to not be equilibrated with soils deeper in the pedon. Rather, it is "mixed" on a volume-weighted basis with waters derived from other horizons plus all water draining from the bottom of the pedon. New pH values and aluminum concentrations are then computed for the "surface water" assuming equilibration with atmospheric pCO_2.

Three options were incorporated into our version of the model regarding the treatment of input nitrogen chemistry. In the original versions of the model ammonium in deposition was ignored, and H^+ effectively served as a surrogate for NH_4^+. This treatment was retained as one option in our code. The second option (used in all model runs for this report) was based on the presumed reaction:

$$NO_3^- + NH_4^+ = \text{org-N} \qquad \text{(Equation 9-6)}$$

in which the two nitrogen species are accreted into the organic nitrogen pool on an equivalent basis. If nitrate concentrations exceed ammonium concentrations in deposition, then the excess nitrate is passed through the soil as a mobile anion. Conversely, if ammonium concentrations exceed nitrate in deposition, the excess ammonium is presumed to be replaced by H^+. The third option is based on the reaction:

$$3\ NO_3^- + 5\ NH_4^+ = 4\ N_2(g) + 9\ H_2O + 2\ H^+ \qquad \text{(Equation 9-7)}$$
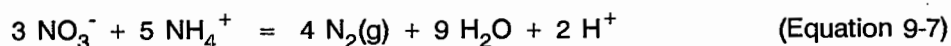
in which nitrate and ammonium combine to form nitrogen gas, water, and hydrogen ion. This process originally was conceived to occur if the organic nitrogen pool attained steady state. As with the second option, excess nitrate is passed on to the soil as a mobile anion, or the excess ammonium is presumed to be replaced by H^+.

These options are not sufficiently comprehensive for modelling of nitrogen species distributions or concentrations in surface waters. As previously indicated, the purpose of the Reuss model is to examine soil exchange phenomena with regard to the effects of acidic deposition, and not to provide detailed information concerning the effects of nitrogen transformations in the soil environment. The different routines, however, provide the user with some degree of flexibility in the treatment of nitrogen transformations.

Finally, the time series computations were converted from deposition volume-controlled increments to time related steps, largely as a matter of convenience for dealing with units and to facilitate use of the model by others.

9.3.2.1.3 Assumptions -

As with any model, assumptions are necessary regarding certain processes, the soil environment, and the characteristics of certain reactions. These assumptions and their justifications are outlined below, along with an assessment of the effect they have on model predictions.

9.3.2.1.3.1 Gibbsite solubility controlling soil Al^{3+} concentrations --

One of the main features of Reuss's model is that the solubility of a gibbsite-like [$Al(OH)_3$] phase controls the concentrations of dissolved aluminum in soil solutions. Objections have been raised to this assumption on several grounds. First, in many acidic forest soils, gibbsite is probably not present as a separate or distinct phase, and thus cannot regulate concentration of an aqueous species. Second, investigators have noted that aluminum activities, $\{Al^{3+}\}$, in forest soil solutions do not behave according to classic gibbsite solubility dynamics in response to changing H^+ activities (Johnson, 1986; Bloom et al., 1979a,b). Theoretically, aluminum activities should decrease by three orders of magnitude for each unit increase in pH, i.e.,

$$\log_{10} \{Al^{3+}\} \quad = \quad C - 3 \text{ pH} \qquad \text{(Equation 9-8)}$$

where C is an arbitrary constant related to the solubility product of gibbsite. In the studies cited, however, aluminum activities appear to be independent of soil pH, or vary in ways different from the above relationship. A third concern focuses on the variability in aluminum solubility behavior observed in natural materials. In natural systems, gibbsite is expected to display a range of solubilities, based on the grain size, crystallinity of the parent material, and conditions under which it was formed. This issue is irrelevant in the context of the Reuss model, as apparent solubility products are computed on a sample-by-sample basis using field data to constrain the aluminum behavior.

Despite these concerns, the solubility of a gibbsite-like phase is assumed in the present analyses to control aluminum activities in soil solutions. Figure 9-23 shows pH vs. $\log_{10} \{Al^{3+}\}$ (both measured in 0.002 M $CaCl_2$) for all samples collected during the DDRP NE Soil Survey. The solid line indicates the theoretical solubility of gibbsite (C = 8.774; May et al., 1979). In computing the aluminum activities, only the hydroxide complexes of aluminum were included in the speciation model. Contributions from sulfate, fluoride, or organic ion pairs or complexes were not incorporated into the speciation model because data on the counter ion species were not available from the analytical solutions. The contributions of the sulfate, fluoride, and organic complexes to total dissolved aluminum concentrations increase with increasing pH, so, effectively, aluminum activities should be increasingly overestimated at successively higher pH values.

For soil samples with pH values greater than about 4.0, i.e., all B and C horizon samples, and about half of the A/E horizon samples, gibbsite solubility appears to provide a reasonable model of aluminum solubility. Regression of the data with pH values greater than 4.0 yields a slope of -1.4. For soils with pH values between 4 and 5, predicted aluminum activities are generally within an order of magnitude of measured values. Soils with higher pH values generally display high aluminum activities. These results are attributed to the inability to incorporate organic complexes of aluminum into the speciation model.

For soils with pH values less than 4.0, i.e., all O horizon soils and about half of the A/E horizons, aluminum activities appear to be independent of soil pH. This observation is interpreted as an indication that the mass of rapidly exchangeable aluminum available on soil exchange sites is limited. Most of the soil buffering is expected to be derived from mineral horizons. Given the behavior of soils illustrated in Figure 9-23, and considering the limitations of the aluminum speciation model used to estimate the
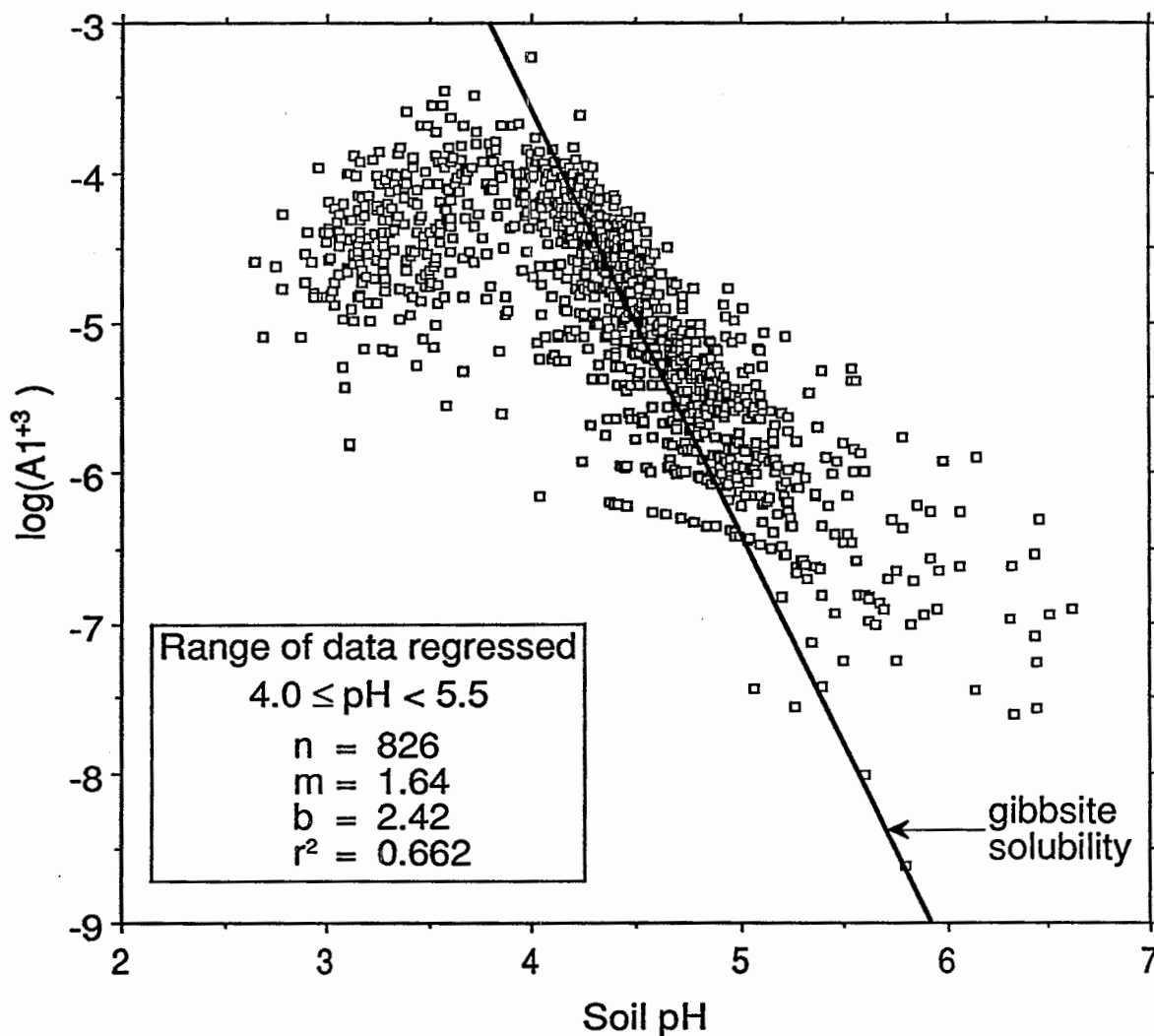
Figure 9-23. Plot of the log of the activity of Al^{3+} vs. soil solution pH for individual soil samples collected for DDRP. Both parameters were measured in a 1:2.5 soil:solution suspension of 0.002 M $CaCl_2$. The cluster of points at pH < 3.9 are O and organic-rich A horizons and do not follow a gibbsite-like mineral solubility behavior. The points on the right side of the graph suggest that solutions are highly oversaturated with respect to gibbsite. However, the speciation model used to estimate activities included only hydroxy complexes. Chloride, sulfate, fluoride, and organic complexes were not considered in these computations. As such, these points probably significantly overestimate actual (Al^{3+}) activities in these solutions.

aluminum activities indicated, the evidence supports the model of a gibbsite-like solubility behavior to describe aluminum availability in soils.

The use of the limited aqueous speciation model to compute aluminum activities potentially introduces one other problem. If aluminum activities are significantly overestimated, then selectivity coefficients computed using the artificially high values should similarly be too large. (The value is calculated as: $K_{ex}^{ac} = \{Al^{3+}\}^2 [X_{Ca}]/\{Ca^{2+}\}^3 [X_{Al}]$. This effect, however, partially compensates for an opposite effect, namely that induced by not considering rational activity coefficients for the solid-phase exchangers (see next subsection).

9.3.2.1.3.2 Constancy in selectivity coefficients as functions of base saturation --

As detailed in Section 9.3.2.1.2, the Reuss model describes exchange reactions using Vanselow-type mass action equations. The equations are developed and used based on data derived from the soils. This approach is reasonable as long as the changes in the base saturation of the soils under study are limited. Problems may be encountered, however, during time dependent simulations if significant changes in base saturation are projected to occur.

Problems may arise because selectivity coefficients are not true thermodynamic constants. As presently formulated, the selectivity coefficients do not incorporate rational activity coefficients for the solid-phase exchangers. Therefore, the selectivity coefficients are only approximately constant, and then only for narrow ranges of base saturation around those levels for which they were calculated. As base saturation declines, the selectivity coefficients would be expected to vary accordingly.

As an example of this behavior, Figure 9-24 illustrates the relationship between $\log_{10}(K_{ex}^{ac})$ (the selectivity coefficient for the Ca/Al exchange reaction) and base saturation for aggregated A/E horizon samples used in the watershed runs. For base saturations between 30 and 40 percent, selectivity coefficients average slightly more than 100. As base saturation decreases, selectivity coefficients increase such that for samples with base saturations between 10 and 12 percent the constants have average values of about 1000. As indicated, this change is a direct result of not having incorporated the rational activity coefficients into the expression for the solid-phase exchangers.

Obviously, the apparent change in the selectivity coefficients as a function of base saturation is of concern in terms of the model results. To determine what the effects of varying selectivity coefficients might be, a modelling experiment was undertaken in which the selectivity coefficients for the Ca/Al exchange reaction were both increased and decreased by an order of magnitude for each of the master horizons in the 145 watersheds. The model was run using these inputs, and the projected surface water ANC was determined. Results for the present-day ANC values are summarized in Figure 9-25.

Changing the selectivity coefficients by an order of magnitude introduces about a 10 μeq L^{-1} change in the projected ANC for any particular system. This change is small, as the predicted total base cation concentrations for most systems fall in the 100 to 200 μeq L^{-1} range. Therefore, errors introduced by having selectivity coefficients that are off by as much as an order of magnitude are approximately 5 to 10 percent. This change is small enough not to affect the long-term projection of depletion of buffering capacity significantly in most systems.
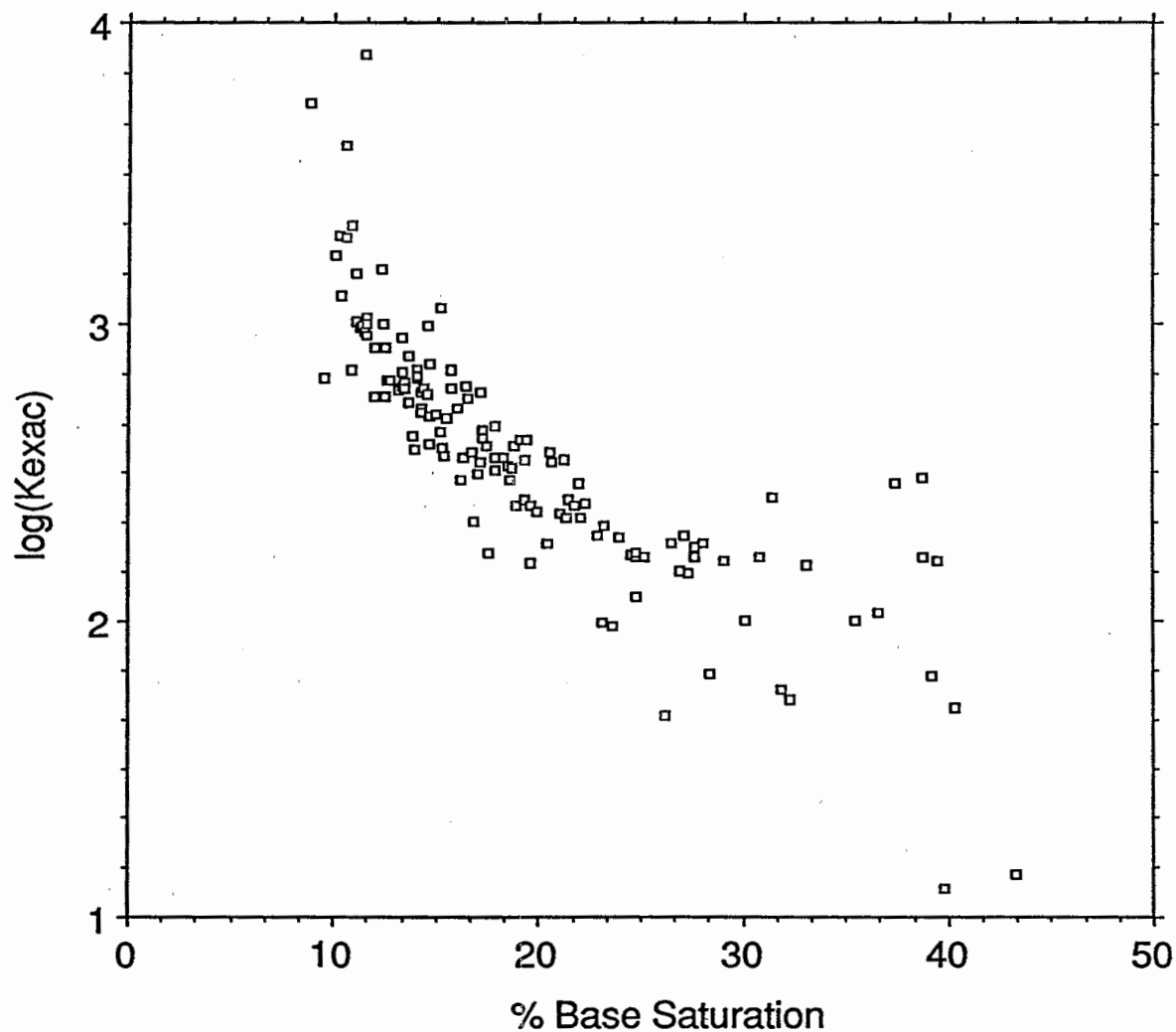
Figure 9-24. Plot of the log of the selectivity coefficient for the calcium-aluminum exchange reaction vs. the measured base saturation in A/E horizons in the NE. The increase in the selectivity coefficients with decreasing base saturation is a direct result of not incorporating rational activity coefficients into the mass action expression used to estimate selectivity coefficients.
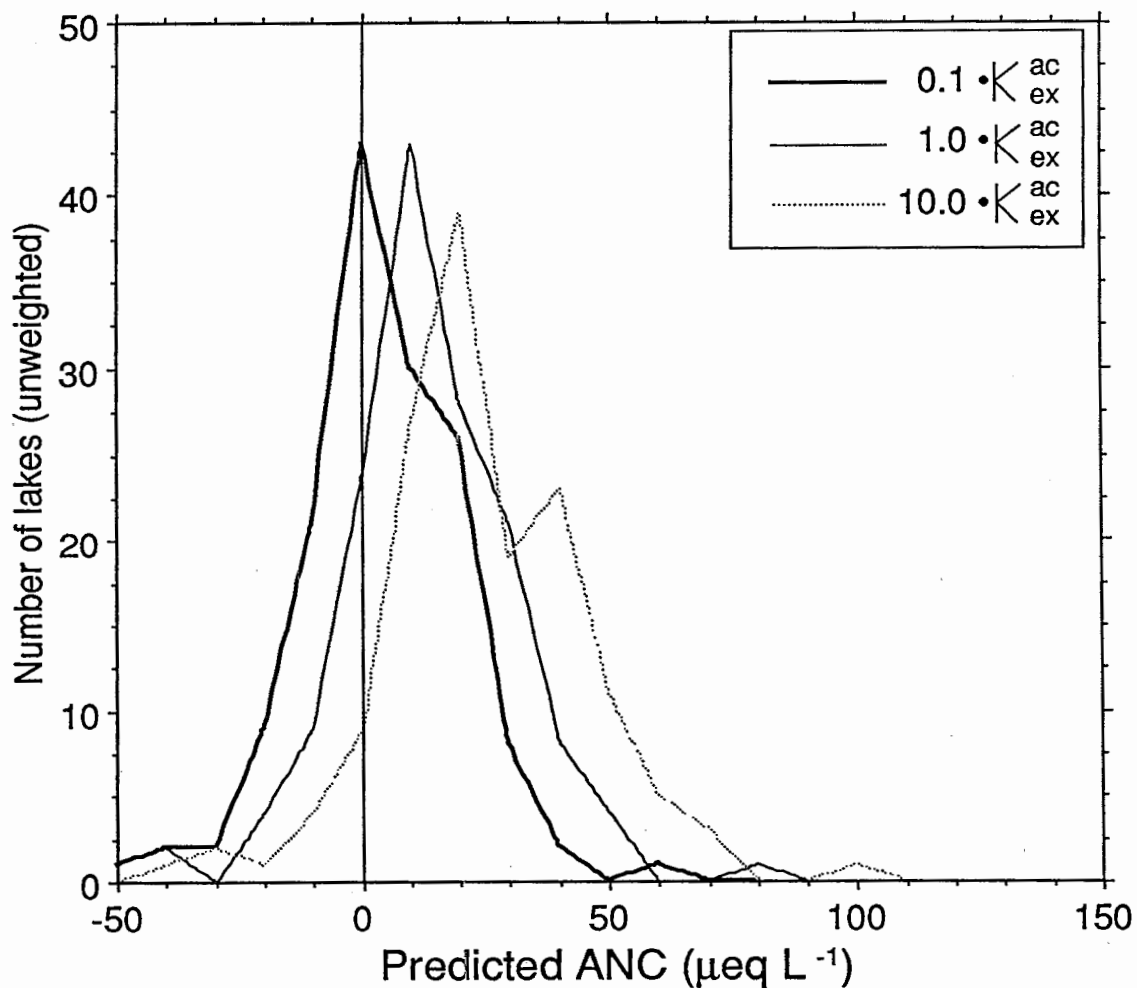
Figure 9-25. Histograms of the (unweighted for the population estimates) projected present-day ANC values for lakes in the NE. The three curves were generated by varying the selectivity coefficient for the calcium-aluminum exchange reaction by ± an order of magnitude from the value estimated from the soils data. Varying the selectivity coefficient by a factor of 10 changes the projected ANC values for any system by about 10 μeq L^{-1} for present-day conditions. This is not of sufficient magnitude to have a significant effect on the projected rates of depletion of buffering capacity for the vast majority of these systems.

9.3.2.1.3.3 Soil gas pCO_2 --

The last major assumption made in running the Reuss model was the selection of an average annual soil gas pCO_2. For the model runs reported here, the partial pressure of CO_2 for all horizons and all soil classes was assumed to be 0.005 atm on an average annual basis. Soil pCO_2 concentrations vary with a number of factors, including temperature, soil productivity, and moisture content. Unfortunately, there are not enough available data for the range of soils included in the DDRP to be able to model values accurately. Data that are available (Solomon and Cerling, 1987; Fernandez and Kosian, 1987; Lam et al., 1988) indicate soil gas CO_2 can exceed 0.5 percent, and in some soils at some times of the year, levels are less than 0.5 percent. A partial pressure of 0.005 atm was selected simply because it appears to be a representative value for forested soils, based on available data.

Reuss model outputs are responsive to increases in soil gas CO_2 concentrations. Figure 9-26 illustrates present-day surface water ANC values predicted using CO_2 concentrations of 0.001, 0.005, and 0.025 atm CO_2. As the partial pressure of CO_2 increases in the soil gas, the ANC of the associated surface water also increases. It is possible, therefore, to adjust predicted present day surface water ANC values up (or down) simply by adjusting the CO_2. In making these adjustments, however, there is a trade-off. By increasing soil gas CO_2 concentrations to increase the predicted ANC values, the rate of base cation leaching from the soil exchange complex is increased significantly. Therefore, the rate at which soil buffering capacity becomes depleted is also increased. This is illustrated in Table 9-10, where changes predicted for surface water ANC at 50 and 100 years are given for the three soil gas CO_2 scenarios.

Finally, it should be clarified that no attempt was made, in selecting the 0.005 atm value for pCO_2, to use this parameter to "calibrate" the Level II models. Admittedly, had the pCO_2 been adjusted on a watershed-by-watershed basis, a much better fit to observed soil pH values could have been obtained. However, the purpose of this part of the modelling exercise was to determine the magnitude of possible responses to acidic deposition. In the absence of more specific data on soil gas CO_2 levels in individual watersheds, the approach taken here yields the least controversial, and most widely applicable, results possible.

9.3.2.1.4 Limitations -

The Reuss model focuses on soil exchange reactions. The model does not consider other processes such as sulfate adsorption, mineral weathering, nitrogen transformations, or afforestation, even though these processes may have equal or greater influence in regulating surface water composition in certain ecological settings (Likens et al., 1977; Johnson et al., 1988b). The purpose of this part of the study, however, was specifically to examine exchange processes and their contribution in regulating surface water composition and buffering against changes caused by acidic deposition.

Most of the other model limitations were alluded to in Section 9.3.2.1.3. The most significant among these is that no provisions are made to consider organo-cations, and especially organo-aluminum interactions. The data are not available to include these interactions in our modelling efforts.
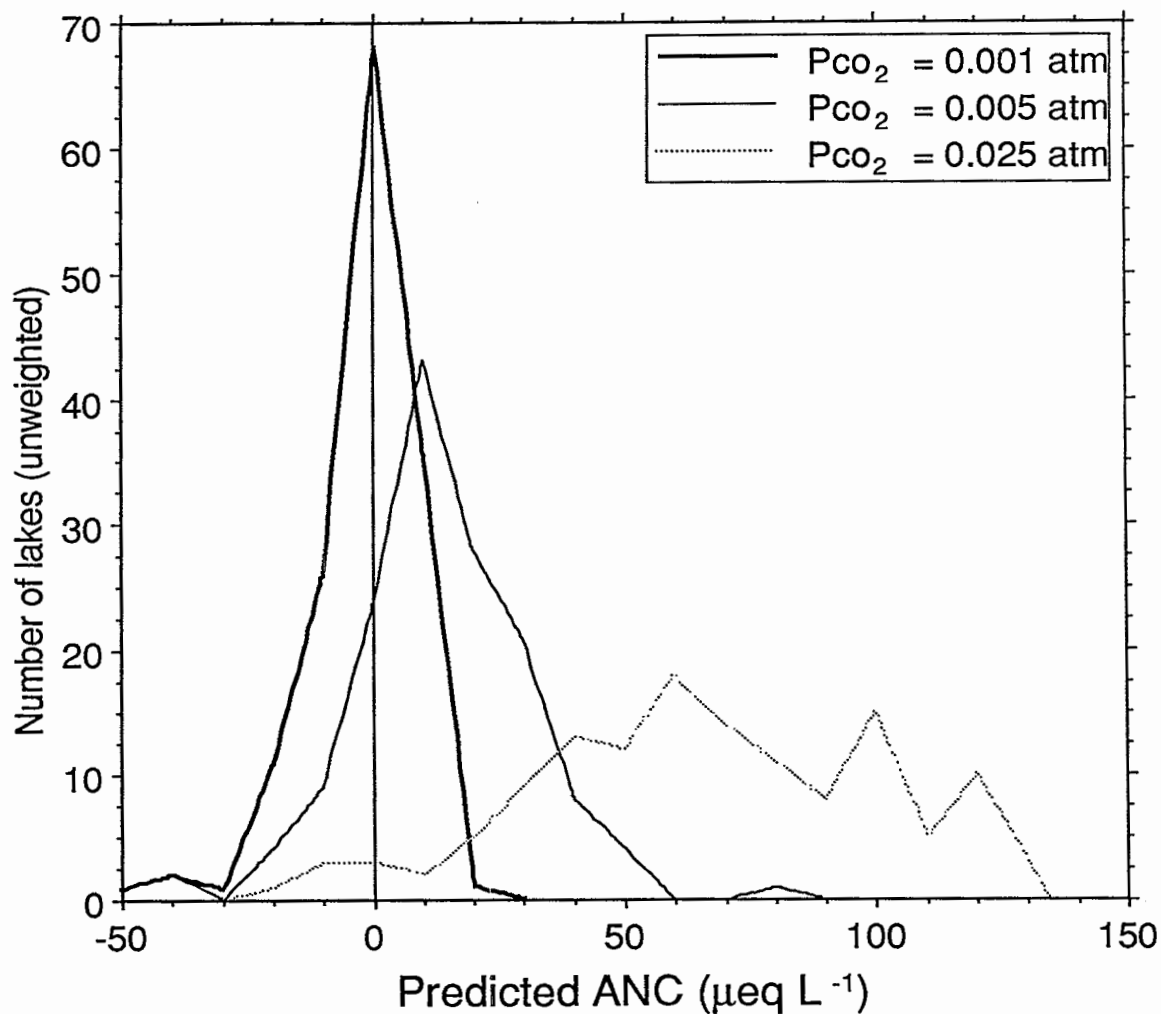
Figure 9-26.   Histograms of the (unweighted for the population estimates) projected, present-day ANC values for lakes in the NE.   The three curves were generated by varying the soil gas partial pressure of carbon dioxide by plus or minus a factor of 5 from the assumed value of 0.005 atmospheres.   Decreasing the partial pressure of CO_2 reduces the projected ANC by about 10 μeq L^{-1} on the average, but does not dramatically affect the projected rates of depletion of buffering capacity of the systems in the NE.   Increasing the partial pressure dramatically increases both the projected mean ANC values for the lakes and the rates of cation depletion from the soil exchange complex.

Table 9-10. Effect of pCO_2 on Changes Projected to Occur in Surface Water ANC Values at 50 and 100 Years Using the Reuss Model. Deposition Used in the Model is LTA. Values Are Given as the Mean, Population-Weighted ANC Values for the NE (see Section 9.3.3.1 for details)

Time Step	ANC@ 0.001 atm	ANC@ 0.005 atm	ANC@ 0.025 atm
Present day ANC	-6.6	10.0	74.5
Δ-ANC @ 50 years	-8.5	-13.7	-50.7
Δ-ANC @ 100 years	-21.3	-32.1	-97.0

Another limitation of the Reuss model is the implicit assumption that the reactions considered can be modelled on an equilibrium basis. Clearly, most ongoing chemical processes in watersheds are subjected to rapidly and constantly changing chemical environments. Fluctuations in temperature, fluid flow, and external cation demands occur on daily, weekly, and seasonal bases. Few if any processes actually attain chemical equilibrium. Nonetheless, the Reuss model assumes exchange processes can be modelled using an equilibrium approach. Given the relatively rapid nature of exchange reactions and the annual time step used in most computations, this assumption is probably not unreasonable.

9.3.2.1.5 Model inputs -

9.3.2.1.5.1 Deposition and associated data --

The model requires deposition data including precipitation quantity (cm yr^{-1}) and average annual concentrations of the major ions in precipitation (SO_4^{2-}, Cl^-, NO_3^-, NH_4^+, Ca^{2+}, Mg^{2+}, Na^+, and K^+). The atmospheric flux of each ion was the combined wet plus dry average annual deposition. Evapotranspiration (% ET) data are required to adjust the concentrations of the non-reactive tracers (e.g., Cl^-) between deposition and runoff. This parameter also helps define the ionic strength of the soil solutions, thereby influencing solution composition.

As described in Section 5.6, a number of deposition scenarios are used for model simulations. The LTA deposition is used as the baseline against which other results are compared. LTA data are the best available estimates of total deposition occurring in each watershed. Typical year (TY) deposition data have also been compiled for these watersheds and are used in model simulations. Two reduced dry deposition scenarios have been examined as part of these efforts. The first scenario, long-term annual average-reduced or LTA-rbc, assumes fluxes of base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) in dry deposition to be half the values used in LTA. This scenario was included because concerns had been raised over the large particle deposition rates incorporated into the LTA baseline estimates. The second scenario, LTA-zbc, assumes zero flux for dry deposition base cations. The LTA-zbc deposition dataset yields maximum H^+ deposition estimates for each watershed and has been included in the Reuss model analyses to ascertain the magnitude of error potentially caused by uncertainty in dry deposition data.

In addition to the above data, which assume constant depositional inputs to the watersheds over the course of the simulations, ramped datasets have been constructed. In these ramped datasets, total (wet plus dry) sulfate and hydrogen ion depositional fluxes are varied during the course of each simulation. Changes are assumed to occur over a 15-year period, from year 10 in the simulation to year 25. The change is linear during this period, and the value attained in year 25 is maintained to the end of the simulation. In the NE Region, the ramp decreases sulfate depositional values to 70 percent of current estimates; in the SBRP, the ramp increases sulfate fluxes to 120 percent of current estimates.

9.3.2.1.5.2 Soils data --

The model requires physical and chemical information about each of the horizons included in the simulations. Required physical parameters are horizon thickness, bulk density, percent coarse fragments, and a hydrologic runoff parameter. Required chemical parameters include cation exchange capacity (CEC), base cation concentrations on the exchange complex, selectivity coefficients for the Ca/Al, Ca/Mg,

Ca/Na, and Ca/K exchange reactions, soil gas pCO_2, the apparent solubility product for $Al(OH)_3(s)$, and the stoichiometric coefficient for H^+ to be used in describing the dissolution of the aluminum solid phase. Multiple-horizon versions of the model require the above information for each of the horizons to be considered. Some minor adjustments were required to incorporate these parameters in the model.

Soil bulk densities in the DDRP database were entered on a coarse fragment-free basis. As a result, two adjustments to the associated field data were necessary. First, the percent coarse fragments parameter, was assigned a value of 0 in all cases. The contribution of coarse fragments is subtracted from the bulk density and soil (horizon) thickness, since these fragments are essentially unreactive mass. Second, to retain the proper reactive soil mass, the horizon thicknesses were adjusted to remove the contribution of the rock fragments. The fragments not only add mass to a horizon, but also contribute to the overall thickness. Had this correction had not been made, the reactive masses of the individual horizons would have been larger than those actually measured.

Another fixed parameter in the input datasets was the soil gas pCO_2 concentrations. As discussed in Section 9.3.2.1.3, a uniform value of 0.005 atm (0.5 percent) was used for all model computations. Finally, for this report, the stoichiometric coefficient for H^+ used to describe the dissolution of the aluminum oxyhydroxide phase is assumed in all cases to be 3.00. Although the model can adjust this parameter (e.g., in response to observed aluminum behavior in O and A/E horizons; see Section 9.3.2.1.3), we retained the gibbsite-like solubility behavior because of data limitations regarding aluminum behavior in individual soil samples.

Other data used as model input were taken directly from the DDRP soil chemistry database. For most of the simulations discussed in the report, data were aggregated according to the procedures and protocols presented in Section 9.3.1.2.2. That is, data from the six to ten pedons in each sampling class were aggregated (Johnson et al., 1988b) to a master horizon level (O, A/E, B and C horizons). Extensive parameters, such as horizon thickness, were aggregated by simple arithmetic averaging. Intensive parameters, such as soil pH or CEC, were aggregated using mass weighting procedures.

In addition to the sampling class-based design, a study was undertaken to evaluate an alternative aggregation procedure. Results from some of the multivariate analyses (see Section 8.3) suggested a significant watershed-specific component to observed variances. Simulations were conducted using only data collected on each individual watershed to model that watershed. Because soils were not sampled on all watersheds, and because difficulties were encountered with some of the analytical data, complete coverage of the DDRP watersheds was not possible using the alternative aggregation scheme. Data were collected on 129 of the 145 systems included in the study, however. Results from this effort are used to determine if changing the aggregation scheme would significantly affect conclusions.

9.3.2.1.6 Model outputs -

For each simulation, the model generates two results files, one containing projections for surface water composition and the other describing soil and soil solution composition for major chemical species. Results are compiled for the first and final years of the computation and at user-specified intervals during the simulation. For example, if the user were running a 13-year simulation and requested output at 5-year intervals, the result files would contain data for years 1, 5, 10, and 13.

Occasionally, results are not available for all soils or watersheds for the duration requested (typically, 100-year simulations). This occurs when the model fails to converge with a particular set of input parameters, which at most is about 7 percent of the simulations. Initially, the failure-to-converge rate was considerably higher than 7 percent. However, by adjusting convergence criteria, the loss of results minimized without sacrificing significant numerical accuracy.

Information on many variables is retained in the two output files. For surface waters, data on pH, ANC, SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+, Al^{3+}, sum-$(Al)_{aq}$, and ionic strength are captured. For soils, information on soil pH, base saturation, and exchangeable Ca, Mg, Na and K are retained for the solids, and ANC, Ca^{2+}, Mg^{2+}, Na^+, and K^+ data are retained for the soil solutions. For this report, analyses focus on a few select parameters, namely surface water pH and ANC and soil pH and base saturations, because these parameters are believed to provide the most easily interpretable indicators of system responses to continued exposure to acidic deposition.

9.3.2.2 Bloom-Grigal Model

In the DDRP, surface water is the principal resource of interest. However, soils play a vital role in maintaining the quality of surface waters because drainage waters entering lakes and streams pass through soils. Soils can buffer drainage waters against changes in several ways, as discussed in other parts of this report. If soils in the study regions were to change dramatically (e.g., become more acidic), these changes would ultimately be reflected in the subtending surface waters and in the status and health of forest vegetation. Characterizing the status of the soils in the DDRP regions and considering the effect of chronic acidic deposition on them is, therefore, important.

Two very different simulation models have been included in the DDRP to assess the impact of acidic deposition on surface waters. The Reuss model was discussed in the previous section. This section describes the Bloom-Grigal model.

9.3.2.2.1 Model description -

The impact of acidic deposition on soils can be modelled following one of two approaches (Bache, 1983). The first approach (used in the Reuss model) is to view the interaction of precipitation with soils as a perturbation of the equilibrium between ions in the soil solution and ions on the soil ion exchange complex. Following the perturbation, the system returns to equilibrium according to the theories of ion exchange equilibria. The second approach is to view this interaction as a simple mass action (non-equilibrium) exchange reaction. Following this approach, the amount of acidity in deposition replaces an equivalent amount of base cations in the soil. The Bloom-Grigal model is a form of this second approach.

The Bloom-Grigal model estimates the loss of base cations on an annual basis using the following equation:

$$S = I - A - C$$

(Equation 9-9)

where S is the sum of base cations, I is the amount of effective acidity in deposition, A is the acid leached from the soil, and C is the correct ion factor for the decrease in acidity due to protonation of bicarbonate. The model is presented graphically in Figure 9-27.

The Bloom-Grigal model is a simple semi-empirical computer simulation model created to project the effects of acidic deposition on soils (Bloom and Grigal, 1985). The model tracks soil pH and base saturation. Unlike the Reuss model, the Bloom-Grigal model is not formulated to project the chemistry of subtending surface waters. The model does, however, follow the concentrations of aluminum in the soil solution during simulation runs which can serve as an indicator of possible changes in surface water chemistry and forest health. The Bloom-Grigal model was initially formulated to assess the effects of acidic deposition on forested soils in northeastern Minnesota. Because the model is based on widely applicable principles, we believe that it can be meaningfully applied to project the effects of acidic deposition on the soils in the DDRP study regions.

9.3.2.2.2 Model formulation -

The Bloom-Grigal model is formulated around the assumption that, in steady-state ecosystems, acidic deposition depletes base cations on the soil ion exchange complex. The model's simplicity lies in the fact that soils are treated as a single homogeneous unit or compartment and all incoming deposition reacts completely with the soil in the compartment. Soils, however, are much more complex. The Bloom-Grigal model seems to be an appropriate tool for assessing the impact of acidic deposition on forested soils.

The Bloom-Grigal model assumes that the acidity in deposition reacts completely with the soil. In other words, the model makes no provision for deposition to be routed around the soil and directly into the surface water or into the subsoil strata. The amount of exchangeable base cations removed from the soil compartment is calculated as the difference between the input acidity and the output of H^+ and Al^{3+}, corrected for the protonation of bicarbonate. The amount of base cations lost is subtracted from the pool of exchangeable base cations and a new base saturation is calculated. The Bloom-Grigal model then calculates a new soil pH based on an equation that relates soil pH to base saturation. After adjusting parameters, the model then simulates the next year of deposition (see Figure 9-27).

This model was created to assess the effect of acidic deposition on non-sulfate adsorbing soils. Soils that adsorb sulfate have lower base cation removal rates than soils that do not. In this regard, the Bloom-Grigal model is probably more appropriate for application to the soils in the NE than in the SBRP.

Another feature of the Bloom-Grigal model is that it incorporates the input of nitrogen in deposition. Because forested soils are generally deficient in available nitrogen, inorganic nitrogen in deposition is removed by plants and organisms in the soil (Bloom and Grigal, 1985). When plants assimilate nitrogen in the form of nitrate (NO_3^-), they release hydroxyls (OH^-) to the soil, which is a non-acidifying reaction. However, when plants assimilate nitrogen as ammonium (NH_4^+), they release protons (H^+). Ammonium uptake is an acidifying reaction. The biological oxidation of NH_4^+ to NO_3^- produces one H^+ for every molecule of NH_4^+ oxidized. The Bloom-Grigal model incorporates these processes in calculating the net or effective acidity of deposition.

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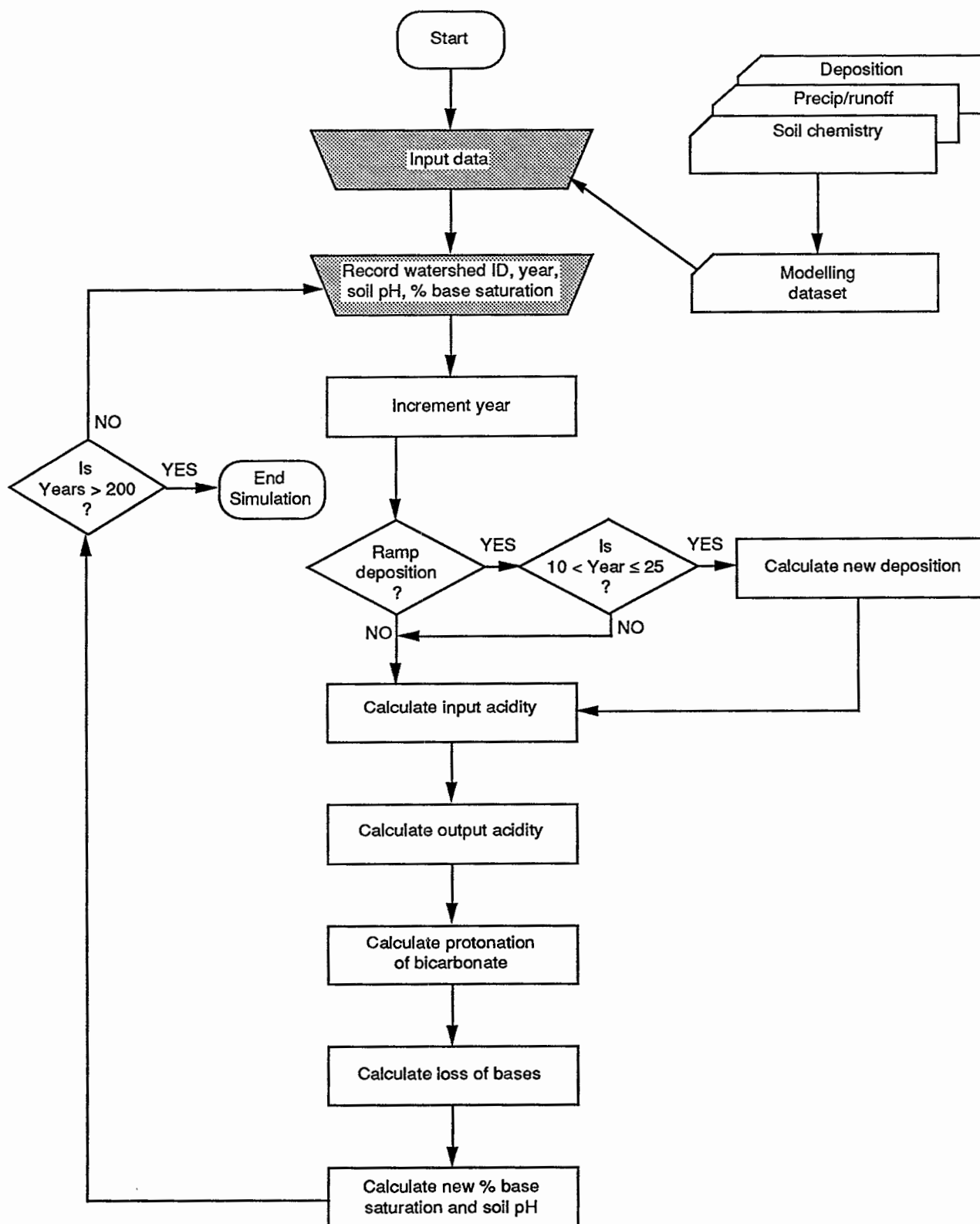
Figure 9-27. Flow diagram for the one-box Bloom-Grigal soil simulation model.

The original versions of the Bloom-Grigal model were coded in FORTRAN and BASIC; the version used in this analysis is coded in a high speed, compilable form of BASIC. In addition to optimizing the code for speed, code has been added that allows the input data to be processed in a batch mode. The output is now formatted to magnetic media to simplify the data reduction process. Additional lines of code have been added to calculate the various deposition scenarios automatically as the model is running. The fundamental equations in the original model have not been altered, however.

9.3.2.2.3 Assumptions --

A number of assumptions are made in modelling the effect of acidic deposition on soils with the Bloom-Grigal model. Some are implicit to the model, others are made to meet the needs of our current application. The assumptions used in implementation of the Bloom-Grigal model are itemized below including additional explanatory discussion or comments.

9.3.2.2.3.1 Sulfate adsorption --

The Bloom-Grigal model assumes that sulfate is not adsorbed by the soil and is treated as a completely mobile anion. As mentioned previously, in soils that have net sulfate adsorption, this assumption may lead to an overestimation of the amount of base cations actually leached from the soil.

9.3.2.2.3.2 Input acidity --

The total effective acidity (H^+_{total}) in deposition is equal to:

$$H^+_{total} = H^+ + NH_4^+ - NO_3^-$$

(Equation 9-10)

9.3.2.2.3.3 Extent of reaction --

The effective acidity in deposition reacts completely with the soil.

9.3.2.2.3.4 Depth of soil --

The depth of reactive soil material equals the mean aggregated thickness of the soil sampling classes represented by the types of soils on the specific watersheds.

In their original paper, Bloom and Grigal (1985) assumed that only the top 25 cm of soil are affected by acidic deposition. We consider the effect, however, on the whole soil compartment. Our soil chemistry input data are aggregated to represent the central tendency of the soil chemical characteristics of the whole soil compartment. The effect of acidic inputs on data aggregated in this way, thus, represents a mean effect. At the same time, this assumption allows for the water that flows in cracks or root channels to lower soil horizons before reacting with the soil.

9.3.2.2.3.5 Volume of drainage water --

The volume of water moving though the watersheds in each year of simulation is equal to the long-term annual average runoff.

9.3.2.2.3.6 Partial pressure of CO_2 --

The partial pressure of ambient CO_2 is approximately 0.0003 atm. Soil air is, however, enriched with CO_2 due to biological respiration and is consequently elevated. In all of the Bloom-Grigal model runs, the partial pressure of CO_2 in the soil air is set at 0.005 atm, a value thought to be reasonable for forested soils.

9.3.2.2.3.7 Activity of Al^{3+} --

To calculate the amount of input acidity that is converted to output acidity by aluminum buffering, the activity of Al^{3+} in soil solutions is calculated using the following equation:

$$\log(Al^{3+}) = 2.60 - 1.66 * \text{soil pH} \qquad \text{(Equation 9-11)}$$

This equation is the empirical part of the Bloom-Grigal model. In developing their model, Bloom and Grigal had a fundamental problem with using the solubility of $Al(OH)_3$ to describe the variation in Al^{3+} with pH. They state that in very acidic soils, such as forested soils, Al^{3+} is undersaturated with respect to the precipitation of $Al(OH)_3$. Therefore, $Al(OH)_3$ solubility is a poor model for the pH-Al^{3+} relationship. To establish a more realistic relationship between Al^{3+} and pH, they developed the above equation from laboratory measurements of Al^{3+} in artificially acidified soils. Although not appropriate for all soils, Bloom and Grigal believe that model results from which their equation was generated were reasonable for selected forested soils of northeastern Minnesota.

9.3.2.2.3.8 Relating soil solution pH to base saturation --

The pH of soil solutions is related to base saturation (BS) by the following equation:

$$\text{pH} = pK_a + n * \log [BS/(1 - BS)] \qquad \text{(Equation 9-12)}$$

where pK_a is the apparent acidity constant for soil (i.e., aggregate watershed/soil compartment) and n is an empirical constant. This equation is an extended form of the Henderson-Hasselbach equation.

The Bloom-Grigal model used here calculates pK_a and n for each watershed using the input values of soil pH and base saturation. These parameters describe the relationship between soil pH and base saturation and are unique for each watershed.

9.3.2.2.3.9 Base cation uptake --

The model assumes no net accretion of base cations in biomass. The uptake of base cations by forest vegetation is an acidifying process by which H^+ is exchanged for an equivalent amount of base

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cations to maintain charge neutrality. At the same time, through litterfall and decomposition, base cations are released to soils. The Bloom-Grigal model only tracks the flux of base cations that are leached from the soil. This no-accretion assumption implies that the uptake of base cations by vegetation is exactly equal to the amount recycled to the soil.

9.3.2.2.3.10 Mineral weathering --

Mineral weathering is the ultimate source of base cations, and the Bloom-Grigal model has a subroutine that calculates the contribution of base cations to the soil solution via mineral weathering. The rate of mineral weathering for these simulations, however, is set to zero for two reasons. First, assuming no base cation resupply a "worst-case" base cation loss scenario is evaluated, thereby bounding the projections. Second, the relationships between weathering and soil solution pH are not sufficiently established to provide accurate parameters for the weathering equations. One complication, in particular, is that mineral weathering rates are a dynamic function of the chemical weathering environment.

9.3.2.2.3.11 Cation exchange capacity --

Cation exchange capacity (CEC) is constant throughout the period of simulation. Scientifically this is not correct. Soil CEC is derived from two sources: (1) secondary clay minerals with permanent charge due to isomorphous substitution of lower valent cations for cations in the clay crystal lattice, and (2) variable charge sites on organic matter, para- and noncrystalline hydrous oxides, and edge sites on permanently charged clays. The variable charge CEC is a function of pH, i.e., the net soil CEC changes as with changes in pH. As pH increases the variable charge CEC increases, and vice versa. Because of scientific and data limitations, we have chosen to hold CEC constant.

9.3.2.2.3.12 Time steps --

The time step for simulations is annual. For assessment purposes, yearly time steps are a useful increment. From a modelling standpoint any shorter time step (e.g., daily) is data intensive and computationally demanding. Shorter time steps may provide more accurate projections, however.

9.3.2.2.4 Limitations -

Soils are highly complex and no simulation models exist that accurately depict the flux of energy and matter in soil systems. As with any attempt to project future events, the Bloom-Grigal soil simulation model is not without limitations. Some of the limitations are due to the state of the science and others are have been imposed by the DDRP.

The scientific limitations center around the factors that control aluminum solubility and the relationship of soil pH to base saturation. Bloom and Grigal (1985) empirically developed equations to describe this relationship for a selected set of northeastern Minnesota forested soils. As described in their paper, the equations appear appropriate for forested soils in Minnesota. In the DDRP, the equations are assumed to be widely applicable and they are not independently verified. It is doubtful, however, that these equations are universally true due to vast differences in soils and vegetation.

Soils are dynamic systems. Soil properties fluctuate on a daily basis, and daily temperature and moisture changes affect a broad range of soil processes. Broader seasonal changes also occur. The use of annual time steps assumes that soils are static, possibly restricting the accuracy of the projections. As mentioned above, however, shorter time steps are data and computationally restrictive.

Individual soil processes are inextricably linked to a number of other processes and considering a single process (e.g., base cation flux) in isolation may distort projections. In the DDRP Level II Analyses, processes are isolated in order to focus on the principal soil reactions associated with surface water acidification. It is recognized that some of the uncertainty in assessing effects is due to this approach of isolating facets of the whole ecosystem.

9.3.2.2.5 Model inputs -

The Bloom-Grigal model was designed not to be data intensive. The data required to run the Bloom-Grigal model fall into four categories: (1) deposition data, (2) precipitation data, (3) soil chemistry data, and (4) fixed parameters. The deposition data are described in Sections 5.6 and 9.3.3. Table 9-11 lists the specific data requirements.

The soil chemistry data used in these simulations has been aggregated to the single compartment, watershed level. These procedures are described in detail in Johnson et al. (1988b). The capacity variables, sum of base cations (SOBC) and CEC are capacity weighted. Soil pH is intensity weighted.

9.3.2.2.6 Model outputs -

The Bloom-Grigal model simulates soil processes relevant to the assessment of impacts of acidic deposition on soils. During model simulation runs, soil pH, soil base cation status (i.e., base saturation), and soil solution Al^{3+} are tracked. Principal interest for this analysis is soil pH and base saturation.

During 200-year simulations, soil pH and percent base saturation are recorded (see Figure 9-27) at years 0, 20, 50, 100, and 200. The results are converted to change in soil pH and change in percent base saturation by subtracting the initial values from the projected values. Because the initial values are higher than the projected values, the reported results are all negative numbers, reflecting a decrease.

The projected changes in soil pH and percent base saturation are presented as cumulative distribution functions (CDF) for graphical comparisons. The CDFs represent regionally weighted projections for soils on the target population of watersheds. Summary statistics for the CDFs also are presented for numerical comparisons.

9.3.3 Model Forecasts

Level II base cation analyses were conducted using Reuss's (Reuss, 1983; Reuss and Johnson, 1985) cation exchange model and Bloom and Grigal's (1985) cation depletion model. Results from the individual models are presented in this section along with a comparison of the projections made using the two models.

Table 9-11. List of Input Data for the Bloom-Grigal Soil Acidification Model

Input Variables	Units
Annual average runoff	cm
Annual H^+, NH_4^+, NO_3^-, and SO_4^{2-} in wet deposition	keq ha^{-1}
Annual H^+, NH_4^+, NO_3^-, and SO_4^{2-} in dry deposition	keq ha^{-1}
Soil pH	pH(H_2O)$^{-1}$
Sum of soil base cations (0.1 M NH_4Cl)	keq ha^{-1}
Soil cation exchange capacity (0.1 M NH_4Cl)	keq ha^{-1}

Fixed Parameters	Value
Length of simulation	NE = 100 years SBRP = 200 years
Partial pressure of CO_2	0.005 atm
Activity coefficient of Al^{3+}	0.82
Activity coefficient of $Al(OH)^{2+}$	0.92

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9.3.3.1 Reuss Model

9.3.3.1.1 Data sources -

Summaries and examples of the various datasets used in running the Reuss model are presented in Section 5. A brief summary of the data used for the simulations also is given below.

The data fall into two categories: deposition data and soils data. Four deposition datasets were used in making population estimates of watershed responses. As described in Section 9.3.3.1.1.1, these datasets were used in model simulation runs assuming constant levels of deposition for the future and in conjunction with a ramping function that adjusted deposition downward by 30 percent in the NE and upward by 20 percent in the SBRP (see Section 5.6). Similarly, soils data were aggregated using two approaches. The sampling class-based aggregation described in Section 9.3.1.2.2 was used with each of the deposition scenarios. In this approach, soils data were aggregated to master horizon/watershed level. The second approach (watershed-based aggregation) was initially undertaken because some preliminary Level I Analyses indicated a substantial "watershed effect". That is, some combination of local variables indicated that a soil from a given watershed was more similar to other soils in the watershed than it was to other soils in the region from the same sampling class. While this preliminary observation was not substantiated by additional investigations (see Section 8.8.1), the watershed-based aggregation procedure was further examined to determine whether substantial differences in the results would be observed. Results from this examination are presented in Section 9.3.3.1.2.1.

Given the number of deposition scenarios and soils aggregation approaches available, 16 distinct sets of results could be generated for the NE. Because the purpose of examining the scenarios and the aggregation schemes was to determine the sensitivity of model results to different conditions, discussions are limited to nine combinations of deposition scenarios and soils aggregation schemes. All of the constant and ramped deposition scenarios are run in conjunction with the master horizon/watershed soils aggregation scheme. The two soils aggregations are run using the constant level, LTA deposition. Thus, results obtained using LTA deposition and the master horizon/watershed soils aggregation scheme serve as the baseline dataset against which other results are compared.

9.3.3.1.1.1 Deposition data --

Four deposition datasets were used. The dataset considered to be most representative of "actual" deposition is the LTA dataset, derived from 5-year averages of species concentrations in deposition and 30-year averages of precipitation quantities (see Section 5.6).

Except for the TY dataset, which is based on data obtained from a year with mid-range depositional values (see Section 5.6), other deposition datasets are variations of LTA. In constructing LTA, transport and deposition of large particles ($> 20 \ \mu m$) were integral components of the dry deposition estimates. The uncertainty in the long-range transport of these larger particles (concern that net H^+ fluxes to watersheds might be underestimated) prompted construction of two additional deposition datasets. LTA-rbc is essentially identical to LTA, except that the estimated dry deposition of base cations (Ca^{2+}, Mg^{2+}, Na^+, and K^+) is reduced by 50 percent. LTA-zbc assumes zero net dry deposition of base cations. Dataset LTA-zbc, as a result, yields the highest hydrogen ion fluxes to watersheds, and, in fact, probably

significantly overestimates net H^+ fluxes. In this context, LTA-zbc can be viewed as a "worst-case" deposition scenario.

9.3.3.1.1.2 Soils data --

Soils data were aggregated using one of two approaches. The primary aggregation scheme uses the soil sampling class concept around which DDRP was designed (see Section 5.5). The other aggregation was based on locale, and is described in more detail in this section.

The aggregation scheme routinely used in the DDRP is the master horizon/watershed aggregation. Data representing each of the four master horizons (O, A/E, B, and C) are obtained. For each master horizon, data are first averaged to within sampling class using protocols described in Johnson et al. (1988b), which are then averaged using areal weighting to obtain estimates for a watershed. Hydrologic routing of water is considered if at least one of the sampling classes has a lower-most horizon that is anything other than a C horizon. For example, overland flow of water for the watershed is set equal to the percentage of precipitation falling directly on rock outcrops and is routed directly to the surface water without equilibration with any of the soil horizons. As another example, for watersheds having soils in sampling class H01 (which has only an O horizon), that fraction of soil water equal to the areal percentage cover of the watershed by H01 is routed to surface water after equilibrating with the O horizon. While this approach is oversimplified, watershed hydrologic characteristics are spatially distributed, and adequate representation of the complexity in natural systems cannot be accomplished in the current formulation. The hydrologic routing was established for these analyses in full cognizance of its limitations. Bedrock outcrops tend to occur along ridgelines, so incident precipitation will not run off directly into the surface water. Histic soils, on the other hand, tend to be concentrated in riparian zones. Histic soils can have extremely low permeabilities, and unless they are dry, incident precipitation will tend to run off from their surfaces. Nonetheless, the model equilibrates incident deposition with these soils. The model also does not consider any aspect of lateral flow, and therefore downward percolation is likely to be considerably, overestimated especially on steeper slopes. Considering the various trade-offs, we feel that the hydrologic routing, as described, yields a reasonable approximation for modelling these complex, spatially-related processes.

Second, a watershed-based aggregation of soils data was undertaken in order to obtain information concerning the sensitivity of model results to the aggregation method. For this approach, only data from those soils sampled on a particular watershed were used to describe the watershed. Therefore, if the only two soils sampled on a watershed were a Histosol and a Spodosol, the data from those two soils were used to represent the watershed regardless of the actual areal coverage. The potential problem with this aggregation is that, for watersheds on which sample classes are minor proportions of the total watershed area, the soils sampled may not be representative of the actual local environment. As described in Section 9.3.3.1, however, preliminary concerns had suggested that, even with this limitation, the aggregation might be more representative of the population of soils in each of the regions than is the sampling class-based information (see Sections 5.2 and 8.8).

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9.3.3.1.2 Projections of surface water ANC -

9.3.3.1.2.1 Northeast --

9.3.3.1.2.1.1 Prediction of current conditions --

The distribution of current surface water ANC values projected for the NE using the Reuss model is illustrated in Figure 9-28, along with upper and lower bounds for 90 percent confidence intervals associated with the projection. The ANC values for each of these lakes, as measured by the Eastern Lake Survey (Linthurst et al., 1986a), are listed in Table 5-3 for comparative purposes. An obvious feature of these projections is the extremely tight clustering of the results in the range of -25 to +50 μeq L^{-1}. This clustering has been observed on virtually all model runs conducted to date, including those runs using data aggregated at the watershed level and those conducted on individual sampling classes. For the individual sampling classes, the upper limit for ANC values exceeds 200 μeq L^{-1}, while for the other 37 classes in the NE an upper limit of 80 μeq L^{-1} is observed.

These results are consistent with the hypothesis that soil exchange reactions can buffer soil and surface water ANC values and that the buffering occurs in the low ANC range. Although surface waters with higher ANC values occur in the NE, they are not typical of the region. Soil exchange reactions, therefore, do not adequately explain the observed distribution of surface water ANC. Figure 9-29 illustrates the relationship between observed and projected ANC values. Clearly, the tight clustering of the predicted values near zero indicate no significant correlation.

In order to explain the observed distribution of ANC values in the population of lakes sampled for this study, it is necessary to invoke some mechanism other than base cation exchange to produce ANC values greater than 100 μeq L^{-1}. Uptake of cations by aggrading vegetation is a possible mechanism, but if cation uptake were a significant process in these watersheds, the observed ANC values would be lower than those computed by the model. The other major process that could explain the distribution is primary mineral weathering, which can significantly alter cation balance. Release of base cations and ANC through reactions such as those listed in Section 3.4 can increase surface water ANC to values well above the 100 μeq L^{-1} limit apparently imposed by soil exchange processes. Other processes that could increase ANC to the levels observed in the lakes are presently unidentified.

For lakes exhibiting ANC values exceeding 100 μeq L^{-1}, mineral weathering apparently is the dominant watershed process controlling ANC. For systems with ANC values less than 100 μeq L^{-1}, either mineral weathering or soil exchange processes could be regulating the observed levels. Given available methods, however, determining which process accounts for the observed ANC values is not possible.

The implications of these findings are significant in terms of projected future changes in surface water chemistry. If mineral weathering is, in fact, regulating ANC levels in those systems with ANC greater than 100 μeq L^{-1}, then these systems probably will not experience significant future declines in ANC at current levels of deposition. Inasmuch as present trends in the NE indicate stable or declining hydrogen ion deposition, lakes with ANC values exceeding 100 μeq L^{-1} are probably not at risk with regard to future acidification.

NE Lakes
Deposition = LTA
Year = 1
Model = Reuss
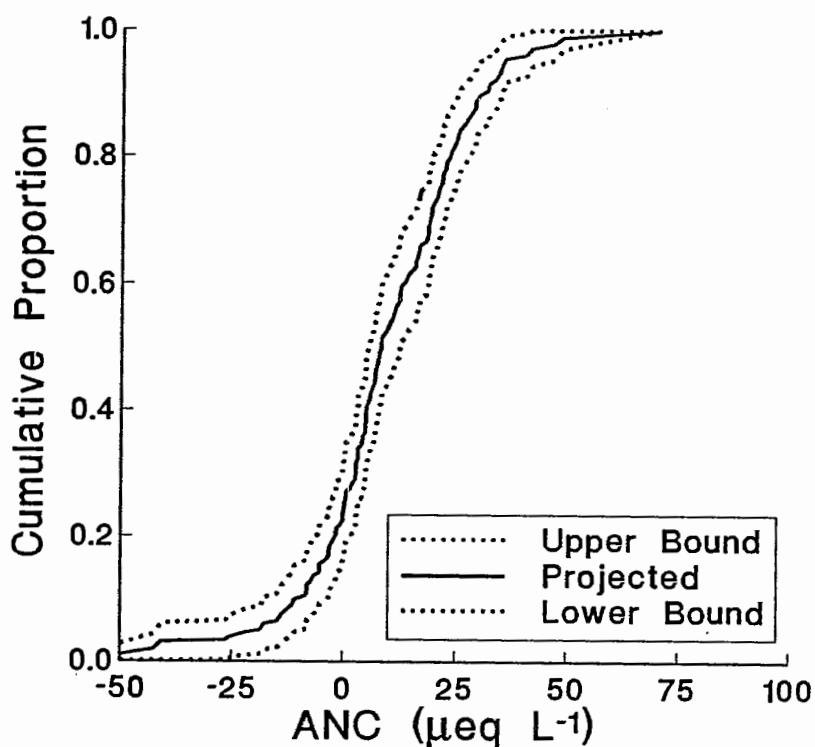
Figure 9-28. Cumulative distribution of projected, present-day ANC values for lakes in the study population in the NE as projected using Reuss's cation exchange model. LTA deposition was used in making these projections. The error bounds on the plot are the 90 percent confidence intervals and were obtained using a Monte Carlo approach, assuming that errors on individual input parameters to the model are normally distributed, and that the only source of error is in those input parameters.
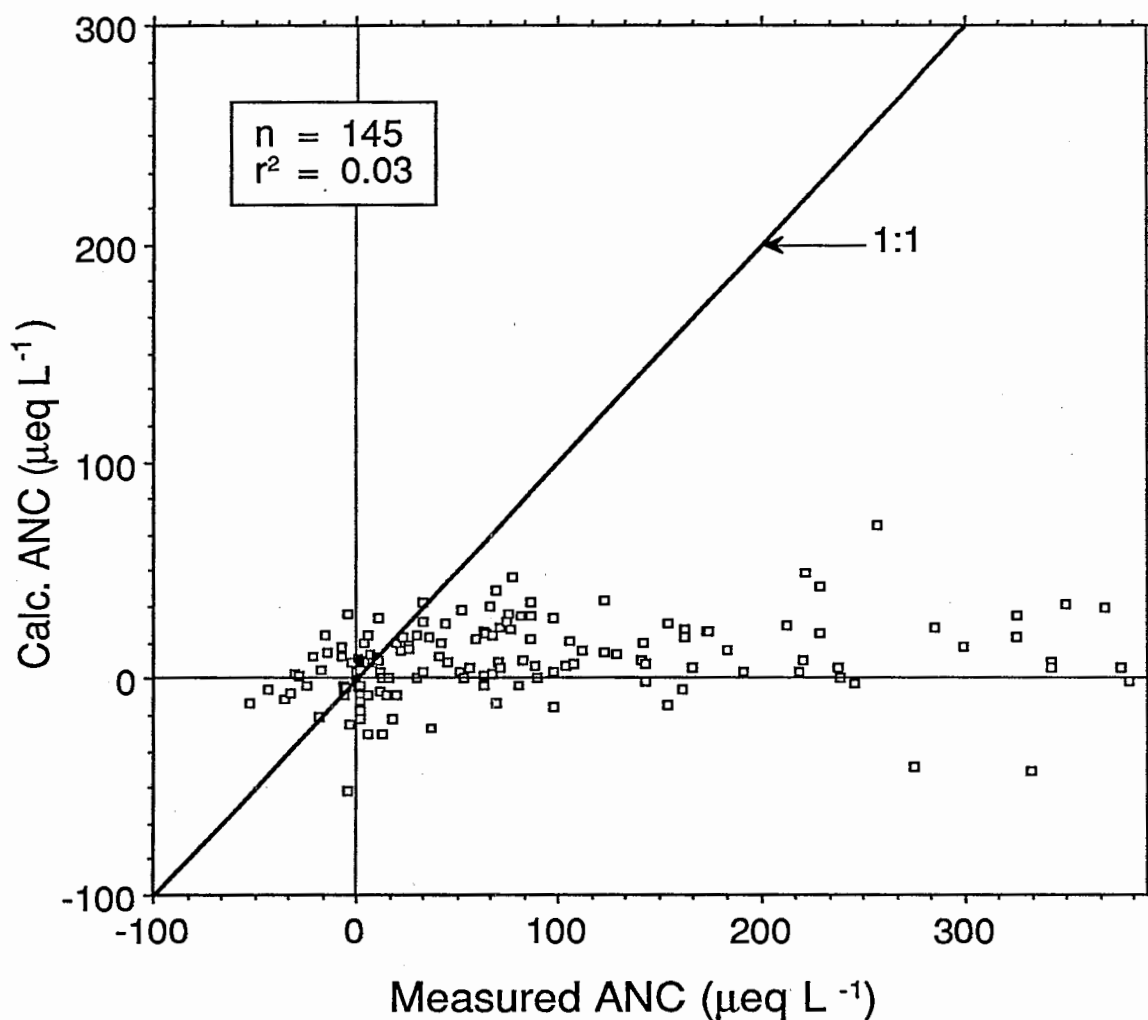
Figure 9-29. Scatter plot of the projected, present-day ANC values for lakes in the NE, obtained using the Reuss model vs. observed (ELS) values. The heavy diagonal line indicates the 1:1, or perfect correspondence, line. As is apparent, the model projects that current ANC values should cluster at values that are slightly in excess of 0 μeq L^{-1}. This is interpreted as indicating the importance of mineral weathering in controlling observed surface water composition for the majority of systems in the NE.

Soil exchange processes might regulate ANC in systems exhibiting ANC levels less than 100 μeq L^{-1}. If so some of these systems might currently be experiencing an increase in base cation leaching rates in response to acid anion inputs from acidic deposition. In the future, these systems could experience significant ANC decline. Unfortunately, given the current state of the science, distinguishing between those systems in which ANC is controlled by mineral weathering and those in which ANC is controlled by soil exchange processes is not currently possible.

To provide an upper bound on the number of systems that may experience additional declines in ANC, summary information from the Eastern Lake Survey can be examined (Linthurst et al., 1986a). Data from this survey suggest that about 1,038 lakes (about 15 percent of the total ELS target population in the NE) have ANC values in the range of 0 to 50 μeq L^{-1}. The largest population of lakes that might be adversely affected by changes to the soil exchange buffering capacities is in the Adirondacks (Subregion 1A), where 321 lakes (25 percent of the target population) have ANC between 0 and 50 μeq L^{-1}. The Poconos/Catskills Subregion (1B) has the fewest lakes in this ANC class: 116 lakes (7.8 percent). As noted, the proportion of these systems that may actually experience future declines in ANC cannot be determined. Some proportion of the systems that currently have low ANC values, however, will probably experience adverse changes.

An issue of concern regarding these conclusions is the sensitivity of the results to the input data used in the simulations. To address this issue, several different versions of input data were used in running the simulations: four deposition scenarios and two soil aggregation schemes (see Sections 9.3.2.1 and 9.3.3.1). Summary results from these model runs for projected present-day ANC values are given in Table 9-12. For the four deposition scenarios, the differences among projected ANC are minimal, with projected population-weighted, mean lake ANC values of 9 $\pm$ 1 μeq L^{-1}; medians, maxima, and standard deviations are equally comparable. The largest differences are observed for the projected minima. The LTA-zbc deposition scenario results in an ANC value that is 10 μeq L^{-1} less than that projected using the LTA and 15 μeq L^{-1} less than that projected using the TY.

The greatest observed differences occur with the use of the different soil aggregation schemes. For the data listed in Table 9-12, the columns under LTA and WBA were obtained using the same deposition data, but different soils aggregation schemes. The data under the LTA column were obtained using the master horizon/watershed aggregation scheme, whereas those under the WBA (or the Watershed Based Aggregation approach) column were aggregated based on soils collected from individual watersheds and used to describe only those watersheds. The WBA data indicate moderate changes in the means and medians for the present-day ANC values. The extremes, however, represent a much broader range of values than are actually represented by the field data. Figure 9-30 illustrates the relationship between the observed and projected ANC values obtained using the WBA scheme. Fifteen of the 129 lakes in the sample have projected ANC values exceeding 100 μeq L^{-1}. Despite the wider range of projected values, the WBA scheme does not improve the correlation between observed and projected values. This finding is not surprising, since the soils sampled on any given watershed were not selected to be representative of the soils on that watershed, but rather to be representative of a group of soils in the region (see Section 5.2.4.1). Therefore, although the WBA scheme may more accurately portray the variability of individual soils in the regions, it does not demonstrably provide a more accurate means for explaining observed surface water composition.

Table 9-12. Summary Statistics for the Population Estimates of Current ANC Conditions for Lakes in the NE Region for Five Different Deposition or Soils Aggregation Schemes (Refer to the text for explanation of the different input scenarios)

	LTA	TY	LTA-rbc	LTA-zbc	WBA
Mean	10.0	8.3	9.4	8.8	35.5
Std Dev.	18.4	19.0	18.9	19.5	87.4
Median	8.3	7.4	7.8	7.4	18.9
P25	0.34	-1.8	-0.7	-0.2	0.3
P75	21.7	20.6	21.0	21.0	43.3
Max	70.8	67.1	70.7	70.6	863.7
Min	-52.0	-46.8	-56.7	-61.3	-121.1
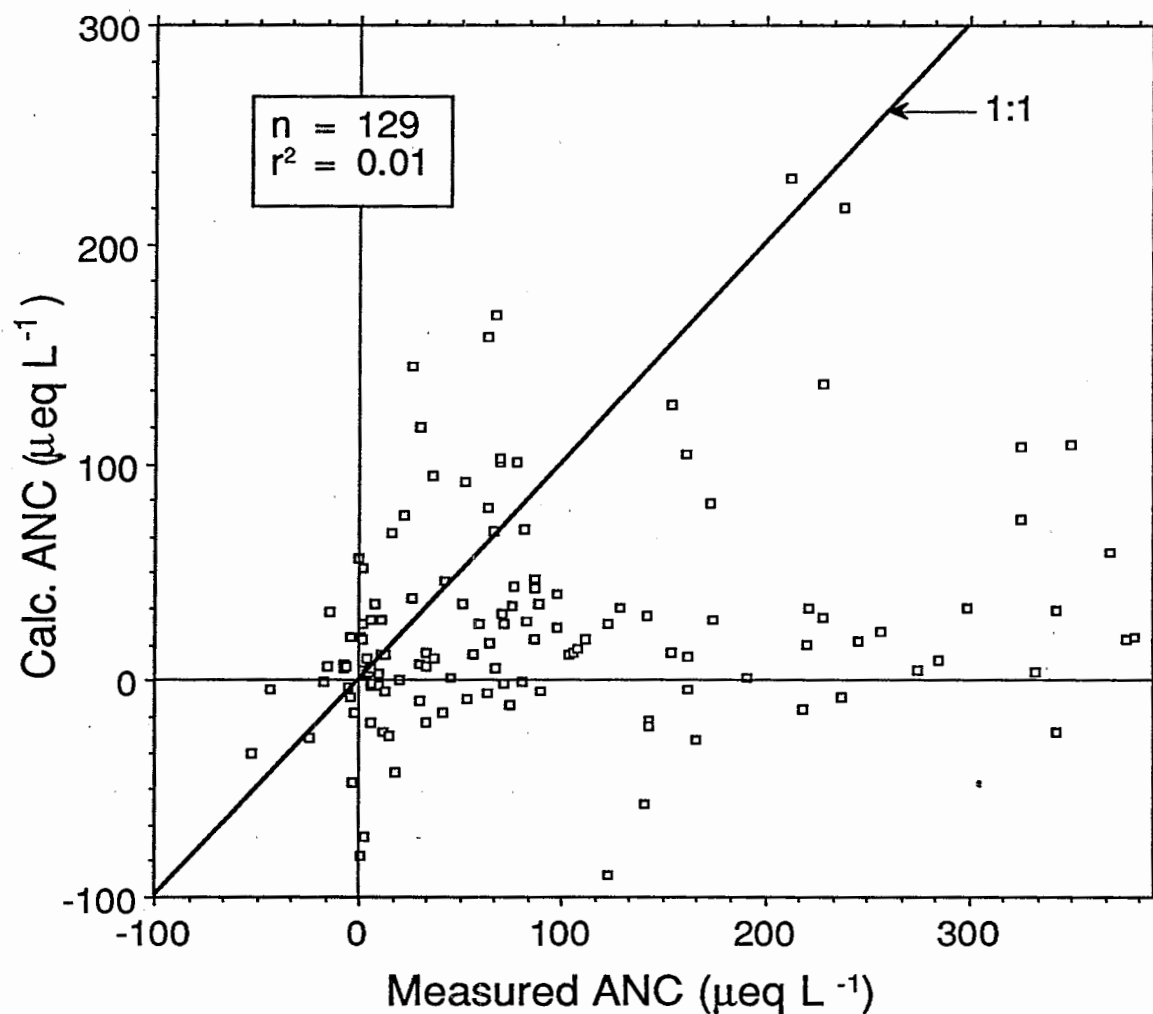
Figure 9-30. Scatter plot of the present-day lake ANC values projected using the Reuss model in conjunction with the Watershed-Based Aggregation (WBA) soils data vs. observed (ELS) ANC values. The range of ANC values projected using this approach is much greater than obtained using the sampling class/watershed-based approach. However, the correlation is not improved. Three projected points with ANC values in excess of 300 μeq L^{-1} are not shown on this plot.

9.3.3.1.2.1.2 Projected future conditions --

In order to project the magnitude of changes in ANC that might occur in the NE, as well as the time frame over which such changes might occur, the Reuss model was run using its mass balance component. The mass balance component of the model tracks the loss (or gain) of base cations from soil exchange sites through time. For these simulations, precipitation quantity (cm yr^{-1}) as well as the depositional fluxes were used to specify the total loadings of ions delivered to the soil. Annual time steps were used in making these computations. For the NE, model simulations were run for a total of 100 years, with results of the computations being collected at 10-year intervals. Results are reported only at the 20-, 50-, and 100-year time increments.

Projected, time-dependent changes in ANC values for the population-weighted results are illustrated in Figures 9-31 and 9-32 and summary statistics are given in Table 9-13. The Reuss model considers only the effects of the soil cation exchange process in making these projections. Mineral weathering reactions would, in general, further delay the response of these systems to the effects of acidic deposition. At 20 and 50 years, most systems in the NE are projected to experience minimal change in ANC. Apparently, the soil buffering capacity in these systems is sufficient to moderate the effects of acidic deposition over these time scales. Only a small percentage of the watersheds (about 10 percent) is projected to experience losses of ANC that exceed about 25 μeq L^{-1} within the 50-year time frame.

The 100-year projections for changes in ANC (Figure 9-32) suggest a bimodal distribution in the way watersheds respond to the effects of acidic deposition. About half of the watersheds in the region are projected to experience minimal changes ($<$-13 μeq L^{-1}) over the 100-year time frame. The other half is projected to experience a median change in ANC of about -50 μeq L^{-1} and a maximum change of almost -200 μeq L^{-1}. The magnitude of these changes is of concern, if mineral weathering reactions do not control ANC. A closer examination of the results (Table 9-13) suggests that projected changes in the ANC values through time are not linear, but rather accelerate to a point where the buffering capacity of soils is depleted. Soils response to acidic deposition is analogous to a buffer effectively being titrated by acidic deposition. As such, any given soil behaves in the same way a dissolved buffer in an aqueous system behaves (Figure 9-33). Assuming that the system is not yet near to or beyond the inflection point of the titration curve, the initial response of a soil to continued loadings of acidic deposition will be a gradual, and almost linear, decline in projected ANC for some period of time. Once the system reaches the inflection point, however, the rate of decline in ANC dramatically accelerates until the buffering capacity of the system is depleted.

For the soils examined to date, these observations have two major implications. First, minimal changes observed in lake water ANC values do not necessarily preclude the possibility that more dramatic changes will occur in the future. If the buffering capacity of a soil is currently being depleted, the full effect might not be immediately apparent. Rates of change in system response can increase with time, unless the process is being moderated by mineral weathering. Second, for the soils included in DDRP, dramatic changes in system response to acidic deposition are projected only for those systems with lower ANC values. Most of the titration curves deviate from relatively flat slopes to steeper slopes as the inflection points approach ANC in the range of -20 to +20 μeq L^{-1}. Therefore, the systems that are most

NE Lakes
Deposition = LTA
Year = 50
Model = Reuss
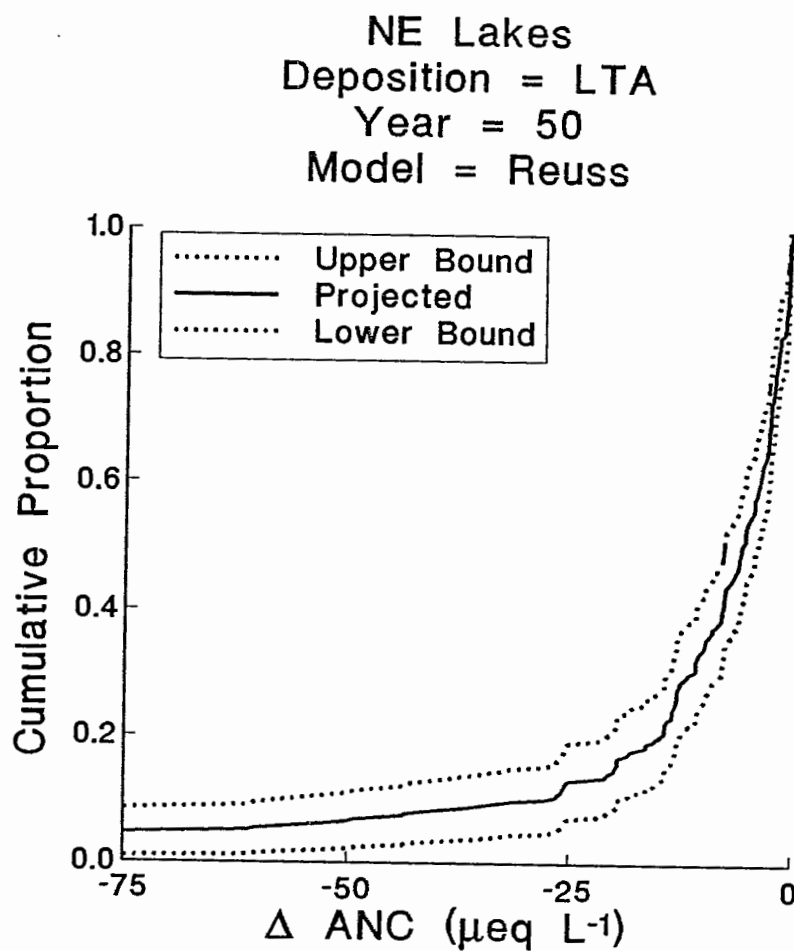
Figure 9-31. Cumulative distribution of the projected surface water ANC values projected for the study population of lakes in 50 years in the NE. The model runs were conducted using LTA (constant level) deposition.

NE Lakes
Deposition = LTA
Year = 100
Model = Reuss
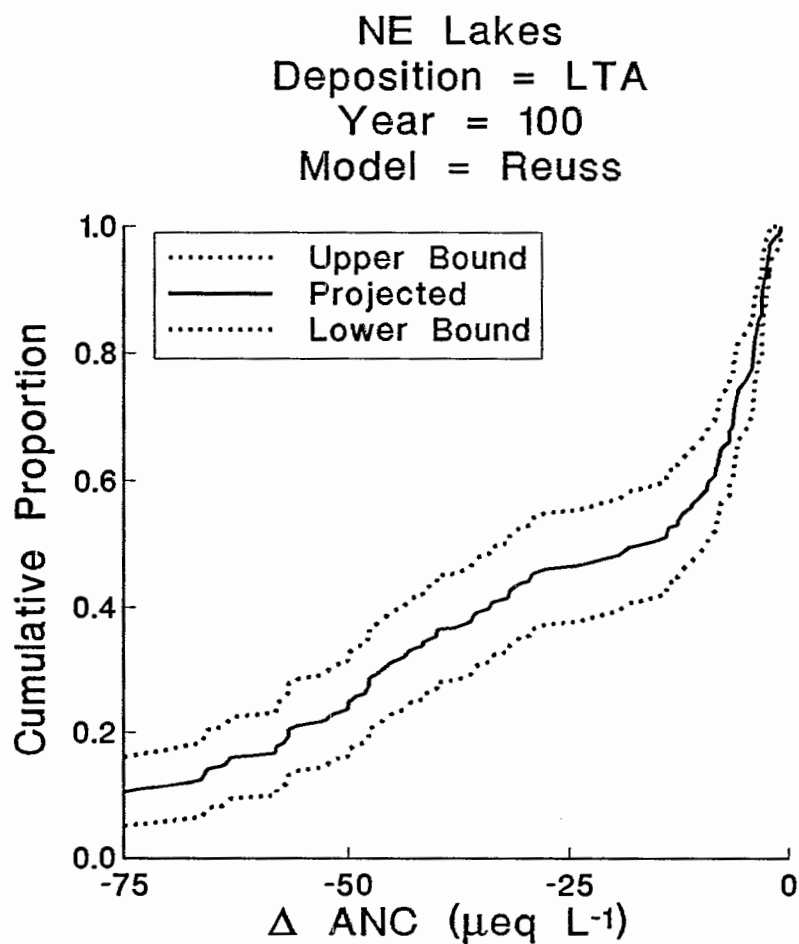
Figure 9-32. Cumulative distribution of the projected surface water ANC values projected for the study population of lakes in 100 years in the NE. The model runs were conducted using LTA (constant level) deposition.

Table 9-13. Descriptive Statistics of the Population Estimates for Changes in Lake Water ANC for Systems in the NE. Mean, Median, Standard Deviations for the Population and the Maximum Changes Projected Are Presented for Each of the Four Deposition Scenarios at the Time Increments 20, 50, and 100 Years

	LTA	TY	LTA-rbc	LTA-zbc
ANC (0) (Mean)	10.0	8.3	9.4	8.8
ANC (20)				
Mean	-6.1	-6.4	-6.5	-6.9
Std	16.4	18.0	17.4	18.3
Median	-2.0	-2.4	-2.3	-2.5
Max	-101.9	-118.3	-107.1	-110.0
ANC (50)				
Mean	-13.7	-16.1	-15.5	-17.5
Std	23.6	26.4	26.4	30.0
Median	-5.2	-6.0	-6.0	-6.4
Max	-127.5	-138.8	-140.0	-160.0
ANC (100)				
Mean	-32.1	-43.1	-39.4	-44.7
Std	36.1	51.5	43.8	49.6
Median	-13.9	-22.0	-16.4	-20.6
Max	-185.4	-231.7	-207.5	-228.7
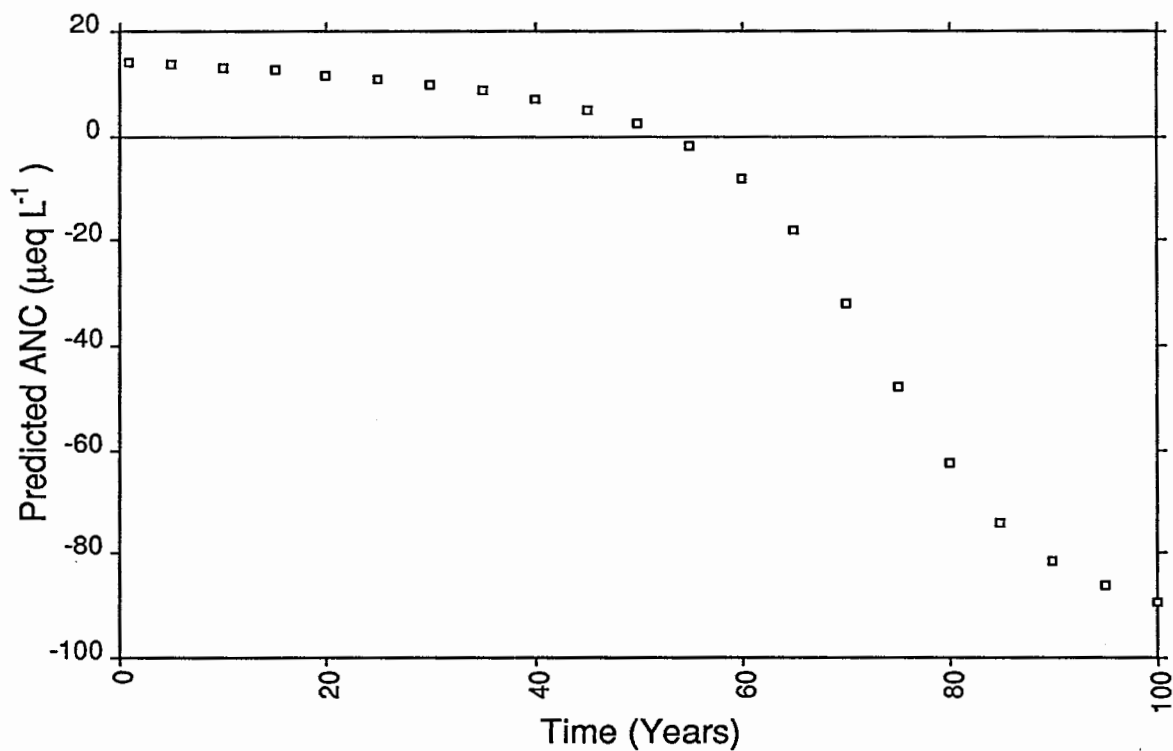
Figure 9-33. Schematic illustration of the titration-like behavior displayed by soils in response to constant loadings of acidic deposition. Initially, soils respond slowly, showing only minor changes in ANC as the base status of the soil is reduced. However, once the base cations have been sufficiently depleted from the exchanger, rapid and dramatic changes in ANC values from the soils can take place. This example was computed using soil sampling class S14 and a mid-range deposition.

vulnerable to dramatic future changes in ANC are those that currently have an associated surface water ANC of about 0 μeq L^{-1}.

The alternative soils aggregation scheme, WBA, yields results that are qualitatively similar to those obtained using the master horizon/watershed aggregation (Table 9-14). Quantitatively, the changes projected using the WBA scheme are two to three times as large as those projected with the routine aggregation method. Also, the WBA scheme projects substantial changes in a small number of watersheds during the early phases of the simulations. These results substantially shift the mean values of the changes to more negative numbers. Because there is a lower limit to values that ANC can attain within the framework of this model, the magnitude of changes that can occur in the population means is limited.

The last group of simulations addresses the effects that ramped deposition has on projected future changes. As discussed in Section 9.3.3.1.1.1, the three LTA deposition datasets, as well as the TY data, were modified using a ramp function that decreased sulfate and hydrogen ion depositional fluxes by 30 percent in the NE between years 10 and 25 of the simulations. Differences between the projections made using ramped and constant deposition are presented in Table 9-15. Not surprisingly, differences between the two scenarios are minor at the 20-year point. By year 50, the median declines projected for ANC using ramped deposition are only half as large as those projected using constant deposition. After 100 years, the differences in the medians are less. Ramped deposition results in changes in surface water ANC that are two-thirds the magnitude of those for constant deposition. Differences in the means are more uniform for both year 50 and year 100. At both years, ramped deposition results in changes that are about 60 percent as large as those obtained using constant deposition.

Incorporation of mineral weathering effects into these results would suggest smaller differences between the constant and ramped depositions than those reported here. A supply of cations from weathering would tend to minimize the changes projected by both datasets, but such effects would be larger for the constant deposition scenario than for the ramped deposition scenario.

9.3.3.1.2.2 Southern Blue Ridge Province --

9.3.3.1.2.2.1 Prediction of current conditions

The distribution of current surface water ANC values projected using the Reuss model for the SBRP is illustrated in Figure 9-34. These values can be compared to the actual distribution of ANC measured for these stream reaches during the Pilot Stream Survey (Messer et al., 1986a) (see Table 5-6). As with the northeastern results, the extremely tight clustering of the results around an ANC value of zero is notable. Mean and median values for each of the four deposition scenarios (Table 9-16) are between 2 and 4 μeq L^{-1} , and the total range for the four scenarios is about -15 to 23 μeq L^{-1}.

As for the northeastern data, these results are interpreted as an indication that the soils of the region are characterized by strong buffering. Additionally, the results suggest a dominant role for mineral weathering in regulating the observed surface water composition, since neither sulfate adsorption nor cation accretion into biomass can readily explain the differences between observed and projected ANC

Table 9-14. Summary Statistics Comparing the Projections Regarding Changes in Surface Water ANC Values Obtained Using Different Soils Aggregation Schemes

	LTA[a]	WBA[b]
ANC (0)	10.0	35.5
Δ-ANC (20)		
Mean	-6.1	-25.1
Std	-16.4	42.0
Median	-2.0	-5.2
Max	-101.9	-216.4
Δ-ANC (50)		
Mean	-13.7	-43.9
Std	23.6	55.1
Median	-5.2	-14.3
Max	-127.5	-241.4
Δ-ANC (100)		
Mean	-32.1	-66.9
Std	36.1	67.6
Median	-13.9	-36.5
Max	-185.4	-275.6

[a] The LTA data have been obtained using a sampling-class-based aggregation, in which soils from the whole region are used to describe specific soils on the watershed (see Section 5.5.1).

[b] The WBA is based on data obtained from only those soils sampled on the watersheds being described. The text contains details of the procedures used.

Table 9-15. Summary Statistics of the Differences Between the Population Estimates for Future ANC Projections Made Using the Constant Level and Ramped Deposition Scenarios[a]

	LTA	TY	LTA-rbc	LTA-zbc
ANC (0)				
Mean	0.0	0.0	0.0	0.0
Δ-ANC (20)				
Mean	2.1	2.3	2.1	2.2
Std. Dev.	1.0	1.6	1.3	1.3
Median	1.7	1.9	1.6	1.7
Max	9.9	10.7	10.6	12.1
Δ-ANC (50)				
Mean	5.7	7.0	5.9	6.3
Std. Dev.	4.8	6.6	5.5	6.4
Median	3.0	3.8	3.1	2.9
Max	25.8	27.5	29.2	33.2
Δ-ANC (100)				
Mean	11.4	15.6	12.7	12.2
Std. Dev.	10.8	14.2	11.3	11.5
Median	4.7	11.3	5.4	4.5
Max	79.9	56.7	57.4	54.8

[a] The values were computed as the difference between ramped and constant deposition. The magnitude of the values can be compared to the descriptive statistics presented in Table 9-13 to obtain estimates of the absolute values of the changes incurred with the ramped datasets. Standard deviations are presented as absolute values.

SBRP Stream Reaches
Deposition = LTA
Year = 1
Model = Reuss
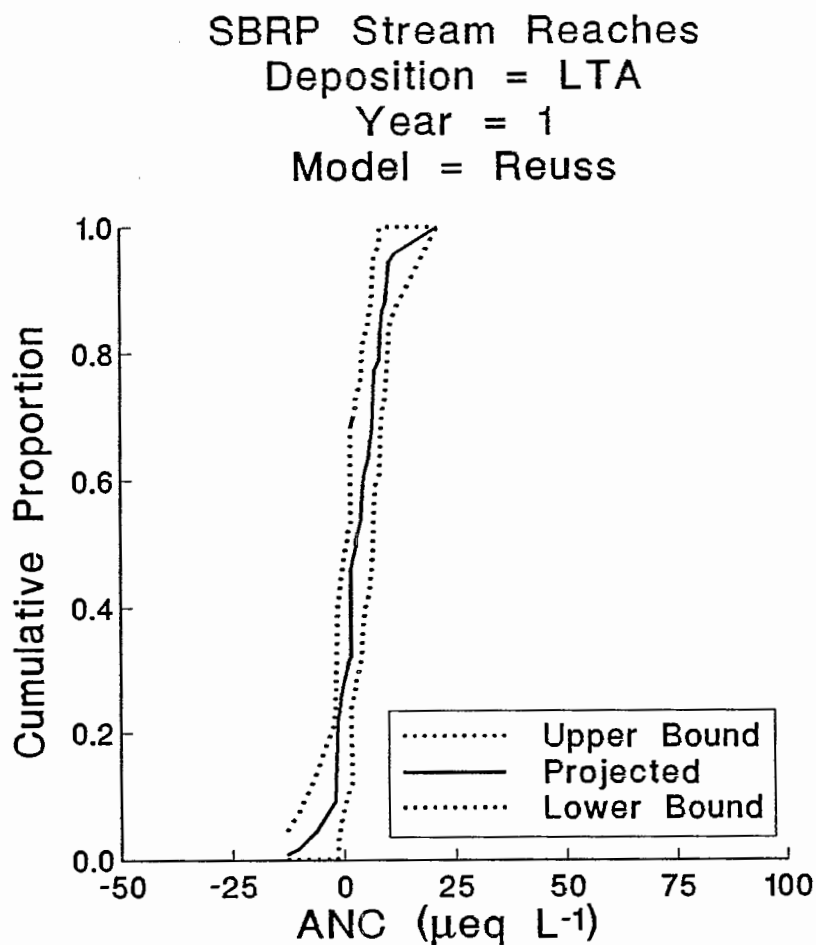
Figure 9-34. Cumulative distribution of projected present-day ANC values for stream reaches in the study population in the SBRP, as projections using Reuss's cation exchange model. Long-term average (LTA) deposition was used in making these projections. The error bounds on the plot are the 90 percent confidence intervals and were obtained using the parameter error estimates developed for northeastern region soils. Then, as completed in the NE, a Monte Carlo approach was used to obtain population estimates of the errors.

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Table 9-16. Summary Statistics for the Population Estimates of Current ANC Conditions for Stream Reaches in the SBRP for Four Different Deposition Scenarios (Refer to the text for explanation of the different input scenarios)

	LTA	TY	LTA-rbc	LTA-zbc
Mean	3.9	2.2	3.7	3.4
Std. Dev.	5.8	6.1	6.0	6.2
Median	2.9	2.3	2.9	2.9
P25	-0.55	-1.5	-0.55	-0.55
P75	7.0	4.7	6.7	6.5
Max	21.2	23.0	21.2	20.8
Min	-12.8	-14.1	-15.3	-17.7
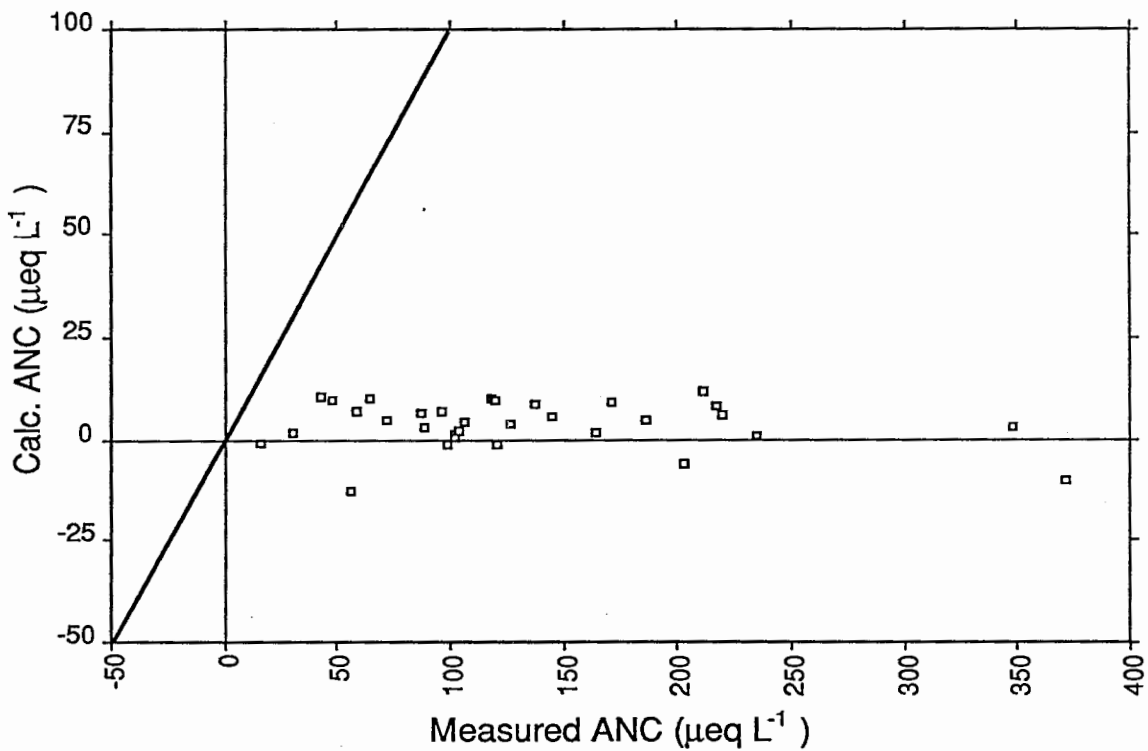
Figure 9-35. Scatter plot of the projected present-day ANC values for stream reaches in the SBRP, obtained using the Reuss model, vs. observed (NSS) values. The heavy diagonal line indicates the 1:1, or perfect correspondence, line. As is apparent, the model projects that current ANC values should cluster at values that are slightly in excess of 0 μeq L^{-1}. This is interpreted as indicating the importance of mineral weathering in controlling observed surface water compositions for the majority of systems in this region.

values (Figure 9-35). Mineral weathering also might explain why the observed ANC values are considerably higher than the model results.

9.3.3.1.2.2.2 Projected future conditions

As described for the NE, simulations of the time-dependent responses of the ANC in the study population stream reaches in the SBRP were conducted. Annual time steps were employed for these runs, and results were collected at 10-year intervals; data are summarized here for the 20-, 50-, 100-, and 200-year increments only.

Changes in the projected surface water ANC values are summarized in Table 9-17. During the first 50 years of these simulations, the Reuss model results suggest that changes, even the maximum changes, are trivial relative to our ability to measure representative ANC values. As base cation supply becomes depleted, these changes become much more dramatic, but this depletion is projected to occur on a century-long time scale. Mean and median changes for this region are estimated to be -20 ± 5 μeq L^{-1} on a 100-year time scale. Over two hundred years, these changes increase by a factor of 5 to approximately -100 ± 20 μeq L^{-1}. These changes are projected to occur regardless of the selected deposition scenario. These results are illustrated in Figures 9-36 and 9-37 for the LTA deposition.

Watersheds in the SBRP are projected to respond relatively uniformly to the different deposition scenarios, unlike the NE, for which a range of responses to acidic loadings was displayed. This observation can be explained by several factors. First, the watersheds in the SBRP were selected from a geographically more limited area than those in the NE. Second, the number of stream reaches studied in the SBRP is considerably smaller than the lake study population in the NE. This smaller subset of systems will limit the observed variability simply because of the reduced sample size being examined.

In examining the changes projected for surface waters in the SBRP, it is important to remember that the Reuss model is a cation exchange model, and it does not consider the effects of increasing anion mobility. At present, the soils in the SBRP are retaining significant percentages of sulfur being deposited in the region (see Sections 7 and 9.2). As a result, rates of base cation leaching from the soil exchange pool are probably less than those presented above because the total anion concentration in soil solutions are lower than considered in the model. The rates of leaching will increase as the soils approach zero net retention of sulfur and will approach the projected levels asymptotically. Therefore, the magnitude of observed changes should be some non-linear combination of the time frames involved in base cation leaching and changes in sulfur retention.

Mineral weathering would even further delay any anticipated changes in observed surface water ANC values. As weathering proceeds, additional cations are provided both to the exchange complex and to surface waters. As in the NE, it is not possible with the data and models currently available to isolate the separate effects of weathering and cation exchange. In a qualitative sense, however, we conclude base cation-related changes in surface water ANC in the SBRP should occur only on century-long time scales once the effects of weathering are incorporated into the projections.

The last major issue concerns the effects of ramped deposition datasets on the response of watersheds to acidic deposition. As discussed in Section 5.6, the ramping functions increased deposition

Table 9-17. Descriptive Statistics of the Population Estimates for Changes in Stream Reach ANC Values for Systems in the SBRP. Mean, Median, and Standard Deviations for the Population and the Maximum Changes Projected Are Presented for Each of the Four Deposition Scenarios at the Time Increments 20, 50, 100, and 200 Years

	LTA	TY	LTA-rbc	LTA-zbc
ANC(0) (Mean)	3.9	2.2	3.7	3.4
Δ-ANC (20)				
Mean	-1.2	-1.2	-1.2	-1.2
Std. Dev.[a]	0.4	0.7	0.5	0.4
Median	-1.2	-2.2	-1.9	-2.0
Max.	-1.8	-2.2	-1.9	-2.0
Δ-ANC (50)				
Mean	-3.0	-3.7	-3.5	-5.3
Std. Dev.	1.1	2.0	1.5	2.8
Median	-2.9	-4.0	-3.7	-4.8
Max.	-5.2	-7.4	-5.9	-10.9
Δ-ANC (100)				
Mean	-14.6	-23.0	-20.3	-33.7
Std. Dev.	6.0	16.2	12.8	23.6
Median	-14.8	-18.5	-18.3	-24.4
Max.	-27.4	-58.8	-48.0	-80.4
Δ-ANC (200)				
Mean	-81.2	-97.8	-97.3	-120.1
Std. Dev.	24.5	36.2	33.1	39.1
Median	-77.8	-103.3	-103.9	-122.7
Max.	-134.8	-161.7	-154.9	-185.3

[a] Standard deviations are reported as absolute values.
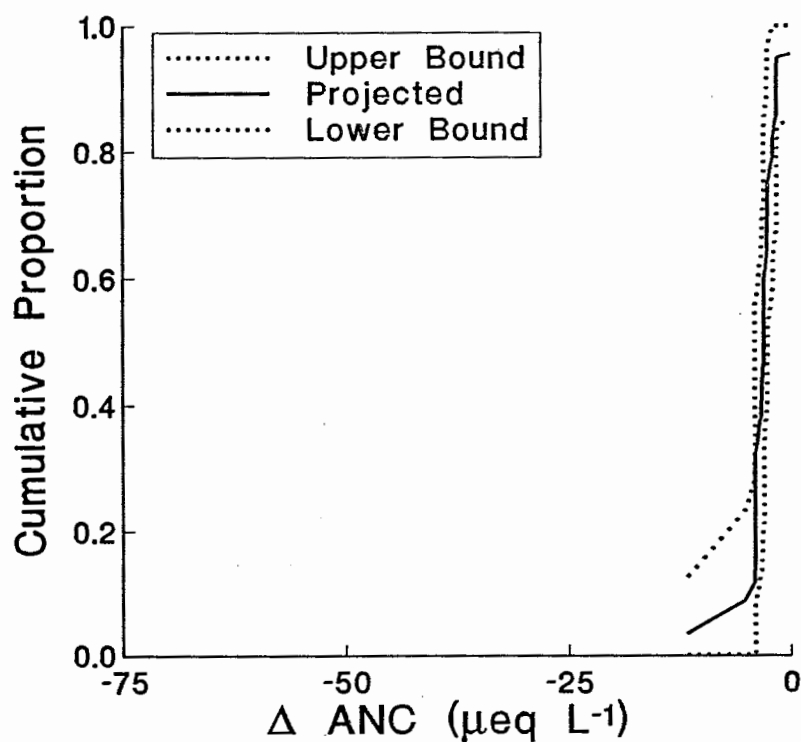
Figure 9-36. Cumulative distribution of projected changes (at 50 years) in surface water ANC obtained using the Reuss model for stream reaches in the SBRP. The deposition scenario used in making these projections was LTA. Confidence intervals around the distribution are based or uncertainty estimates of the individual parameters used in the model.

SBRP Stream Reaches
Deposition = LTA
Year = 100
Model = Reuss

Figure 9-37. Cumulative distribution of projected changes (at 100 years) in surface water ANC obtained using the Reuss model for stream reaches in the SBRP. The deposition scenario used in making these projections was LTA. Confidence intervals around the distribution are based on uncertainty estimates of the individual parameters used in the model. The "choppiness" of the curve is due, in part, to the smaller number (n=20) of watersheds for which 100-year projections were obtained.

by 20 percent during the 10- to 25-year time interval of each simulation. This ramping function was used in conjunction with each of the deposition datasets.

Differences in the projections of surface water ANC between the ramped and constant scenarios are given in Table 9-18. Not surprisingly, projected differences are minor during the first 50 years of the simulations, although the increased levels of deposition in the ramped dataset nearly double the median projected changes at 50 years (from -2.9 μeq L^{-1} to -5.0 μeq L^{-1}). At 100 years, the projections using the ramped deposition are double those for constant levels of deposition. Median changes between the deposition scenarios are not as large, but the ramped scenario projections result in changes that are 50 percent larger than those for the constant deposition. At 200 years, the medians of the population projections for the ramped and constant deposition scenarios continue to diverge. However, the differences in the population means have not changed substantially from those observed at 100 years, suggesting that the limiting values proscribed by the composition of the deposition are being attained.

9.3.3.1.2.3 Comparison of results from the Northeast and Southern Blue Ridge Province --

Comparison of the effects projected by the Reuss model in the two regions indicates both similarities and differences between the two regions. In both regions the soils behave initially as strong buffers for surface water ANC. Also, in both regions the projected present-day ANC values are generally substantially less than the actual observed values. These observations are interpreted to indicate the key role that mineral weathering plays in regulating ANC in surface waters of the two regions.

The soils in the two regions, however, are projected to respond differently to continued exposure to acidic deposition. At present levels of deposition, soils in the NE appear to be more susceptible to significant changes in the future than are the soils in the SBRP. In a sense, this conclusion is counter-intuitive because the soils in the NE tend to exhibit higher levels of base saturation (see Section 9.3.3.1.3.1.3). The soils in the NE, however, are also younger than those in the SBRP, and as a result, tend to have less clay-size materials. Because the bulk of the exchange capacity is associated with fine particles (see Section 8.8.1) and because the soils in the NE tend to be shallower than those in the SBRP, soils in the NE apparently have a lower overall capacity to supply base cations to surface waters from exchange processes.

9.3.3.1.2.4 Summary --

Several conclusions can be drawn from the observations made using the Reuss model and the projected behavior of watersheds in both the NE and SBRP.

- For lakes in the NE currently exhibiting ANC values in excess of 100 μeq L^{-1}, mineral weathering is probably the dominant watershed process controlling observed ANC values.

- At present levels of deposition, NE lakes with ANC values in excess of 100 μeq L^{-1} will probably not experience declining ANCs in the foreseeable future.

Table 9-18. Summary Statistics of the <u>Differences</u> Between the Population Estimates for Future ANC Projections Made Using the Constant Level and Ramped Deposition Scenarios for Stream Reaches in the SBRP[a]

	LTA	TY	LTA-rbc	LTA-zbc
ANC (0)				
Mean	3.9	2.2	3.7	3.4
Δ-ANC (20)				
Mean	-0.9	-1.0	-1.0	-1.0
Std. Dev.[a]	0.1	0.0	0.0	0.0
Median	-1.0	-0.9	-1.0	-1.0
Maximum	-1.1	-1.1	-0.9	-0.9
Δ-ANC (50)				
Mean	-1.5	-3.3	-2.9	-3.6
Std. Dev.	0.6	1.7	1.4	2.5
Median	-2.1	-3.2	-2.2	-2.6
Maximum	-6.9	-8.7	-18.1	-30.8
Δ-ANC (100)				
Mean	-8.7	-20.6	-15.6	-25.8
Std. Dev.	7.1	17.3	8.9	12.0
Median	-6.3	-11.9	-11.7	-31.5
Maximum	-41.1	-94.5	-35.9	-53.3
Δ-ANC (200)				
Mean	-24.3	-25.9	-26.8	-23.3
Std. Dev.	11.5	3.1	3.2	0.7
Median	-29.1	-19.6	-20.7	-18.3
Maximum	-95.9	-64.9	-90.2	-74.0

[a] The values were computed as the difference between ramped and constant deposition. The magnitude of the values can be compared to the descriptive statistics presented in Table 9-17 to obtain estimates of the absolute values of the changes incurred with the ramped datasets. Standard deviations are reported as absolute values.

- For lakes in the NE currently exhibiting ANC values of less than 100 μeq L^{-1}, soil exchange processes may be regulating the observed ANCs, although in most systems, the observed levels are probably controlled by a combination of cation exchange and mineral weathering.

- As an upper limit, over 1000 additional lakes in the NE region could become acidic (i.e., ANC $\leq$ 0 μeq L^{-1}) within a 50- to 100-year time frame. This is four times the number of lakes that are currently acidic. This number is considered to be extreme because the contribution of weathering is not included in these projections. However, some lakes are expected to become acidic during the next several decades.

- In the SBRP, changes in observed ANC values due to changes in the base status of soils during the next century should be minimal. Observed changes in this region will be driven primarily by changes in anion mobility in these soils (see Sections 7.3.4 and 9.2.3.2.3).

9.3.3.1.3 Projections of soil pH and percent base saturation -

Another concern regarding the effects of acidic deposition is the changes in soil pH and base saturation status. As discussed in Section 9.3.1.1, soils can be used as indicators of potential future changes. As with the ANC results, these model results are presented on a regional basis.

9.3.3.1.3.1 Northeast --

Unlike the ANC projections, for which the correspondence between observed and predicted values was only a secondary concern, the Reuss model should be able to predict observed soil pH values with a reasonable degree of accuracy. (Present day base saturation is an input to the model and, as such, cannot be used in this type of an analysis.) Figure 9-38 illustrates the correlation between the observed and predicted soil pH values for all of the master horizon/watershed combinations considered in the NE. Two features are immediately apparent from this plot.

First, there is a high correlation between the observed and predicted values. In general, the model tends to over-predict individual observations. For measured pH values greater than about 4.0, the model results exceed measured values by 0.20 $\pm$ 0.10 pH units. The divergence between the two increases substantially at pH values below 4.0. Therefore, the Reuss model reasonably predicts the relative differences in soil pH among soils (for pH values exceeding 4.0).

Second, the model predicts very few soil pH values of less than 4.0, and, in fact, the data appear to reach a plateau at soil pH values of about 4.25 $\pm$ 0.25. Effectively, the lower limit to soil-water acidity is defined by hydrogen ion content of deposition after it has undergone evapotranspirative concentration. This lower limit is about 3.8 in the NE region (precipitation with a pH of 4.2, concentrated by 40 percent through evapotranspiration). Within the Reuss formulation, no provisions are available to address acidity generated by organic processes, and only limited acidity can be added to soil solutions by the exchange of base cations in deposition for acid cations on soil exchange sites. For these reasons, the model has difficulty predicting the extremely low pH values observed in most O horizons and in the organic-rich A

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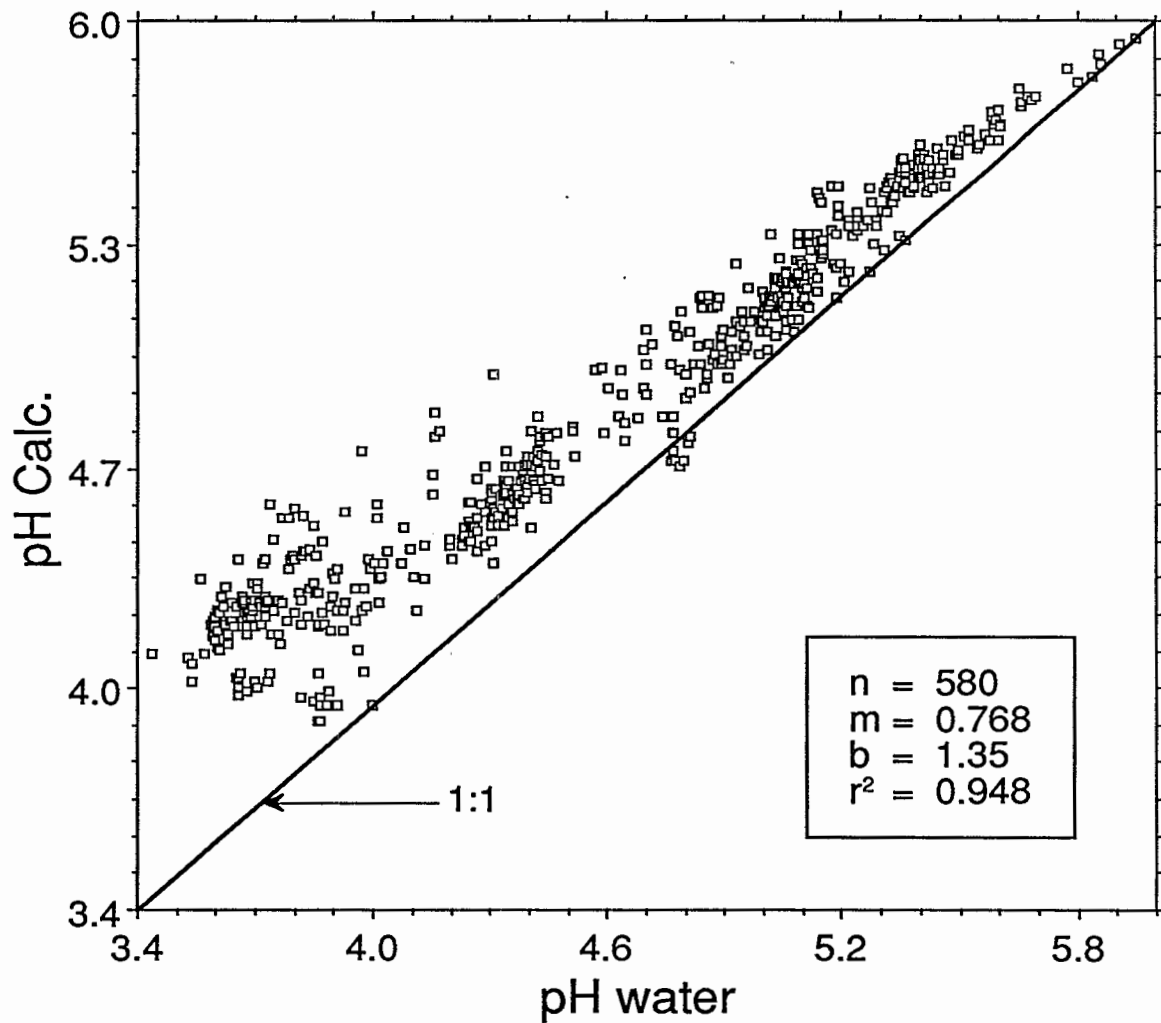
Figure 9-38. Comparison of measured vs. calculated soil pH values for the 580 aggregated master horizons in the NE. The heavy diagonal line is the 1:1, perfect correspondence line. In general, the model slightly over-projects soil pH values.

Table 9-19. Summary Statistics of the Projected Changes in Soil Base Saturations in the NE Region, Obtained Using the Different Deposition Scenarios or Soil Aggregation Schemes. The Time Increments Included in the Table Are 20, 50, and 100 Years

	LTA	TY	LTA-rbc	LTA-zbc	WBA
% BS (Initial)					
Mean	20.9	20.9	20.9	20.9	24.4
Std. Dev.[a]	10.5	10.5	10.5	10.5	20.3
Median	17.6	17.6	17.6	17.6	16.7
Δ-% BS (20 years)					
Mean	-1.4	-1.4	-1.4	-1.4	-1.7
Std. Dev.	0.9	0.9	0.9	0.9	1.6
Median	-1.3	-1.3	-1.3	-1.3	-1.5
Max.	-6.0	-6.0	-6.0	-6.0	-5.0
Δ-% BS (50 years)					
Mean	-3.5	-3.7	-3.7	-3.8	-4.2
Std. Dev.	1.7	2.0	1.8	1.8	3.9
Median	-3.4	-3.5	-3.5	-3.6	-4.3
Max.	-11.0	-13.0	-11.0	-12.0	-20.0
Δ-% BS (100 years)					
Mean	-7.6	-7.9	-8.0	-8.4	-7.5
Std. Dev.	3.2	3.4	3.3	3.6	6.5
Median	-7.5	-8.1	-7.9	-8.1	-6.4
Max.	-17.0	-21.0	-18.0	-20.0	-33.0

[a] Standard deviations are reported as absolute values.

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Table 9-20. Summary Statistics of the Projected Changes in Soil pH in the NE Region, Obtained Using the Different Deposition Scenarios or Soil Aggregation Schemes. The Time Increments Included in the Table are 20, 50, and 100 Years

	LTA	TY	LTA-rbc	LTA-zbc	WBA
Soil pH (initial)					
Mean	5.32	5.30	5.32	5.32	5.30
Std. Dev.[a]	0.194	0.206	0.194	0.194	0.206
Median	5.34	5.33	5.34	5.34	5.33
Δ-Soil pH (20 years)					
Mean	-0.075	-0.075	-0.078	-0.081	-0.046
Std. Dev.	0.140	0.132	0.143	0.145	-0.131
Median	-0.032	-0.040	-0.036	-0.037	-0.011
Maximum	-0.68	-0.67	-0.71	-0.73	-0.65
Δ-Soil pH (50 years)					
Mean	-0.167	-0.181	-0.181	-0.192	-0.116
Std. Dev.	0.187	0.198	0.194	0.203	0.177
Median	-0.086	-0.105	-0.108	-0.114	-0.048
Maximum	-0.88	-0.90	-0.91	-0.94	-0.84
Δ-Soil pH (100 years)					
Mean	-0.355	-0.385	-0.389	-0.418	-0.289
Std. Dev.	0.278	0.298	0.295	0.310	0.274
Median	-0.272	-0.326	-0.299	-0.344	-0.210
Maximum	-1.10	-1.12	-1.12	-1.15	-1.01

[a] Standard deviations are reported as absolute values.
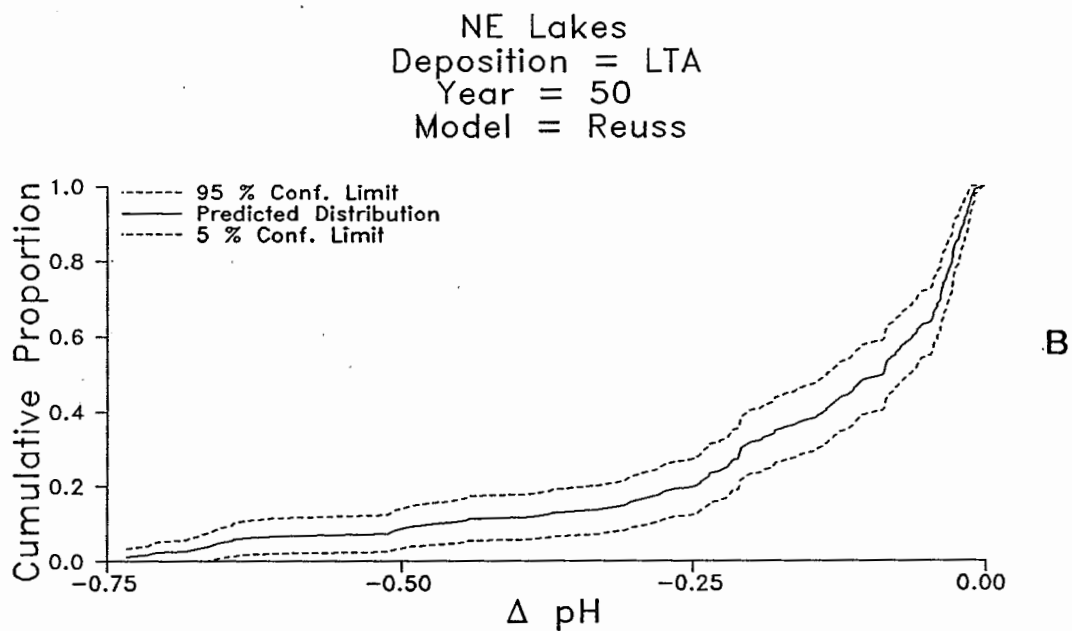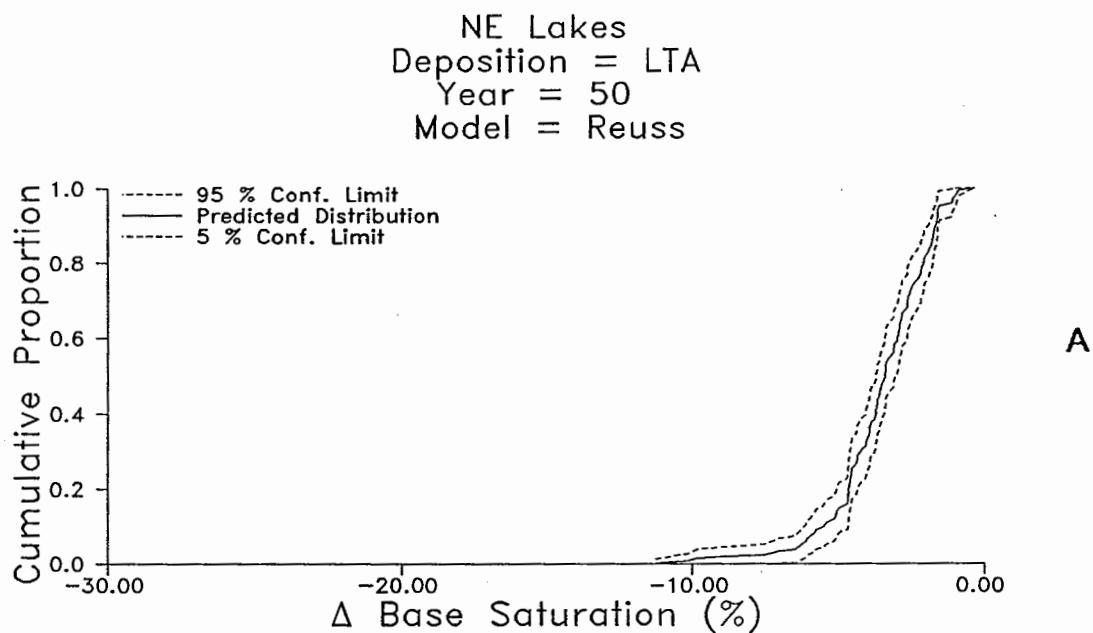
Figure 9-39. Cumulative distribution of projected (a) base saturations and (b) soil pH values for soils in NE. Projections were made using the Reuss model in conjunction with the LTA (constant level) deposition. The results are presented for 50 years.

NE Lakes
Deposition = LTA
Year = 100
Model = Reuss

A

NE Lakes
Deposition = LTA
Year = 100
Model = Reuss

B
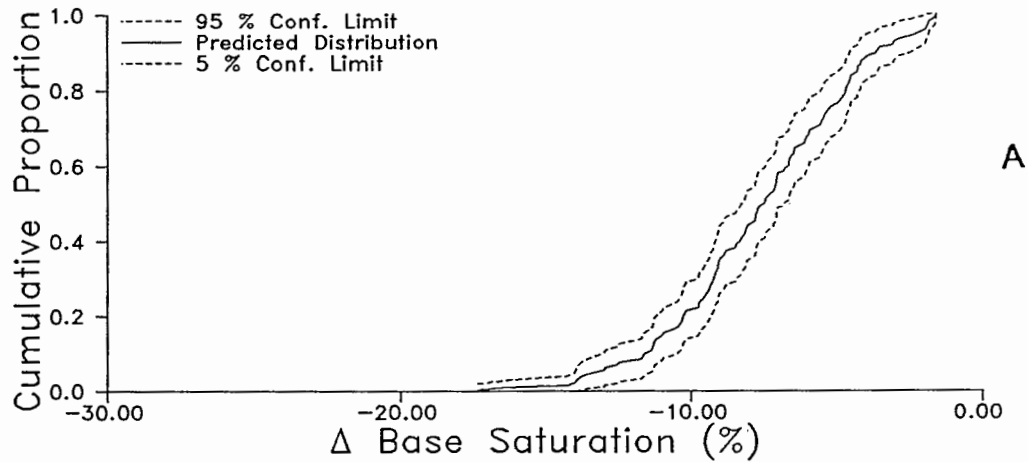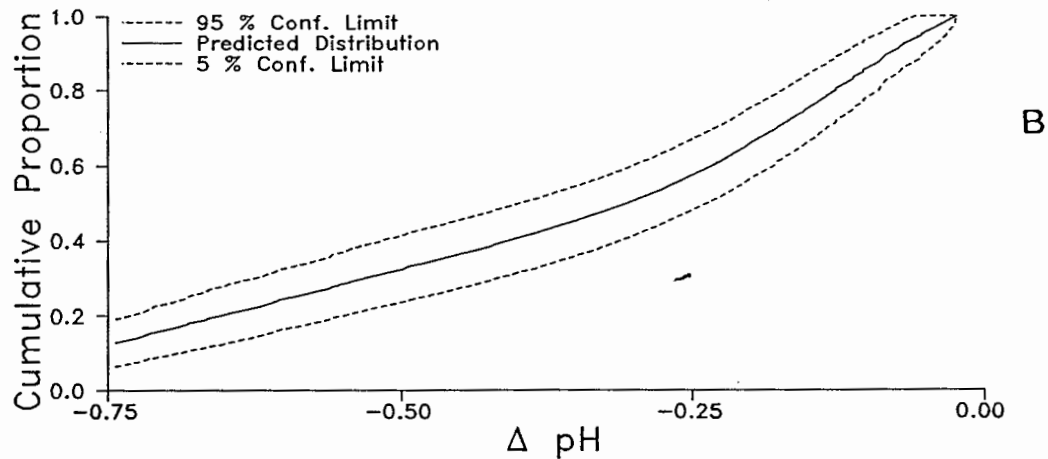
Figure 9-40. Cumulative distribution of projected (a) base saturations and (b) soil pH values for soils in the NE. Projections were made using the Reuss model in conjunction with the LTA (constant level) deposition. The results are presented for 100 years.
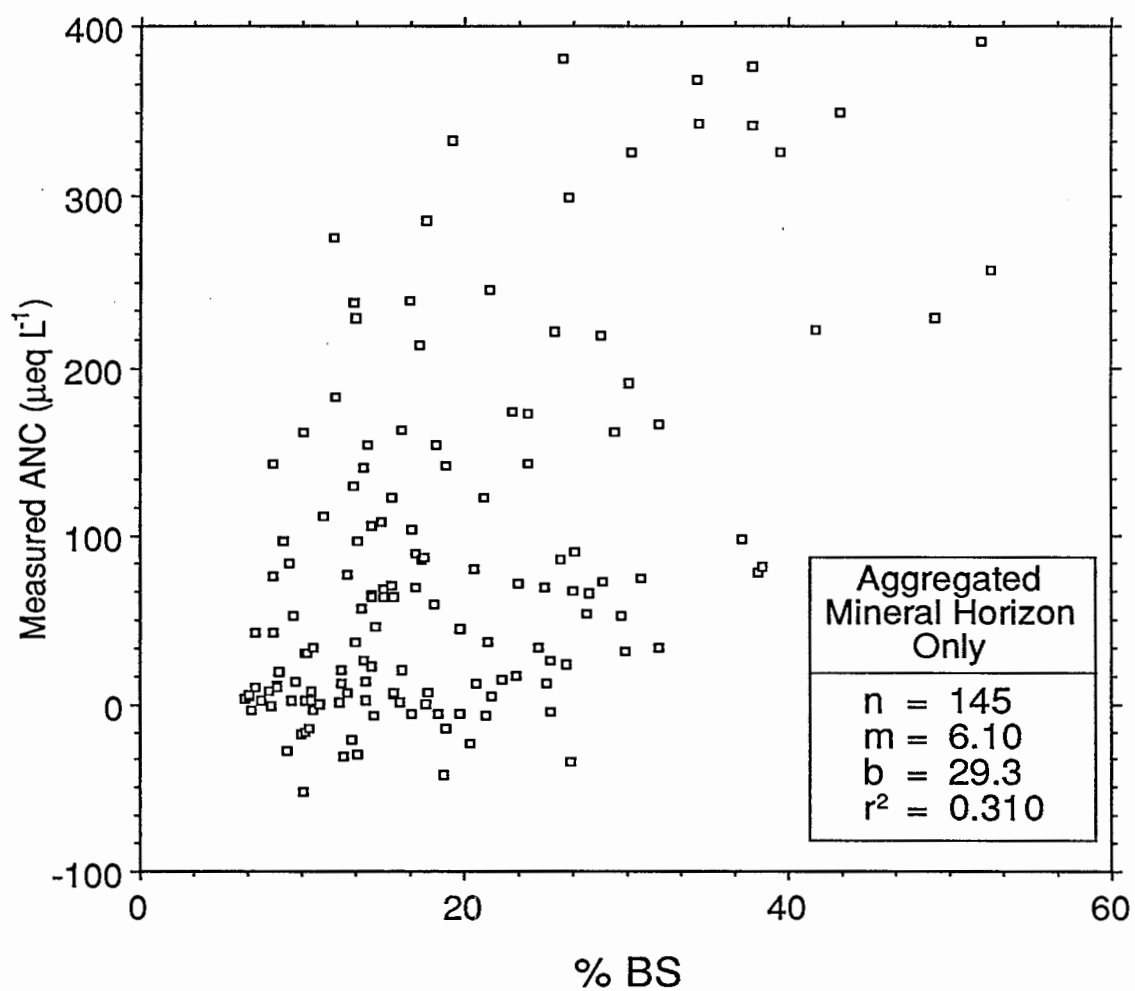
Figure 9-41. Plot of the measured (ELS) ANC values for lakes in the NE vs. the estimated, watershed-level base saturations for mineral horizons in those watersheds.
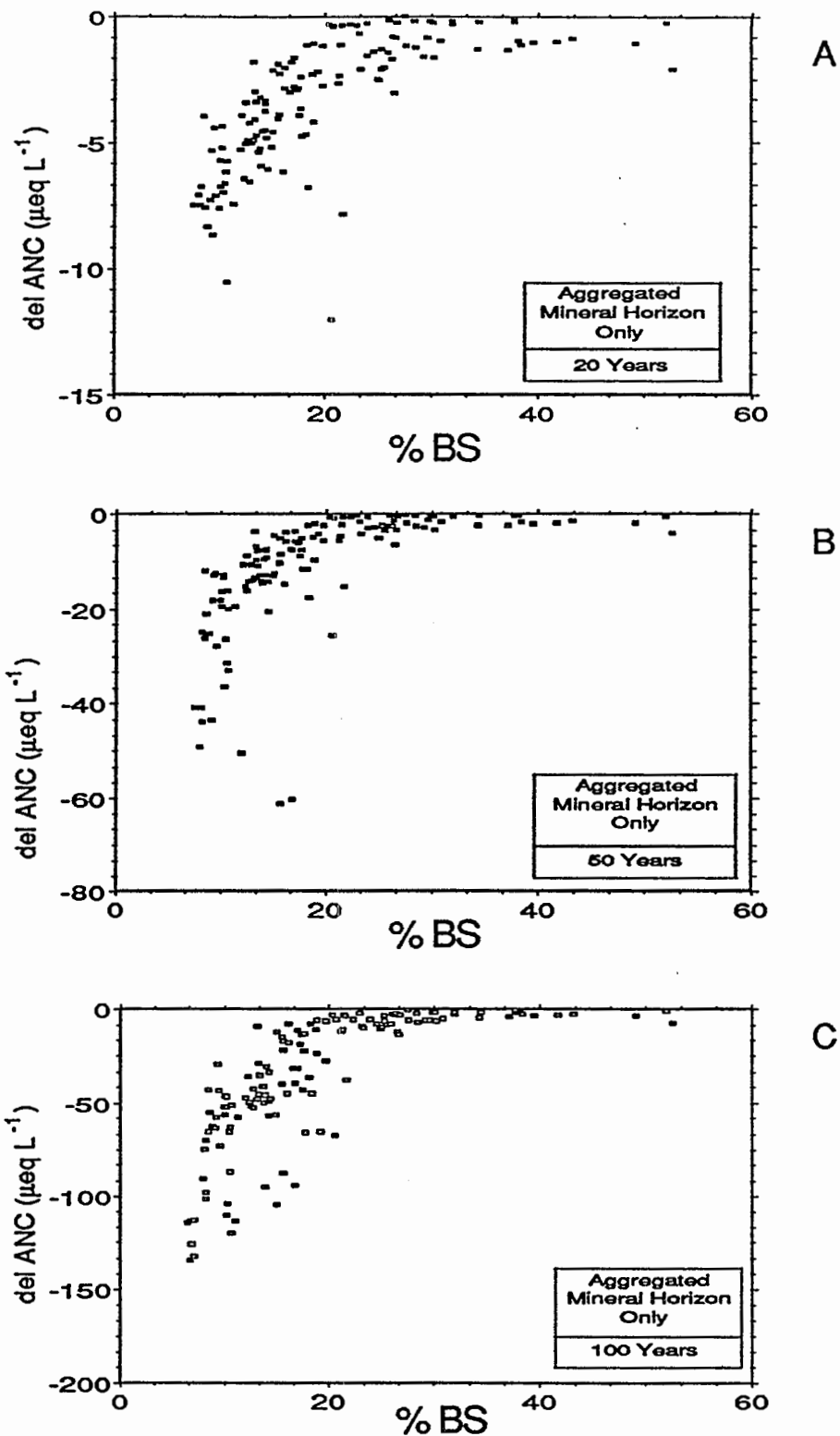
Figure 9-42. Plot of the changes in surface water ANC values at (a) 20, (b) 50, and (c) 100 years as projected by the Reuss model vs. the estimated, present-day, watershed-level base saturations for mineral horizons in those watersheds. The deposition used in computing these differences is the LTA deposition.
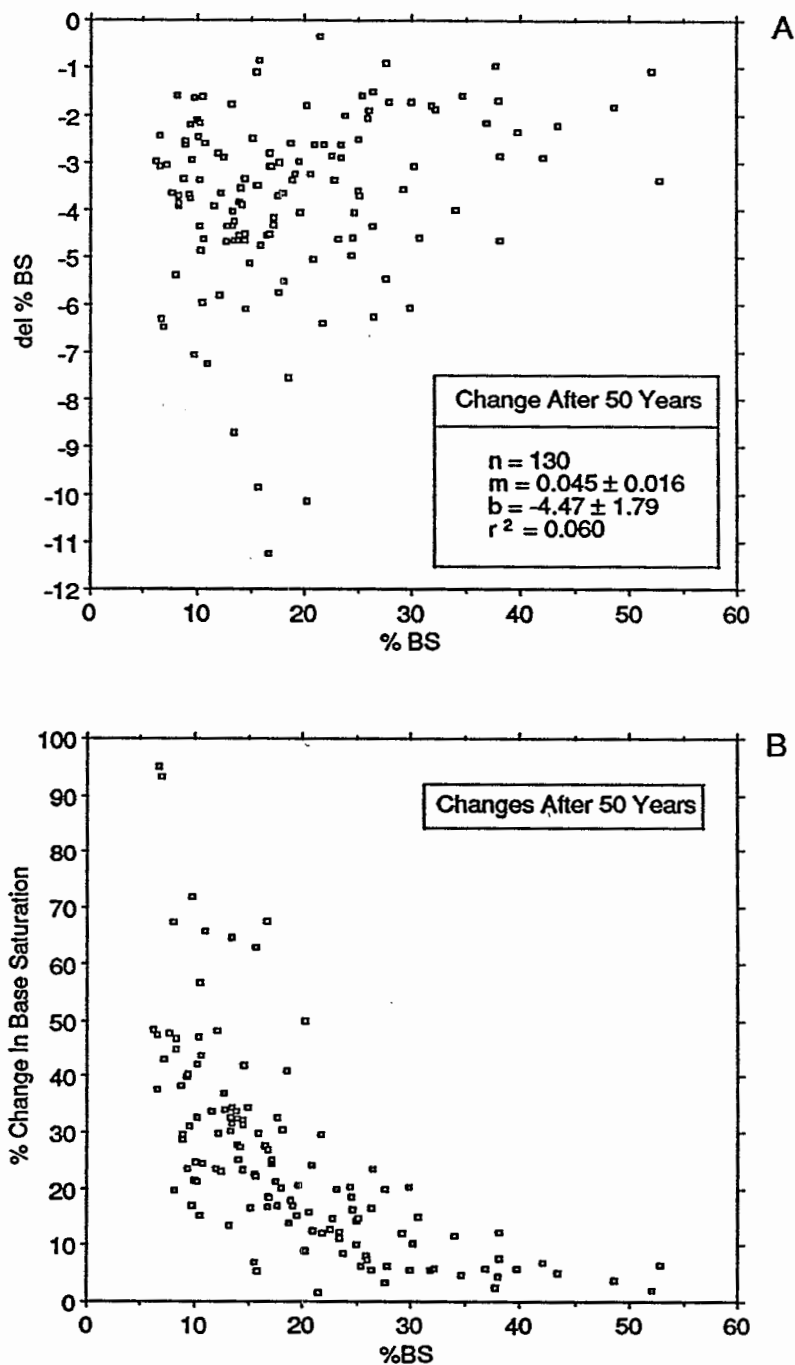
Figure 9-43. Plot of the projected changes in soil base saturations vs. the observed, present-day, aggregated base saturations for mineral horizons in the NE. The projections were made with the Reuss model using LTA deposition. The data are presented for 50-year projections. Data in plot (A) illustrate the absolute changes that are projected using the model. Plot (B) illustrates the relative changes that are projected to occur.

horizons. For most other horizons, however, the relationship between observed and predicted soil pH values are acceptable.

Projections regarding future changes in base saturation and pH of soils in the NE are listed in Tables 9-19 and 9-20, respectively. The projections are illustrated in Figures 9-39 and 9-40 for 50 and 100 years, respectively. Mean and median changes in soil base saturation exhibit uniform rates of depletion of about 0.75 percent ± 0.05 percent per year throughout the simulations regardless of the deposition scenarios used. The rates of depletion are slightly higher for the reduced base cation loading scenarios, as expected. Extreme values are only about three times the magnitude of the mean changes observed for the population of systems being studied. Soil pH values show similar time-dependent changes (Table 9-20). Soil pH values decline at a mean rate of about 0.04 pH units per year throughout the simulation, with only minor, but consistent, differences projected among the different deposition scenarios.

The data presented here are based on the results aggregated from mineral horizons only. An issue of concern with these results, therefore, is the possible effect that organic horizons might have on the magnitude or direction of changes projected by the model. To evaluate this issue, the model runs using data aggregated both with and without the presence of organic layers would need to be conducted. These model runs have not been performed. However, this issue, is addressed in Section 9.3.3.2 for the Bloom-Grigal model. The importance of organic horizons in regulating changes to soil chemistry are presented there.

9.3.3.1.3.2 Soils as an indicator of possible future changes in ANC --

Soils may serve as indicators of future changes occurring because of acidic deposition. An analysis of this hypothesis is useful for identifying those systems that are most susceptible to adverse changes. This information also could be used in the design phases of a monitoring program. To conduct this analysis, aggregated, watershed-level estimates of mineral horizon base saturations were obtained for the 145 watersheds in the NE. These data were plotted against (1) the observed lake water ANC values for each of the lakes and (2) the projected changes in ANC at 20, 50 and 100 years. Figure 9-41 shows the relationship observed between aggregated soil base saturations and surface water ANC. These data support a significant relationship between these variables (see Section 8.8.1). Although there is considerable scatter in the results, lakes with lower ANC values tend to have soils with lower aggregated base saturations.

The relationship between current base saturation and projected changes in ANC is more pronounced, as illustrated in Figure 9-42. In this analysis, the projected magnitude of change in ANC at 20-, 50-, and 100-year intervals is related to the current, aggregated watershed base saturation. At each of these time steps, watersheds with aggregated soil base saturations in excess of 20 percent exhibit little or no significant decline in projected ANC over the course of the simulations. As the base saturations decrease below 20 percent, however, there is a marked increase in the magnitude of the response of individual systems to the effects of acidic deposition. These results suggest that systems with aggregate base saturation of less than 20 percent should be most susceptible to the effects of acidic deposition, at least in terms of projected changes in surface water ANC.

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An alternative approach is to examine changes in soil base saturations as a function of the current state of the systems. Figure 9-43A shows the relationship between current, aggregated, mineral soil base saturations and projected changes in base saturation at 50 years. A significant relationship does not exist between the magnitude of the projected changes and the current base saturation of the systems being studied. This result is interesting, especially in light of the rather strong relationship observed between base saturation and the projected change in surface water ANC. The observation suggests that the largest changes in soil base saturation (in the absence of weathering) occur independently of the present base status of soils. The magnitude of the changes may be mediated by physical factors, such as the thickness or bulk density of the soils. There are some chemical limitations on these changes as well.

Current base saturation is related to the relative magnitude of changes expected to occur in the base status of these soils (Figure 9-43B). Although the data are scattered somewhat (probably due to differences in soil physical parameters and to variations in soil exchange properties) the lower the initial base saturation, the greater the projected relative depletion of base cations from the soil exchange complex. This result is consistent with the observations concerning surface water ANC changes and demonstrates that the soils are behaving in an internally consistent manner.

As noted throughout this section, the Level II models are, by and large, single-process models, used in this context to determine the contribution of individual processes to the integrated responses of watersheds as complete systems. The suggestion that systems with base saturations in excess of 20 percent are at minimal risk to future change needs to be considered in the context of the complete system. Therefore, watersheds with higher aggregate base saturation could experience significant acidification if other processes, such as hydrologic routing of water within the soils and ground water, restrict the degree of interaction between soils and soil-water. Similarly, the present base saturation status of soils probably plays only a limited role in regulating episodic acidification (as opposed to chronic acidification, the principal issue of concern in this report).

Conversely, soils with base saturations of less than 20 percent might not experience significant chronic depletions in ANC if related processes, such as mineral weathering, were able to sustain current base saturations. The above analysis, however, suggests that these systems are more susceptible to adverse changes. Programs designed to monitor future changes should consider using soil base saturation status as one criterion for site selection.

9.3.3.1.3.3 Southern Blue Ridge Province --

Summaries of the results for the SBRP are given in Tables 9-21 and 9-22 and in Figures 9-44 and 9-45. Soils in the SBRP currently have base saturations that are half as large as those in the NE (see Section 5.5.1.3). For this reason, it is reasonable to expect both larger and more rapid responses to the effects of acidic deposition in the SBRP compared to the NE. Examination of the model results, however, suggests that the soils in the SBRP respond more slowly to acidic deposition than do the soils in the NE.

At 50 years, the average base saturations in SBRP soils have declined by between 20 percent and 30 percent, depending on the deposition scenario considered. These declines are equivalent to absolute changes in base saturation of 2 to 3 percent. By 100 years, the average base saturation for the soils

Table 9-21. Summary Statistics of the Projected Changes in Soil Base Saturations in the SBRP, Obtained Using the Different Deposition Scenarios. The Time Increments Included in the Table Are 20, 50, 100, and 200 Years

	LTA	TY	LTA-rbc	LTA-zbc
%_BS (initial)				
Mean	10.5	10.5	10.5	10.5
Std. Dev.[a]	5.7	5.7	5.7	5.7
Median	9.3	9.3	9.3	9.3
Δ-%_BS (20 years)				
Mean	-0.49	-0.55	-0.59	-0.70
Std. Dev.	0.27	0.29	0.30	0.32
Median	-0.44	-0.51	-0.51	-0.59
Max	-1.09	-1.18	-1.18	-1.26
Δ-%_BS (50 years)				
Mean	-1.89	-2.41	-2.37	-2.94
Std. Dev.	0.37	0.58	0.37	0.49
Median	-1.90	-2.52	-2.42	-2.96
Max	-2.80	-4.26	-3.28	-3.82
Δ-%_BS (100 years)				
Mean	-5.16	-6.04	-6.00	-7.16
Std. Dev.	0.76	1.14	0.70	0.99
Median	-5.06	-5.64	-5.84	-7.15
Max	-7.24	-9.22	-7.93	-8.90
Δ-%_BS (200 years)				
Mean	-8.83	-9.03	-9.36	-9.44
Std. Dev.	0.99	1.38	1.45	1.32
Median	-8.78	-9.10	-9.44	-9.68
Max	-12.41	-12.41	-13.03	-12.41

[a] Standard deviations are reported as absolute values.

Table 9-22. Summary Statistics of the Projected Changes in Soil pH in the SBRP, Obtained Using the Different Deposition Scenarios. The Time Increments Included in the Table Are 20, 50, 100, and 200 Years

	LTA	TY	LTA-rbc	LTA-zbc
Soil pH (initial)				
Mean	5.15	5.12	5.15	5.15
Std. Dev.[a]	0.10	0.10	0.10	0.10
Median	5.13	5.12	5.12	5.13
Δ-Soil pH (20 years)				
Mean	-0.03	-0.03	-0.03	-0.04
Std. Dev.	0.01	0.01	0.01	0.01
Median	-0.03	-0.03	-0.04	-0.04
Maximum	-0.06	-0.06	-0.06	-0.06
Δ-Soil pH (50 years)				
Mean	-0.10	-0.13	-0.13	-0.19
Std. Dev.	0.03	0.05	0.05	0.06
Median	-0.10	-0.15	-0.14	-0.20
Maximum	-0.19	-0.21	-0.21	-0.27
Δ-Soil pH (100 years)				
Mean	-0.34	-0.40	-0.41	-0.52
Std. Dev.	0.09	0.14	0.12	0.14
Median	-0.35	-0.47	-0.45	-0.57
Maximum	-0.49	-0.64	-0.58	-0.68
Δ-Soil pH (200 years)				
Mean	-0.66	-0.65	-0.69	-0.74
Std. Dev.	0.15	0.16	0.15	0.17
Median	-0.67	-0.64	-0.71	-0.81
Maximum	-0.82	-0.81	-0.84	-0.86

[a] Standard deviations are reported as absolute values.

SBRP Stream Reaches
Deposition = LTA
Year = 50
Model = Reuss

A

SBRP Stream Reaches
Deposition = LTA
Year = 50
Model = Reuss

B
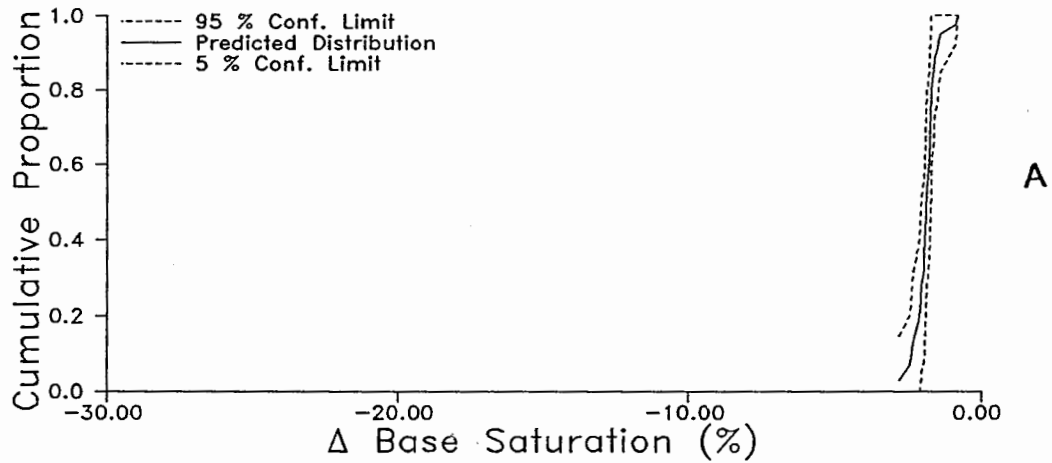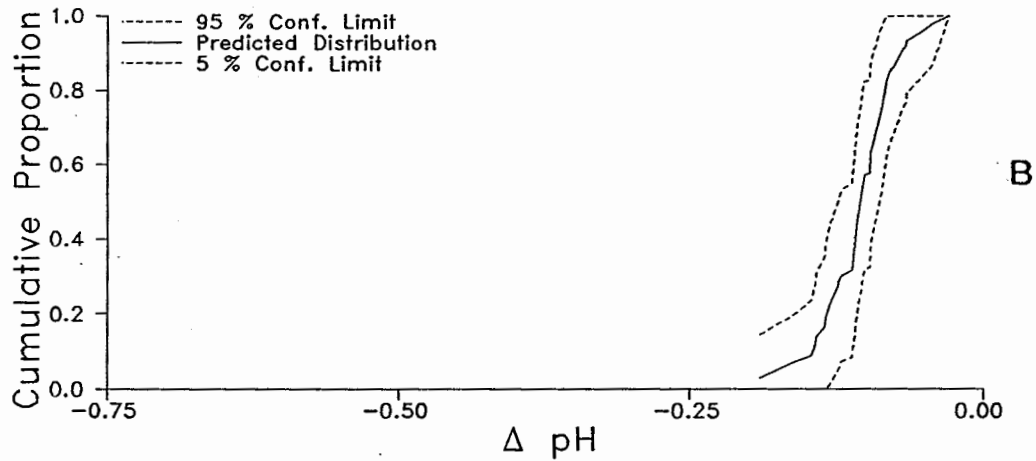
Figure 9-44. Cumulative frequencies of changes in (a) soil base saturation and (b) soil pH for the population of soils in the SBRP. The projections are for year 50 and have been computed using LTA deposition data.
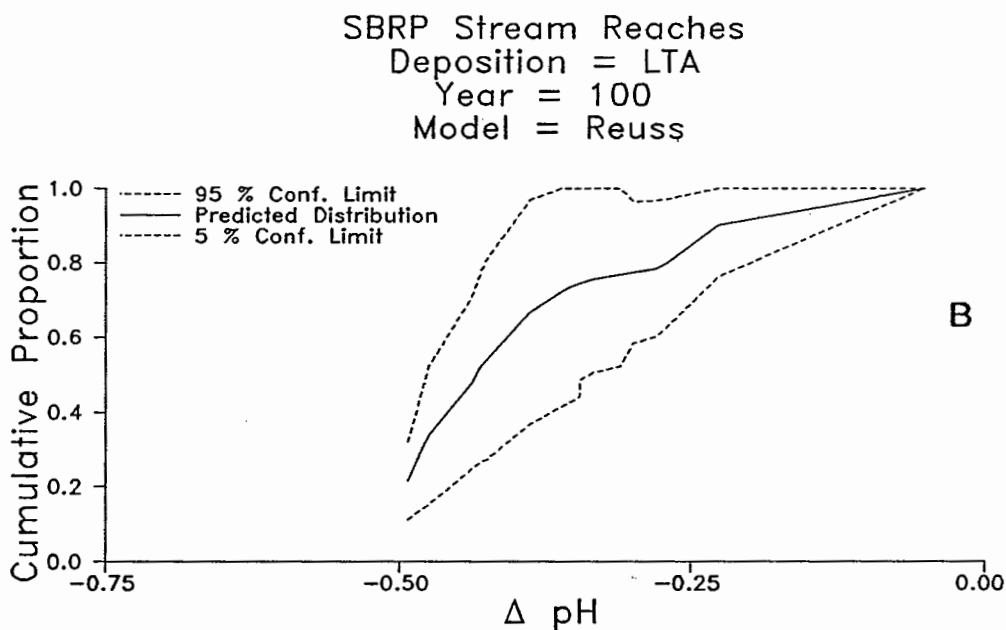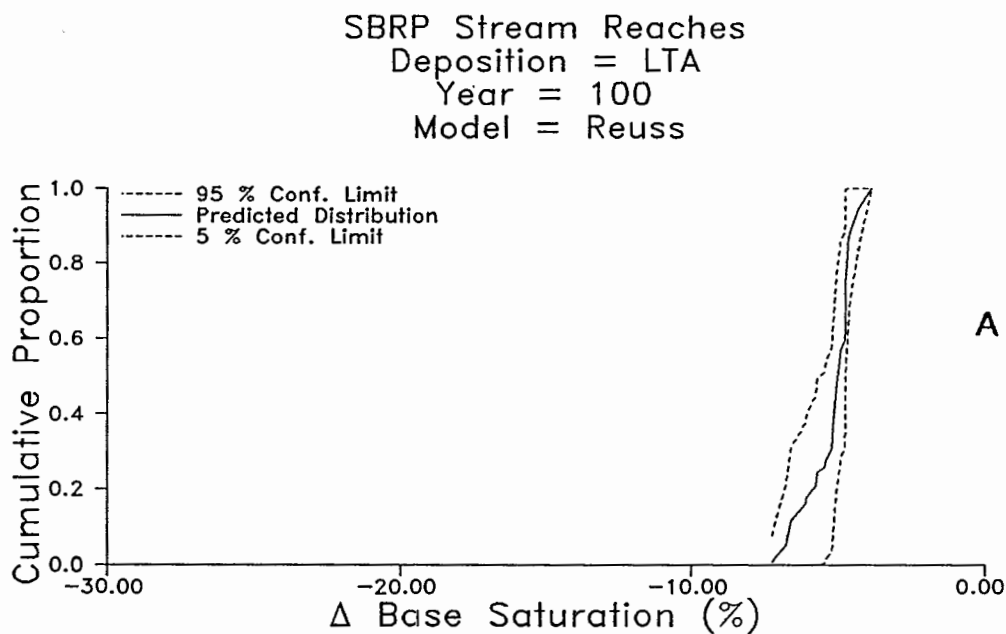
Figure 9-45. Cumulative frequencies of changes in (a) soil base saturation and (b) soil pH for the population of soils in the SBRP The projections are for year 100 and have been computed using LTA deposition data.

in this region have declined by 60 percent ± 10 percent, and by 200 years, by approximately 90 percent. Again, these projections are made with the assumption that weathering is not supplying base cation to the soils of the region. Clearly, primary mineral weathering supplies base cations to these soils and, hence, soil acidification will be slower than the rates projected here.

Changes in soil pH projected using the Reuss model are parallel to those projected for the soil base cations. Changes are minimal at 20 years, with an absolute magnitude of the projected changes of0.04 pH units, regardless of the deposition scenario used. By 50 years, the changes are significant. Within this time frame, soil pH values have declined by an average of about 0.13 pH units, depending on the deposition scenario. The rate of decline in soil pH increases between 50 and 100 years. At this point, the soil is projected to be losing much of the buffering capacity, with a resultant drop in soil pH. By 200 years, when much of the soil buffering capacity has been depleted, the average soil pH has declined to values near the minimum that can be reached in the context of the Reuss model framework.

9.3.3.1.3.4 Regional comparisons --

Results from the Reuss modelling effort have led to many observations concerning the soil behavior in the two regions and how that behavior affects the ANC of waters passing through those soils (see Table 9-23). First, the absolute rate of cation depletion is slower in the SBRP than it is in the NE. Within the first 50 years, mean base saturations have declined by about 3.5 percent in the NE, while they have declined by only slightly less than 2 percent in the SBRP. However, in terms of the percentage of available cations, cation depletion is severe in the SBRP. After 50 years, between 20 and 30 percent of the cations on soil exchange sites have been lost through leaching, whereas in the NE only about 15-20 percent of the available cations are lost during the same time period. These trends continue at 100 years. In the NE, base saturations have declined by about 7.5 percent, or about one third of the total supply of available cations on soil exchange sites. In the SBRP, base saturations have declined by only slightly more than 5 percent. However, this decline constitutes more than half of the available buffering capacity.

For soil pH, parallel trends to those describe above are observed. In the NE, soil pH values decline by about 0.2 pH units during the first 50 years of the simulations, while in the SBRP, the average change is on the order of 0.1 pH units. However, because soil pH values in the NE are initially higher than those in the SBRP by an average of about 0.15 pH units, the observed differences result primarily in a lessening of the disparity between the two regions in terms of their characteristic pH values. By 100 years, changes in soil pH in the SBRP have started to accelerate such that the absolute magnitude of the differences observed between the two regions are, again, equal to about 0.15 pH units. We interpret this observation as an indication that the loss of buffering capacity occurs later in the SBRP relative to the NE. This difference is attributable to differences in soil physical properties, such as soil thickness and bulk density, rather than to differences in soil chemical characteristics. The absolute magnitude of the changes projected for the two regions is equal to about 0.35-0.4 pH units (depending on the deposition scenario considered).

Results from the Reuss model suggest that, in the absence of mineral weathering, both regions will sustain substantial losses of base cations from their soils. In translating these changes into the effects on surface water chemistry, the model results suggest that the largest effects (on the time scale of 100

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Table 9-23. Comparison of the Changes in Soil Base Saturation and Soil pH that Are Projected to Occur in the NE and SBRP. The Projections Have Been Obtained Using Reuss's Cation Exchange Model and Are Presented for Two Deposition Scenarios, the LTA and TY Depositions

	LTA		TY	
	NE	SBRP	NE	SBRP
Δ_ANC (year 50)				
Mean	-13.7	-2.96	-16.1	-3.7
Std. Dev.[a]	23.6	1.05	26.4	2.0
Δ_%BS (Year 50)				
Mean	-3.5	-1.9	-3.7	-2.4
Std. Dev.	1.7	0.4	2.0	0.5
Δ_Soil pH (Year 50)				
Mean	-0.17	-0.10	-0.18	-0.13
Std. Dev.	0.19	0.03	0.20	0.05
Δ_ANC (Year 100)				
Mean	-32.1	-14.6	-43.1	-23.0
Std. Dev.	36.1	6.04	51.5	16.2
Δ_% BS (Year 100)				
Mean	-7.6	-5.2	-7.9	-6.0
Std. Dev.	3.2	0.8	3.4	1.1
Δ_Soil pH (Year 100)				
Mean	-0.36	-0.34	-0.39	-0.40
Std. Dev.	0.28	0.09	0.30	0.14

[a] Standard deviations are reported as absolute values.

years) will be observed in the NE. Larger changes are projected to occur much earlier in the NE. For example, after 50 years, the mean change in projected surface water ANC in the SBRP is less than -3 μeq L^{-1}, whereas it is more than -13 μeq L^{-1} in the NE. At 100 years, the rate of ANC decline has increased in the SBRP. At this point, the projected change for the SBRP is about -15 μeq L^{-1} (using the LTA deposition; this change is about -23 μeq L^{-1} for the TY deposition). However, this change is still only half the magnitude of that projected to occur in the NE, regardless of the deposition scenario. Therefore, larger relative changes in the base cation pool are projected for the soils in the SBRP; the larger projected effects of those changes appear in the surface waters of the NE region.

9.3.3.1.3.5 Summary --

A number of observations and conclusions can be drawn from results obtained using the Reuss model to evaluate changes in soil pH and base saturations in the NE and SBRP regions.

- In the absence of mineral weathering, significant depletions of base cations are projected for the soils of both the NE and SBRP regions.

- The absolute magnitude of base cation depletion is greater in the NE than it is in the SBRP. The relative projected changes, however, are greater in the SBRP.

- Current base saturation of soils in the regions can be used as indicators of potential future change in surface water ANC. Soils with base saturations currently in excess of about 20 percent appear to undergo minimal changes on the time scale of the next 100 years. For soils with base saturations less than 20 percent, however, projected changes in surface water ANC appear to increase with decreasing aggregate base saturation. This effect is more pronounced in the NE region than it is in the SBRP.

- Current base saturation can be used as an indicator of the anticipated relative changes that might occur in the soil base status over the next 100 years. The percentage decline in base saturation increases with decreasing base saturation, although other factors, such as soil thickness or bulk density, probably influence the relationship as well.

9.3.3.2 Bloom-Grigal Model

9.3.3.2.1 Data sources -

In the DDRP, the basic unit of investigation is the watershed. Instead of characterizing the effects of acidic deposition on individual soils, the research focus is the integrated effect of the soils on a particular watershed. Consequently, all of the Bloom-Grigal modelling input data are at the watershed level. Because the DDRP sample of watersheds serve as the basic link to the target population of watersheds, watershed level results can be extrapolated to the target population of watersheds.

The data required to run the Bloom-Grigal model include total annual wet and dry deposition, total annual runoff, and selected soil chemistry data. All of these data were collected as a part of the DDRP and are discussed in detail in Section 5.

9.3.3.2.1.1 Deposition data --

The deposition data are from four sources: (1) Typical Year (TY), (2) Long-Term Annual Average (LTA), (3) LTA Reduced Base Cation (LTA-rbc)--LTA with a 50 percent reduction in dry base cations, and (4) LTA Zero Base Cation (LTA-zbc)--LTA with a 100 percent reduction in dry base cations. Both of these reductions in dry base cations are offset by concomitant increases in dry H^+. The details on the acquisition/generation of the DDRP deposition data sets are given in Section 5.6.

A summary of the regionally weighted median deposition inputs in the four deposition data sets (LTA, LTA-rbc, LTA-zbc, and TY) used in the Bloom-Grigal modelling is presented in Table 9-24 by region. In the NE there appears to be little difference between LTA and TY. A priori, we expect to see only minor differences in the forecasts made with these two deposition data sets. The SBRP TY median value of H^+ is 22 percent greater than the LTA value. The NH_4^+ is, however, lower and NO_3^- is greater. Consequently, the total effective acidity ($H^+_{total} = H^+ + NH_4^+ - NO_3^-$) is only slightly larger.

The largest differences in H^+_{total} are between the LTA and the reduced (LTA-rbc) and zero (LTA-zbc) deposition data sets. In the NE the difference between the median H^+_{total} in the LTA and median value of H^+_{total} in the LTA-zbc is 0.19 keq ha^{-1}, while in the SBRP this difference is 0.24 keq ha^{-1}. Such differences should result in differences in projections, especially for the higher levels of H^+_{total}.

9.3.3.2.1.1.1 Deposition scenarios --

The Level II base cation models are run with three deposition scenarios. The scenario common to both the NE and SBRP is the constant deposition scenario. In this scenario the annual load of deposition is held constant for the duration of the simulation.

9.3.3.2.1.1.2 Northeast --

In addition to the constant deposition scenario in the NE, a ramp down scenario is used to simulate a 30 percent decrease in wet and dry SO_4^{2-} deposition. Deposition is held constant for the first 10 years of the simulation. Beginning with the eleventh year, deposition is decreased by 2 percent per year for 15 years for a total decrease of 30 percent. This new level is then held constant for the duration of the simulation.

9.3.3.2.1.1.3 Southern Blue Ridge Province --

In addition to the constant deposition scenario in the SBRP, a ramp up scenario is used to simulate a 20 percent increase in wet and dry SO_4^{2-} deposition. Deposition is held constant for the first 10 years. Beginning with the eleventh year, deposition is increased by (20/15) percent per year for 15 years for total increase in deposition of 20 percent. This new level is then held constant for the duration of the simulation.

Table 9-24. Regionally Weighted Median Values of Initial Annual Deposition Inputs to the Bloom-Grigal Model for the Northeastern Region and the Southern Blue Ridge Province[a]

	H^+	NH_4^+	NO_3^-	Total Acid Input[b]
NE				
LTA	0.71	0.15	0.44	0.43
LTA - rbc	0.79	0.15	0.44	0.49
LTA - zbc	0.91	0.15	0.44	0.62
TY	0.78	0.14	0.45	0.44
SBRP LTA	0.67	0.22	0.42	0.47
LTA - rbc	0.82	0.22	0.42	0.61
LTA - zbc	0.97	0.22	0.42	0.77
TY	0.82	0.16	0.46	0.51

[a] Values are in keq ha^{-1} yr^{-1}

[b] Total Acid Input = $[H^+ + NH_4^+ - NO_3^-]$

9.3.3.2.1.2 Soils data --

The Bloom-Grigal model uses one value for the following soil chemistry variables to depict the soil chemistry of a particular watershed: soil pH, cation exchange capacity (CEC), and the sum of exchangeable base cations (SOEBC). To obtain results that represent the central tendency of the DDRP regions, a large number of observations for these variables were aggregated to obtain values for each of the DDRP watersheds. Combining or aggregating these data can be accomplished in several ways. It is not correct to use a simple average for all variables; rather, capacity and intensity variables should be weighted differently. Of the variables used in the Bloom-Grigal model simulations, soil pH was aggregated using an intensity variable aggregation method, whereas CEC and SOEBC were aggregated using a capacity variable aggregation method. The details of these methods are provided in Johnson et al. (1988b).

To evaluate the role of soil organic horizons (Oa, Oe, and Oi) in the chemistry of soils, the soils data for the Bloom-Grigal data were aggregated two ways: (1) including organic horizons and (2) excluding organic horizons.

A summary of the regionally weighted median values of the Bloom-Grigal soil chemistry input data (aggregated with and without organic horizons) is presented in Table 9-25. In the NE, inclusion of the organic horizons decreases the median pH by 0.30 and base saturation by slightly more than 1 percent. In the SBRP the changes are even more negligible. Although the pH and SOEBC values are similar between the regions, CEC in the SBRP is more than twice that in the NE. Simply stated, the soils in the SBRP have greater exchangeable acidity than those in the NE with similar SOEBC.

The regional initial soil pH and percent base saturation with and without organic horizons are presented in Figure 9-46 as cumulative distribution functions (CDFs). This manner of presentation allows interregional and intraregional differences to be easily observed. The soil pH in the SBRP is less affected by the exclusion of the organic horizons than in the NE.

9.3.3.2.2 Projections of soil ph and percent base saturation -

In all, Bloom-Grigal model simulations representing more than 300,000 years were needed to obtain the results for the four deposition data sets and different deposition scenarios. A subset of these is presented below by region, and a regional comparison follows in Section 9.3.3.2.3.

9.3.3.2.2.1 Northeast --

The results of the Bloom-Grigal simulations in the NE with LTA, LTA-rbc, and LTA-zbc are presented in Figures 9-47 and 9-48 for the change in soil pH and percent base saturation, respectively. Statistical summaries of the CDFs are presented in Tables 9-26 and 9-27.

The projected changes in soil pH and percent base saturations using the constant LTA deposition scenario are quite small (Figure 9-47). The median change after 100 years is only -0.04. Of the systems in the target population, less that 25 percent of the watersheds have a projected decrease in soil pH greater than -0.10. The largest decrease is projected to be -0.35. Most of these changes are probably

Table 9-25. Regionally Weighted Median Values of Annual Initial Soil Chemical Values Input Into the Bloom-Grigal Model for the Northeastern Region and the Southern Blue Ridge Province[a]. With and Without Organic Soil Horizons

		pH	SOEBC	CEC	BS
NE					
	With[b]	4.62	40.04	183.8	21.98
	W/O	4.92	34.11	177.4	20.60
SBRP					
	With	4.85	40.42	433.3	9.22
	W/O	5.01	40.62	436.4	9.20

pH	=	intensity weighted soil pH
SOEBC	=	mass weighted sum of exchangeable base cations
CEC	=	mass weighted cation exchange capacity
BS	=	base saturation [(SOEBC/CEC)*100]

[a] All values in keq ha^{-1} except BS which is percent.
[b] "With" means that organic soil horizons were included. "W/O" means that organic soil horizons were excluded.
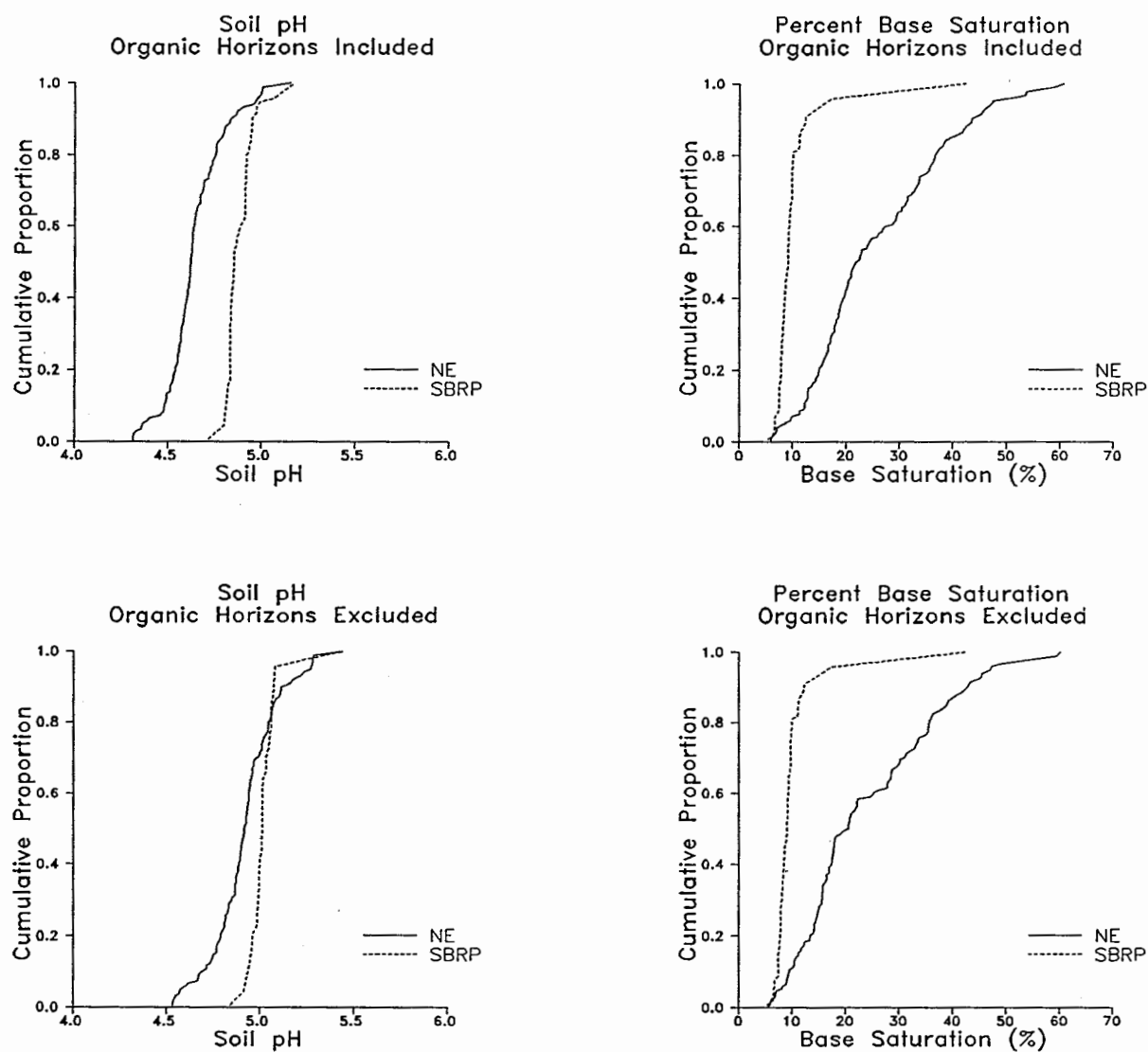
Figure 9-46. Cumulative distributions of aggregate initial soil pH and percent base saturation in the NE and SBRP, with and without organic horizons.
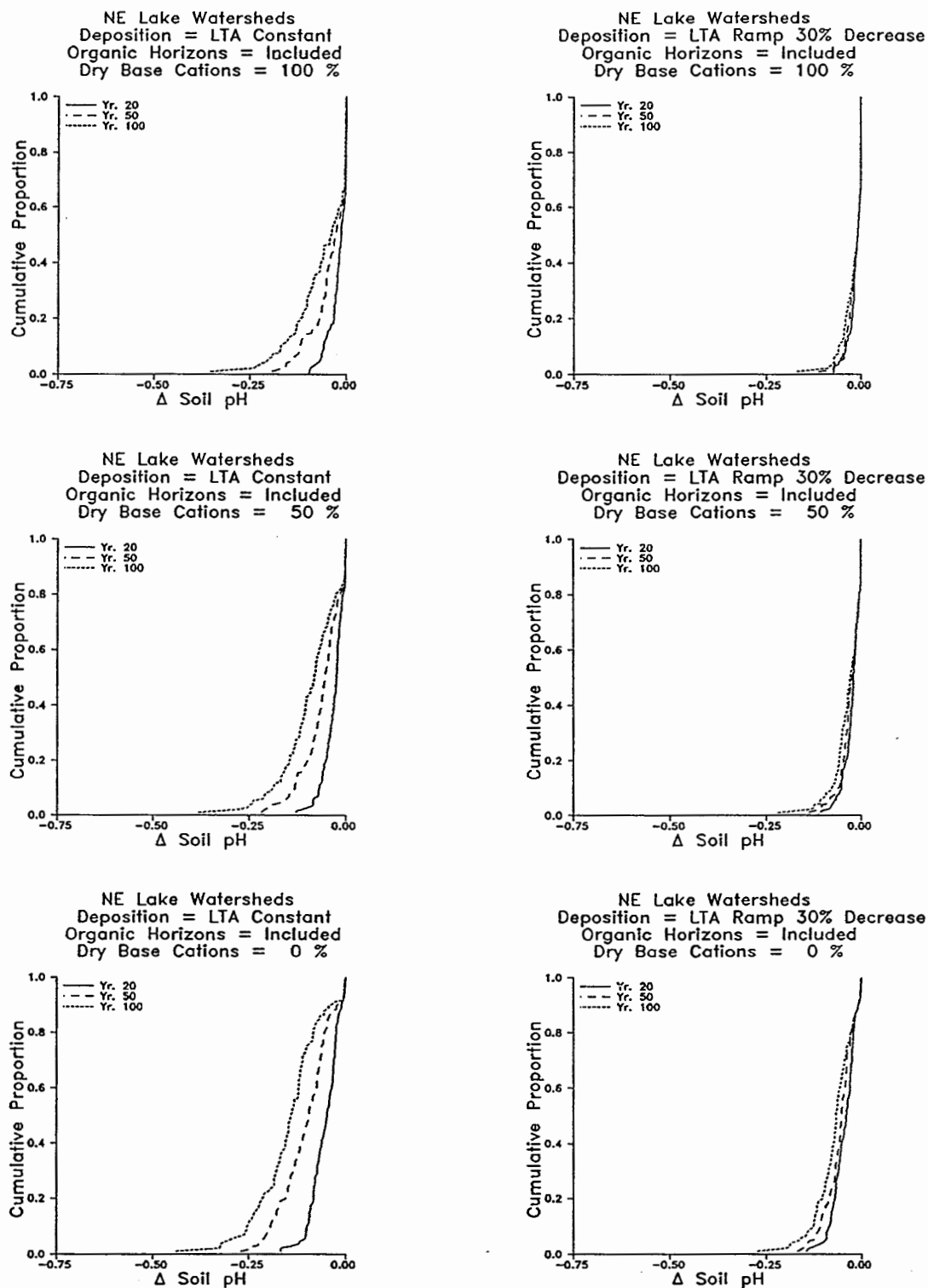
Figure 9-47. Regional CDFs of the projected change in the pH of soils on NE lake watersheds under constant and ramp down (30 percent ↓) deposition scenarios after 20, 50, and 100 years of LTA, LTA-rbc, and LTA-zbc deposition. Organic horizons are included.
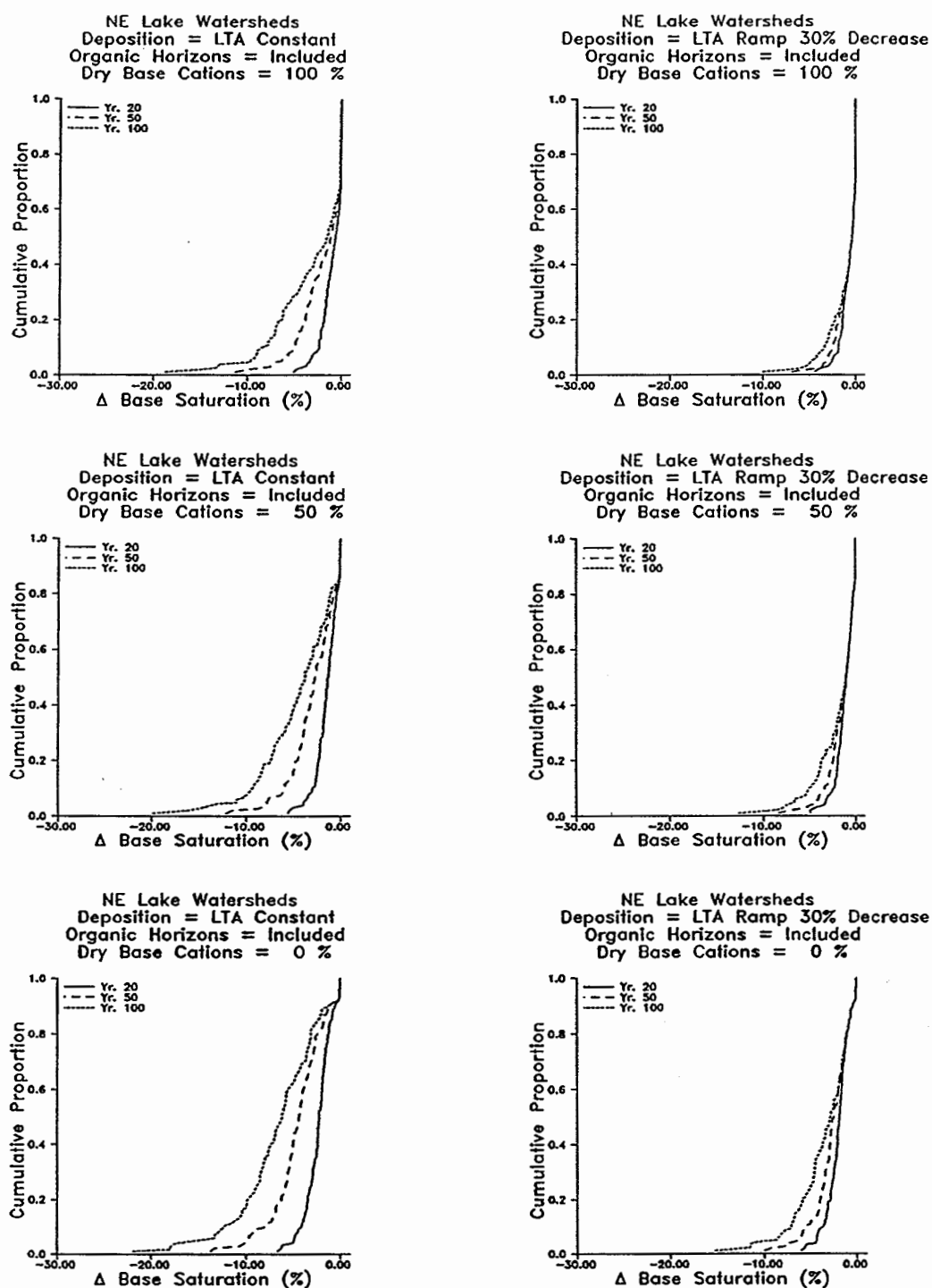
Figure 9-48. Regional CDFs of the projected change in the percent base saturation of soils on NE lake watersheds under constant and ramp down (30 percent ↓) deposition scenarios after 20, 50, and 100 years of LTA, LTA-rbc, and LTA-zbc deposition. Organic horizons are included.

Table 9-26. Bloom-Grigal Model Regional Projections for the Change in Soil pH in the Northeastern United States. Projections Made Using LTA, LTA-rbc, and LTA-zbc Deposition with Constant and 30% Ramped Down Deposition Scenarios at Three Levels of Base Cations in Dry Deposition. Results Reported for 20-, 50-, and 100-Year Projections. Organic Soil Horizons Included

Deposition = Constant ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.02	0.02	-0.10	-0.03	-0.01	0.00	0.00
50	-0.04	0.05	-0.19	-0.06	-0.03	0.00	0.00
100	-0.06	0.07	-0.35	-0.10	-0.04	0.00	0.00

Deposition = Constant ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.03	0.03	-0.13	-0.04	-0.02	-0.01	0.00
50	-0.06	0.05	-0.22	-0.09	0.05	-0.02	0.00
100	-0.09	0.07	-0.38	-0.13	-0.08	-0.04	0.00

Deposition = Constant ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.05	0.04	-0.17	-0.08	-0.05	-0.03	0.00
50	-0.10	0.06	-0.27	-0.14	-0.09	-0.06	0.00
100	-0.14	0.08	-0.44	-0.18	-0.14	-0.10	0.00

Deposition = 30% Decrease ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.01	0.02	-0.07	-0.02	-0.01	0.00	0.00
50	-0.02	0.02	-0.11	-0.03	0.01	0.00	0.00
100	-0.02	0.03	-0.17	-0.03	-0.01	0.00	0.00

Table 9-26. (Continued)

| | | Deposition = 30% Decrease ** Dry Base Cations = 50% ** LTA - rbc | | | | | |
YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.02	0.02	-0.11	-0.03	-0.02	-0.01	0.00
50	-0.03	0.03	-0.14	-0.04	-0.02	-0.01	0.00
100	-0.04	0.04	-0.22	-0.05	-0.03	-0.01	0.00

| | | Deposition = 30% Decrease ** Dry Base Cations = 0% ** LTA - zbc | | | | | |
YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.05	0.03	-0.15	-0.07	-0.04	-0.02	0.00
50	-0.06	0.04	-0.17	-0.07	-0.05	-0.03	0.00
100	-0.07	0.05	-0.27	-0.10	-0.07	-0.04	0.00

Table 9-27. Bloom-Grigal Model Regional Projections of the Change in Percent Base Saturation in the Northeastern United States. Projections Made Using LTA, LTA-rbc, and LTA-zbc Average Deposition with Constant and 30% Ramped Down Deposition Scenarios at Three Levels of Base Cations in Dry Deposition. Results Reported for 20-, 50-, and 100-Year Projections. Organic Soil Horizons Included

Deposition = Constant ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.97	1.11	-5.00	-1.58	-0.57	0.00	0.00
50	-2.00	2.34	-11.26	-3.49	-1.05	0.00	0.00
100	-3.15	3.79	-18.70	-5.83	-1.46	0.00	0.00

Deposition = Constant ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-1.43	1.20	-5.56	-2.09	-1.25	-0.49	0.00
50	-2.90	2.47	-12.11	-4.14	-2.63	-0.96	0.00
100	-4.45	3.95	-19.88	-6.96	-3.68	-1.26	0.00

Deposition = Constant ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-2.32	1.41	-6.63	-3.05	-2.24	-1.50	0.00
50	-4.52	2.80	-13.72	-5.74	-4.29	-2.70	0.00
100	-6.58	4.33	-21.94	-8.82	-6.16	-3.36	0.00

Deposition = 30% Decrease ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.74	0.90	-4.38	-1.32	-0.38	0.00	0.00
50	-0.90	1.20	-6.86	-1.43	-0.38	0.00	0.00
100	-1.14	1.69	-10.03	-1.57	-0.38	0.00	0.00

Table 9-27. (Continued)

Deposition = 30% Decrease ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-1.18	1.07	-4.94	-1.69	-1.00	-0.31	0.00
50	-1.49	1.54	-8.36	-2.25	-1.03	-0.31	0.00
100	-1.91	2.26	-12.66	-2.55	-1.03	-0.31	0.00

Deposition = 30% Decrease ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-2.02	1.29	-6.02	-2.71	-1.86	-1.19	0.00
50	-2.68	1.97	-10.01	-3.57	-2.50	-1.21	0.00
100	-3.49	2.95	-15.27	-4.83	-2.85	-1.21	0.00

within the uncertainty of the model and are not significant. With the LTA-rbc and LTA-zbc deposition larger decreases in soil pH in a greater proportion of the systems is evident. Yet, even at the highest level of acidic input (LTA-zbc), the median change in soil pH is only -0.14. Larger decreases are evident in a few systems (<10 percent).

Ramping the deposition down by 30 percent reduces the projected declines significantly. With LTA-zbc the median decline in soil pH is -0.07, one half that projected for the constant LTA scenario. The results for the projected change in base saturation are similar to those for pH. However, when the initial median base saturation is only 17 percent, a decrease of 6 percent (LTA-zbc) after 100 years (to 11 percent) is projected. The 30 percent decrease in deposition results in smaller changes.

Excluding the organic horizons results in an amplified decrease in soil pH and base saturation (Figures 9-49 and 9-50, Tables 9-28 and 9-29). Without the contribution of the organic horizons, the median change in soil pH and percent base saturation after only 20 years is nearly equal to or greater than the 100-year projections for soils with organic horizons. This result is misleading, however. The initial median pH of the soils without the organic horizons is 4.92, and after 100 years of LTA deposition the median change is -0.21. For the soils with the organic horizons the initial median pH is 4.62, and after 100 years the median change is only -0.04. Thus, although pH of the soils without the organic horizons had greater projected changes, their pH values were still projected to be higher at the end of the 100-year simulation.

As for pH, the decrease in percent base saturation for the soils with the organic horizons is greater than for the soils without the organic horizons. However, because percent base saturation is initially lower for the soils without the organic horizons, the projected percent base saturation is much lower than for the soils with the organic horizons.

There are two principal explanations for the above results. First, soils without organic horizons have higher initial pH values. At higher pH values less Al is available to buffer the losses of base cations. Recalling Equation 9-9 (S = I - A - C), the tendency of a system to lose bases (S) increases if the inputs of acidity (I) are held constant and the buffering of Al (A) and protonation of bicarbonate (C) are decreased. Such is the case at higher pH values. Second, the large decreases in soil pH result from low base saturation, as reflected by the equation that relates soil pH to base saturation (see Equation 9-12). For low base saturation (<20 percent), the slope of the pH versus percent base saturation line increases dramatically and small changes in base saturation result in large changes in pH. Because the systems without organic horizons have higher pH values, their base cation losses are greater than for other soils with lower pH values (e.g., the soils with the organic horizons) assuming all other soils characteristics are the same. The loss rate of base cations decreases, however, as the soil pH decreases. Turchenek et al. (1987) and Turchenek et al. (1988), also using the Bloom-Grigal model, demonstrated similar results.

The median change in base saturation after 50 years of constant LTA deposition on soils without organic horizons is -4.38, and the pH change is -0.12. After an additional 50 years, the percent base saturation decreases by an additional -2.44 and the pH by -0.09.
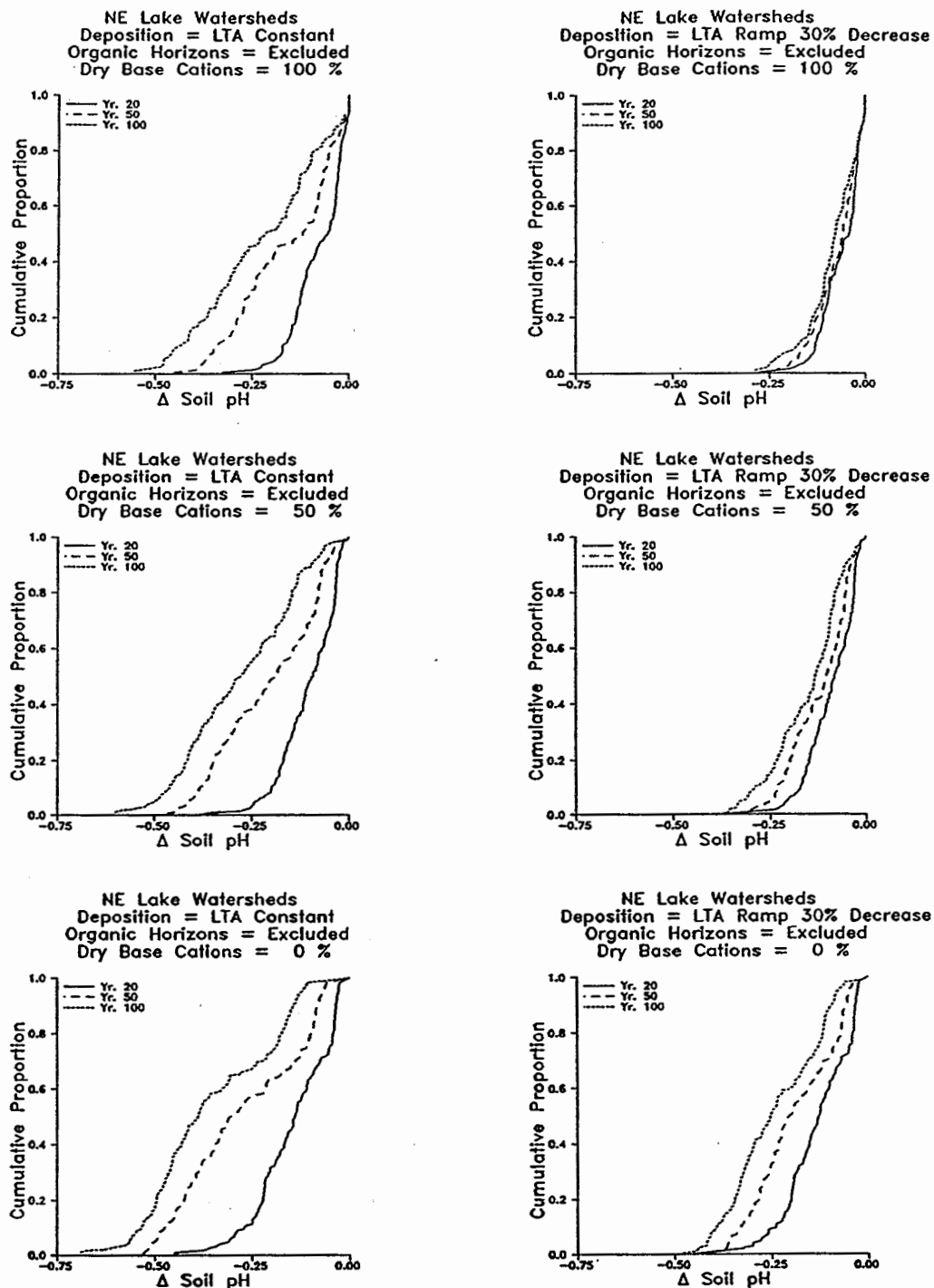
Figure 9-49. Regional CDFs of the projected change in the pH of soils on NE lake watersheds under constant and ramp down (30% ↓) deposition scenarios after 20, 50, and 100 years of LTA, LTA-rbc, and LTA-zbc deposition. Organic horizons are excluded.

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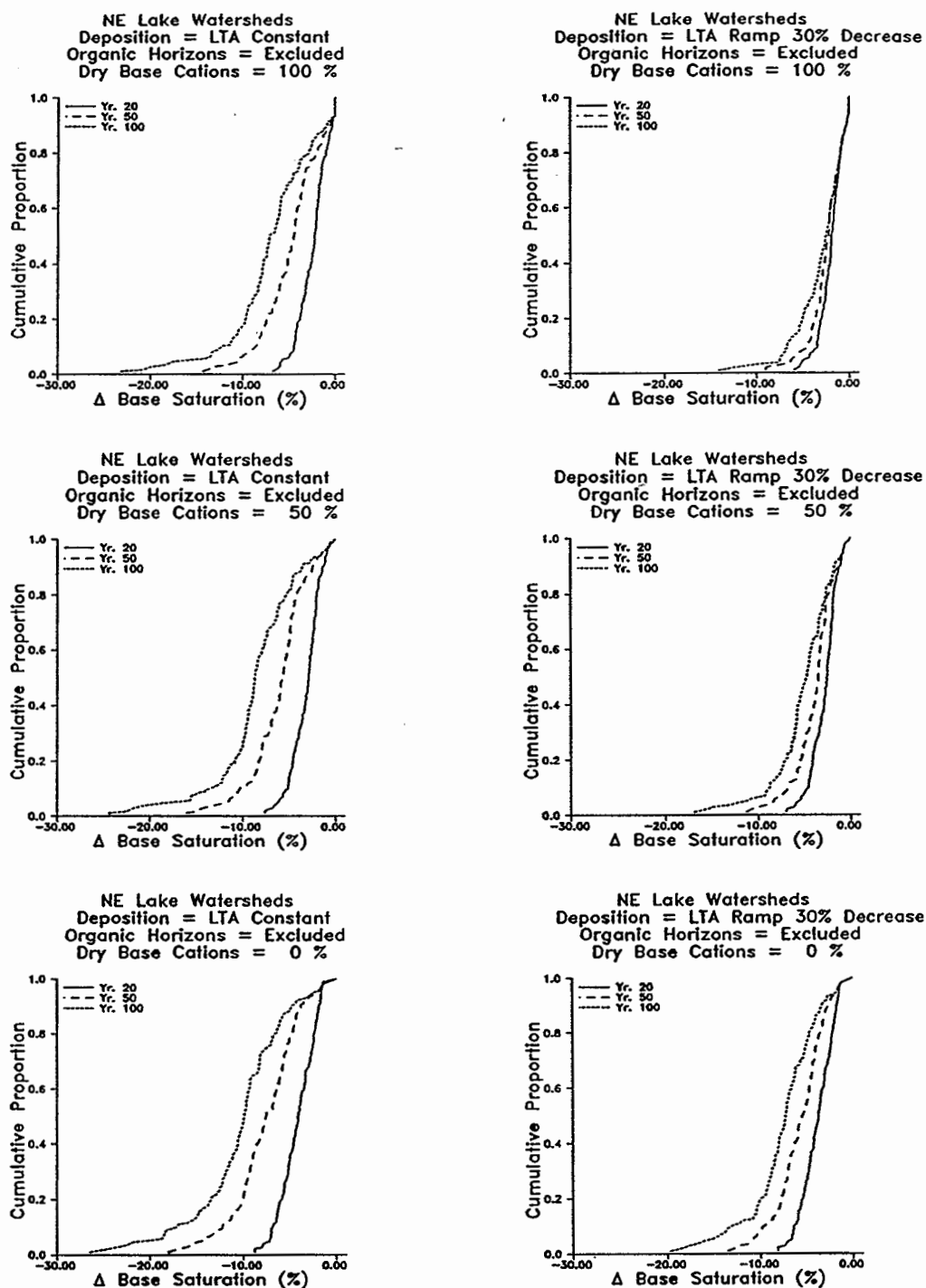
Figure 9-50. Regional CDFs of the projected change in the percent base saturation of soils on NE lake watersheds under constant and ramp down (30% ↓) deposition scenarios after 20, 50, and 100 years of LTA, LTA-rbc, and LTA-zbc deposition. Organic horizons are excluded.

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Table 9-28. Bloom-Grigal Model Regional Projections of the Change in Soil pH in the Northeastern United States. Projections Made Using LTA, LTA-rbc, and LTA-zbc Deposition with Constant and 30% Ramped Down Deposition Scenarios at Three Levels of Base Cations in Dry Deposition. Results Reported for 20-, 50-, and 100-Year Forecasts. Organic Soil Horizons Excluded

Deposition = Constant ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.08	0.07	-0.33	-0.13	-0.05	-0.02	0.00
50	-0.16	0.12	-0.45	-0.27	-0.12	-0.06	0.00
100	-0.22	0.15	-0.55	-0.34	-0.21	-0.10	0.00

Deposition = Constant ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.10	0.07	-0.38	-0.16	-0.09	-0.04	0.00
50	-0.21	0.13	-0.47	-0.33	-0.18	-0.08	0.00
100	-0.28	0.14	-0.60	-0.40	-0.27	-0.15	0.00

Deposition = Constant ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.14	0.09	-0.45	-0.22	-0.14	-0.05	0.00
50	-0.27	0.15	-0.53	-0.41	-0.31	-0.11	0.00
100	-0.35	0.16	-0.69	-0.48	-0.39	-0.19	0.00

Deposition = 30% Decrease ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.06	0.05	-0.28	-0.10	-0.04	-0.02	0.00
50	-0.07	0.06	-0.28	-0.11	-0.06	-0.03	0.00
100	-0.08	0.07	-0.29	-0.12	-0.08	-0.03	0.00

Table 9-28. (Continued)

Deposition = 30% Decrease ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.09	0.06	-0.37	-0.13	-0.08	-0.03	0.00
50	-0.12	0.08	-0.37	-0.19	-0.10	-0.06	0.00
100	-0.15	0.09	-0.37	-0.22	-0.13	-0.08	0.00

Deposition = 30% Decrease ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.13	0.08	-0.44	-0.19	-0.13	-0.05	0.00
50	-0.19	0.10	-0.44	-0.28	-0.20	-0.09	0.00
100	-0.24	0.11	-0.48	-0.33	-0.25	-0.13	0.00

Table 9-29. Bloom-Grigal Model Regional Projections for the Change in Percent Base Saturation in the Northeastern United States. Projections Made Using LTA, LTA-rbc, and LTA-zbc Average Deposition with Constant and 30% Ramped Down Deposition Scenarios at Three Levels of Base Cations in Dry Deposition. Results Reported for 20-, 50-, and 100-Year Projections. Organic Soil Horizons Excluded

Deposition = Constant ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-2.40	1.58	-6.74	-3.56	-2.16	-1.41	0.00
50	-4.79	3.11	-14.34	-6.51	-4.38	-2.72	0.00
100	-6.93	4.54	-23.19	-8.95	-7.08	-3.87	0.00

Deposition = Constant ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-3.12	1.57	-7.64	-4.21	-2.81	-2.04	0.00
50	-6.05	3.02	-16.04	-7.87	-5.59	-4.47	0.00
100	-8.56	4.39	-24.40	-9.99	-8.65	-6.06	0.00

Deposition = Constant ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-4.14	1.89	-8.79	-5.55	-4.04	-2.49	0.00
50	-7.66	3.51	-18.03	-9.72	-7.51	-5.28	0.00
100	-10.36	4.97	-26.41	-12.25	-9.86	-7.03	0.00

Deposition = 30% Decrease ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-1.96	1.31	-5.98	-2.66	-1.87	-1.06	0.00
50	-2.45	1.83	-9.04	-3.20	-2.19	-1.07	0.00
100	-3.07	2.65	-14.13	-4.37	-2.46	-1.08	0.00

Table 9-29. (Continued)

Deposition = 30% Decrease ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-2.79	1.43	-7.00	-3.83	-2.50	-1.85	0.00
50	-3.87	2.16	-11.30	-5.03	-3.48	-2.64	0.00
100	-5.06	3.12	-16.92	-6.35	-4.68	-2.97	0.00

Deposition = 30% Decrease ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-3.81	1.75	-8.13	-5.07	-3.68	-2.32	0.00
50	-5.69	2.68	-13.55	-7.34	-5.34	-3.90	0.00
100	-7.52	3.78	-19.69	-9.06	-7.21	-5.01	0.00

Organic horizons apparently influence the soil chemistry in at least two ways. First, because organic horizons have abundant base cations, they increase the size of the exchangeable base cation pool (see Table 9-25). Because of the concomitant addition of CEC, however, the relative magnitude of the median percent base saturation remains the same. Second, because organic horizons are inherently acidic, the lower soil pH values decrease the rate of base cation removal from the soil cation exchange complex. At lower soil pH values, potentially toxic acid cations, such as Al^{3+} and Mn^{2+} become more prevalent and may be transported in drainage waters to surface water or groundwater.

The Bloom-Grigal modelling results using the TY deposition in the NE are similar to those using the LTA deposition. For this reason they are not presented here.

9.3.3.2.2.2 Southern Blue Ridge Province --

Although the median aggregated soil pH values are higher in the SBRP target population of watersheds than in the NE, SBRP soils have dramatically lower percent base saturation. Because of these chemical properties, and for the larger reasons described in the preceding section, the soils in the SBRP are projected to experience decreases in pH and percent base saturation than soils in the NE.

The changes projected for the soils without the organic horizons differ only slightly from those for the soils with the organic horizons. Unlike the NE, omitting the organic horizons does not appreciably affect the initial aggregate soil pH and percent base saturation. As for the NE, the forecasts using the TY deposition data are only slightly higher than those using the LTA. (These data are not presented.)

The CDFs for the projected changes in soil pH and percent base saturation using the LTA, LTA-rbc, and LTA-zbc deposition data sets are presented in Figures 9-51 and 9-52. The summary statistics for these CDFs are presented in Tables 9-30 and 9-31. These results are for the soils with the organic horizons included.

After 50 years under the constant deposition scenario, the median predicted change in soil pH is -0.16. After 100 years it is -0.24. From year 100 to year 200 the change is only -0.07. The change in percent base saturation after 100 years is -3.22, and after 200 years of the change is only -3.39. These results imply that between year 100 and 200 the buffering mechanism these soils shifts with the latter mechanism buffering soil pH to more acidic levels.

Projected changes with the increased acid loadings of the LTA-rbc and LTA-zbc are much more rapid. After 50 years under constant LTA-rbc deposition, the projected change in soil pH equals that under the LTA deposition after 100 years. With the LTA-zbc, an equivalent projected change occurs in less than 50 years. The 20 percent ramped increase in deposition further increases the rates of projected change: increased acid inputs increase the initial rate of change, i.e., the decrease in base saturation and soil pH. The convergence of the CDFs for 50, 100, and 200 years demonstrates these results. These results are explained by the initial conditions: the greater the pH and the lower the base saturation, the faster the base cation depletion rate (see Section 9.3.3.2.2.2).

This convergence of the CDFs may represent the limit of change, at least for the next two centuries. In order to consider the limit of change, assume that the median value of change represents the central tendency for change. The limit for change in soil pH, therefore, is approximately -0.40 and
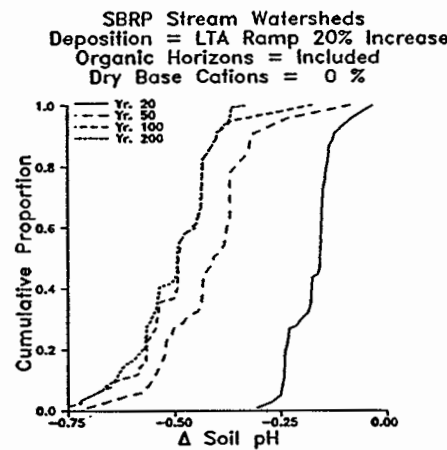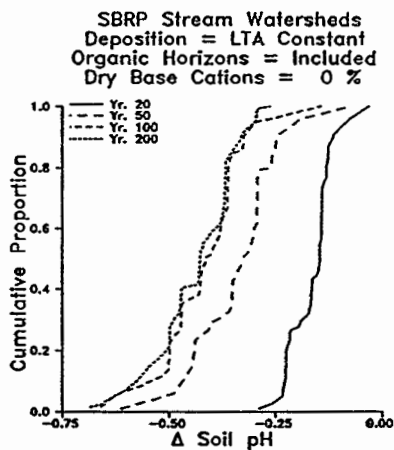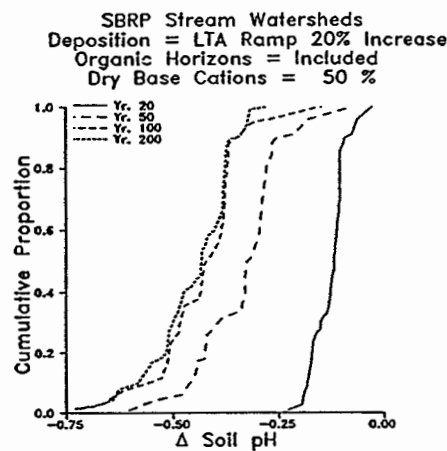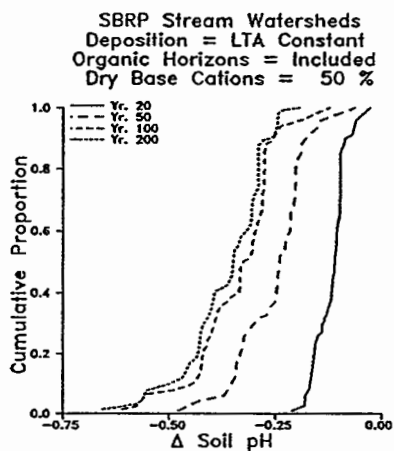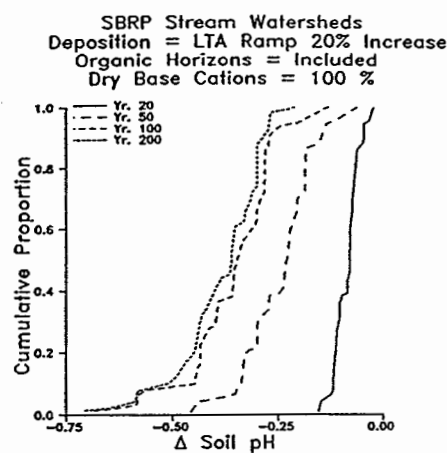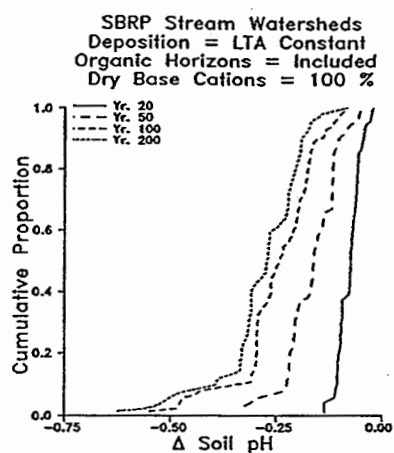
Figure 9-51. Regional CDFs of the projected change in the pH of soils on SBRP stream watersheds under constant and ramp up (20% ↑) deposition scenarios after 20, 50, 100, and 200 years of LTA, LTA-rbc, and LTA-zbc deposition. Organic horizons are included.

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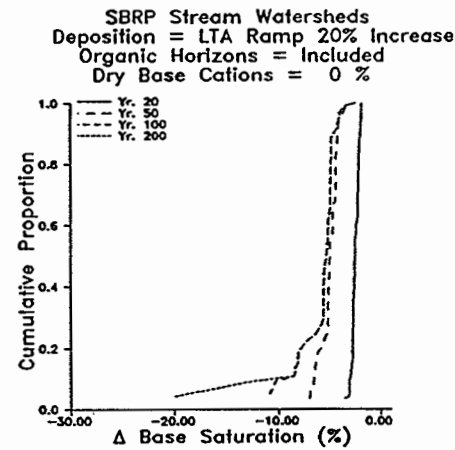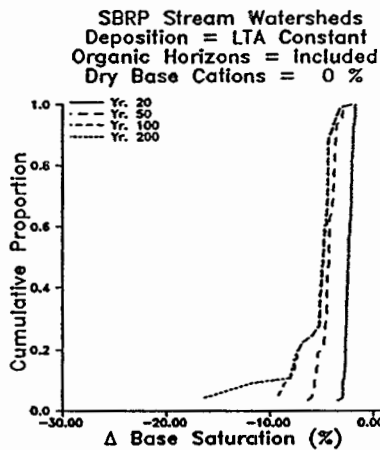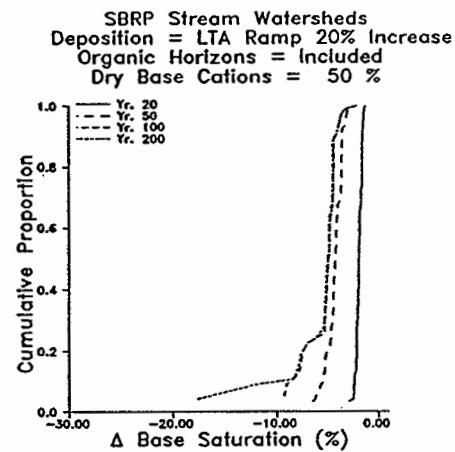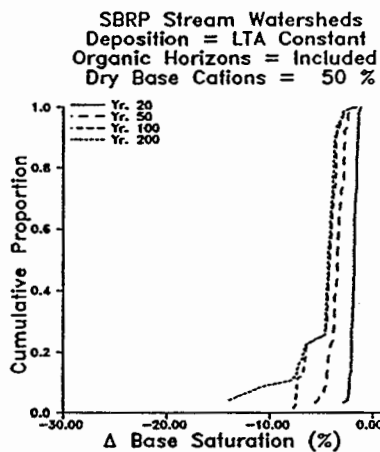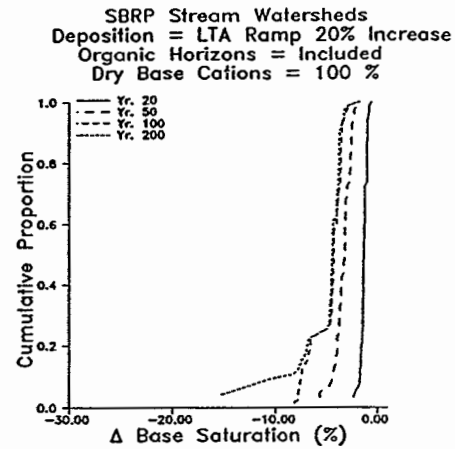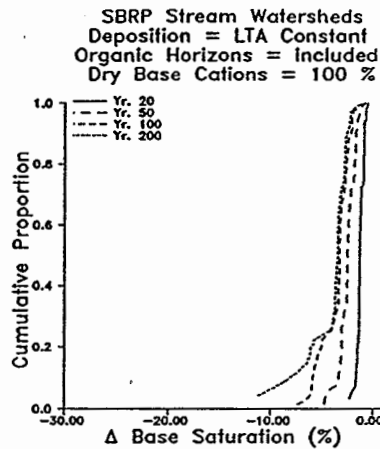
Figure 9-52. Regional CDFs of the projected change in the percent base saturation of soils on SBRP stream watersheds under constant and ramp up (20% ↑) deposition scenarios after 20, 50, 100, and 200 years of LTA, LTA-rbc, and LTA-zbc deposition. Organic horizons are included.

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Table 9-30. Bloom-Grigal Model Regional Projections for the Change in Soil pH in the Southern Blue Ridge Province. Projections Made Using LTA, LTA-rbc, and LTA-zbc Deposition with Constant and 20% Ramped Up Deposition Scenarios at Three Levels of Base Cations in Dry Deposition. Results Reported for 20-, 50-, 100-, and 200-Year Projections. Organic Soil Horizons Included

Deposition = Constant ** Dry Base Cations = 100% ** LTA

| YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.07	0.03	-0.14	-0.10	-0.07	-0.05	-0.02
50	-0.16	0.06	-0.32	-0.21	-0.16	-0.11	-0.05
100	-0.24	0.09	-0.55	-0.29	-0.24	-0.17	-0.08
200	-0.28	0.10	-0.62	-0.32	-0.27	-0.19	-0.08

Deposition = Constant ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.11	0.04	-0.21	-0.15	-0.11	-0.09	-0.03
50	-0.25	0.08	-0.48	-0.32	-0.24	-0.20	-0.06
100	-0.34	0.10	-0.61	-0.40	-0.31	-0.27	-0.12
200	-0.36	0.09	-0.66	-0.42	-0.35	-0.29	-0.19

Deposition = Constant ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.16	0.05	-0.29	-0.22	-0.14	-0.13	-0.03
50	-0.33	0.10	-0.61	-0.42	-0.32	-0.29	-0.07
100	-0.41	0.10	-0.66	-0.47	-0.41	-0.36	-0.14
200	-0.43	0.09	-0.68	-0.50	-0.43	-0.37	-0.26

Deposition = 20% Increase ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.08	0.03	-0.15	-0.11	-0.08	-0.06	-0.02
50	-0.24	0.08	-0.46	-0.30	-0.23	-0.18	-0.06
100	-0.35	0.11	-0.68	-0.42	-0.33	-0.28	-0.13
200	-0.38	0.10	-0.71	-0.44	-0.36	-0.30	-0.21

Table 9-30. (Continued)

Deposition = 20% Increase ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.13	0.04	-0.23	-0.16	-0.12	-0.10	-0.03
50	-0.33	0.10	-0.60	-0.42	-0.32	-0.28	-0.07
100	-0.43	0.10	-0.72	-0.49	-0.41	-0.37	-0.15
200	-0.45	0.09	-0.73	-0.51	-0.43	-0.37	-0.27

Deposition = 20% Increase ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-0.17	0.06	-0.31	-0.23	-0.16	-0.14	-0.03
50	-0.41	0.12	-0.71	-0.51	-0.41	-0.37	-0.08
100	-0.49	0.11	-0.75	-0.55	-0.49	-0.43	-0.17
200	-0.50	0.09	-0.75	-0.57	-0.49	-0.43	-0.33

Table 9-31. Bloom-Grigal Model Regional Projections for the Change in Percent Soil Base Saturation in the Southern Blue Ridge Province. Projections Made Using LTA, LTA-rbc, and LTA-zbc Deposition with Constant and 20% Ramped Up Deposition Scenarios at Three Levels of Base Cations in Dry Deposition. Results Reported for 20-, 50-, 100-, and 200-Year Projections. Organic Soil Horizons Included

Deposition = Constant ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-1.20	0.35	-2.21	-1.30	-1.23	-0.88	-0.46
50	-2.44	0.79	-4.67	-2.98	-2.43	-1.83	-0.68
100	-3.50	1.33	-7.27	-3.96	-3.22	-2.69	-0.74
200	-4.14	2.20	-11.16	-4.10	-3.39	-2.77	-0.74

Deposition = Constant ** Dry Base Cations = 50% ** LTA - rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-1.75	0.35	-2.82	-1.99	-1.72	-1.39	-1.15
50	-3.43	0.78	-5.55	-3.73	-3.36	-2.71	-1.54
100	-4.53	1.41	-7.71	-4.59	-4.11	-3.52	-1.57
200	-5.09	2.55	-13.94	-4.62	-4.23	-3.62	-1.57

Deposition = Constant ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-2.32	0.40	-3.41	-2.59	-2.33	-1.99	-1.67
50	-4.31	0.84	-6.34	-4.67	-4.25	-3.65	-2.02
100	-5.28	1.61	-9.19	-5.16	-4.70	-4.27	-2.03
200	-5.77	2.89	-16.35	-5.17	-4.75	-4.31	-2.03

Deposition = 20% Increase ** Dry Base Cations = 100% ** LTA

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-1.32	0.36	-2.39	-1.45	-1.34	-0.98	-0.57
50	-3.35	0.84	-5.65	-3.75	-3.20	-2.69	-1.5
100	-4.67	1.48	-8.19	-4.94	-4.29	-3.53	-1.67
200	-5.28	2.74	-15.15	-4.97	-4.39	-3.71	-1.67

Table 9-31. (Continued)

Deposition = 20% Increase ** Dry Base Cations = 50% ** LTA-rbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-1.89	0.36	-2.99	-2.13	-1.87	-1.52	-1.28
50	-4.27	0.84	-6.45	-4.64	-4.16	-3.59	-2.08
100	-5.40	1.65	-9.24	-5.29	-4.78	-4.32	-2.10
200	-5.93	3.08	-17.57	-5.30	-4.91	-4.37	-2.10

Deposition = 20% Increase ** Dry Base Cations = 0% ** LTA - zbc

YEAR	MEAN	STD_DEV	MIN	P_25	MEDIAN	P_75	MAX
20	-2.46	0.42	-3.57	-2.74	-2.48	-2.12	-1.80
50	-5.00	0.92	-7.01	-5.21	-4.97	-4.34	-2.41
100	-5.91	1.88	-10.86	-5.78	-5.28	-4.84	-2.42
200	-6.41	3.43	-19.96	-5.78	-5.31	-4.85	-2.42

Table 9-32. Summary of the Bloom-Grigal Projected Changes in Soil pH and Percent Base Saturation in the NE and SBRP Under Constant LTA Deposition

Region	Parameter	Initial Value	Change in Parameter After Selected Years		
			20	50	100
NE	pH	4.62	-0.01	-0.03	-0.04
SBRP	pH	4.85	-0.07	-0.16	-0.24
NE	% B.S.	21.98	-0.57	-1.05	-1.46
SBRP	% B.S.	9.22	-1.23	-2.43	-3.22

for base saturation is about -4.75. The results of subtracting these values from the current median values suggest that the new median pH value will be about 4.5 and for percent base saturation about 4.5. Both of these values are quite low considering that they represent aggregate values--i.e., the weighted average of all soil horizons.

Such changes are likely to affect surface waters. While Al buffering prevents the occurrence of even lower soil pH values, Al^{3+} and other acid cations (e.g., Mn^{2+} and Fe^{3+}) will become the dominant cations in the soil. These elements are toxic to plants and soil microbes and are also potentially toxic in the aquatic environment.

These projections may represent the worst-case estimates of the effects of acidic deposition on soils of the NE and SBRP. Several key points should, however, be reiterated: (1) these projections were made in the absence of mineral weathering and biomass accretion; (2) sulfate was treated as a completely mobile anion; (3) the projected changes are sensitive to the relationships between soil pH and percent base saturation, and these relationships were empirically derived for a selected subset of soils outside the DDRP regions; and (4) many types of soils were aggregated to derive a single value for initial soil pH, cation exchange capacity, and the sum of base cations.

9.3.3.2.3 Regional comparisons

Soils in the NE currently are somewhat lower in pH than soils in the SBRP. Soils in the SBRP, however, have much lower percent base saturation. These two differences lead to very different projections of the change in soil pH and percent base saturation with the Bloom-Grigal model. The median estimates of total effective acidity (H^+_{total} = H^+ + NH_4^+ - NO_3^-) inputs in LTA deposition datasets for the NE and SBRP are similar (see Table 9-24). The output from the simulations using these two datasets, therefore, can be compared (Table 9-32).

The regional response of soils to acidic deposition (changes in soil pH and percent base saturation) differ. Because the soils in the SBRP are older and more extensively weathered, their initial percent base saturation is markedly lower than that of the younger, less weathered soils in the NE. Aggregate soil pH values for the SBRP are, at the same time, slightly higher, which may be due to lower organic matter content. These two conditions, moderate to high pH (high for forested soils) and low percent base saturation result in rapid and severe projected decreases in soil pH and percent base saturation in soils that are already low in base cations. Only minor changes in soil pH and percent base saturation are projected for the NE.

A series of buffer ranges proposed by Ulrich (1983), assist, in part, with the interpretation of these results. He suggested that soil-water pH is indicative of the mineral phases that buffer the soil. He proposed five distinct buffer ranges:

(1)   Calcium carbonate (pH > 6.2)
(2)   Silicate (pH 6.2 - 5.0)
(3)   Cation exchange (pH 5.0 - 4.2)
(4)   Aluminum (pH 4.2 - 2.8)
(5)   Iron (pH 3.8 - 2.4)

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In the NE, the soils are generally in the Al buffer range (as defined by Ulrich), which is consistent with the model predictions. In the SBRP, soils are principally in Ulrich's cation exchange buffer range. When the pool of exchangeable base cations is depleted, the cation exchange buffer is exhausted, and the buffering of the system becomes controlled by Al. In Section 9.3.3.2.2.2, the convergence of the CDFs were suggested as bounding the change in soil pH and percent base saturation, and pH 4.5 was proposed as the limit. The apparent buffering of the NE against changes in soil pH (despite significant acid inputs) suggests that soil pH values near 4.5 are likely to be in the Al buffer range rather than the cation buffer range. The Al buffer range should be extended from pH 4.2 - 2.8 (as suggested by Ulrich) to a range of pH 4.5 - 2.8.

9.3.3.2.4 Summary and conclusions

Based on model projections, the soils in the NE appear to be buffered against changes in soil pH and percent base saturation by an Al buffering mechanism. Soils in the SBRP may experience significant decreases in soil pH and percent base saturation because of their current status and the level of acid inputs. While currently buffered against changes in pH via cation exchange buffering, the effectiveness of this buffer will be exceeded with the current levels of acid input. pH of these soils is projected to decrease until changes in soil pH become controlled by the Al buffering system.The major conclusions of this analysis using the Bloom-Grigal model are:

- Organic horizons contribute sufficient base cations to increase the size of the base cation pool, which slows the rate of acidification.

- In the NE, organic horizons contribute acidity and base cations, which results in lower cation leaching rates.

- Soils in the NE are buffered against changes in soil pH and percent base saturation via an Al buffering mechanism.

- Soils in the SBRP may experience significant decreases in soil pH and percent base saturation. The median soil pH could decrease as much as 0.5 pH units, and the median percent base saturation may decrease from its current level of 9.2 percent to 4.5 percent. They are thought to be worst case estimates because sulfate is considered to be a mobile anion in this analysis. The extent of change in the SBRP soils will be limited by the Al buffer range.

- The soil pH buffer ranges by Ulrich (1983) provide a good basis for interpreting the model-based projections.

9.3.4 Comparison of the Bloom-Grigal and Reuss Model Projections

Results from two soil cation exchange models have been presented in detail. The behavior modelled by the two formulations is remarkably different in some respects and more comparable in others. A summary of the median, mean, and maximum changes in percent base saturation and soil pH in the NE is presented in Table 9-33 for 50- and 100-year projections. Specific comparisons between the models can be made at two levels. First, model results can be compared for the entire population

of lakes in the NE or stream reaches in the SBRP. Because the primary purpose of the DDRP is to obtain such regional estimates, this comparison is of particular importance. On a more detailed level, model results can be compared for individual lakes or stream reaches. While a high degree of correspondence between the model outputs for individual systems should be expected, the comparison at this level may help to increase our understanding of the behavior of the individual models.

With respect to the estimates for the changes expected at the population level, several observations are of interest here. The dynamics of the two models are quite different. Initially, the Bloom-Grigal model projects substantially larger changes in percent base saturations than does the Reuss model (Table 9-33 and Figure 9-53). Both the mean and median values for changes in percent base saturation projected using the Bloom-Grigal model are larger at 20 and 50 years than those projected using the Reuss formulation. At 100 years, however, the relative magnitude of the changes projected by the two models is reversed. At 100 years, both the mean and median changes projected by the Reuss model are larger than those projected by the Bloom-Grigal model. Overall, the CDFs for the projected changes in soil base saturation for systems in the NE using the two models are reasonably similar.

In contrast to model behavior for percent base saturation, the models project quite different distributions for the response of soil pH to acidic deposition. Results from the Reuss model suggest that the rate of change in soil pH increases over the course of the 100-year simulation. The Bloom-Grigal model results, on the other hand, suggest that any changes in soil pH over this period are generally linear. Another major difference between the two models is that, with the Reuss model, a small number of systems experience extreme changes in soil pH during the simulation period. The Bloom-Grigal model results, in contrast, suggest that extremes should not be observed. The effect of the longer tail on the Reuss model population distributions is an increase in the mean projected change in soil pH over a 100-year period. Although the population medians, as projected by both models, are more similar than the medians, they still differ significantly as illustrated for the NE (Figure 9-54).

Comparison of the results for individual systems in the NE supports and reinforces the information obtained from the population-level evaluations. Figure 9-55 shows a scatter plot of the changes in percent base saturation projected for individual systems by the two models at 50- and 100-year intervals. Surprisingly, no correlation between the two model outputs is evident. Clearly, the two approaches used to model cation loss from the soil exchange complex differ. Nevertheless, when integrated over the population of systems in the NE, the differences between the models become sufficiently small to yield similar population estimates.

A greater degree of correlation appears to exist between the models for soil pH projections (Figure 9-56). At 50 years, the Reuss model appears to project smaller changes in soil pH for most of the systems. However, the Reuss model projects some extreme changes for small number of systems, relative to the magnitude of changes projected by the Bloom-Grigal model. After an additional 50 years, the Reuss model projections have increased in magnitude relative to those made with the Bloom-Grigal model. The number of systems projected to have extreme changes in soil pH also increases.

The patterns for individual systems and for populations observed in the NE also are observed in the SBRP. Because the simulations were extended to 200 years in the SBRP, however, some of the differences are more pronounced. Table 9-34 summarizes the results for changes in soil pH and percent

Table 9-33. Comparison of the Results from the Reuss and Bloom-Grigal Models with Regard to the Magnitude of Changes in Soil pH and Base Saturation Projected in Soils of the NE. Results Are Shown for 50 and 100 Years

|	Median	Mean	s.d.[a]	Maximum
Δ_% BS (20 years)				
Reuss	-1.3	-1.4	0.9	-6.0
Bloom-Grigal	-2.2	-2.4	1.6	-6.7
Δ_% BS (50 years)				
Reuss	-3.4	-3.5	1.7	-11.0
Bloom-Grigal	-4.4	-4.8	3.1	-14.3
Δ_% BS (100 years)				
Reuss	-7.5	-7.6	3.2	-17.0
Bloom-Grigal	-7.1	-6.9	4.5	-23.2
Δ_soil pH (20 years)				
Reuss	-0.03	-0.08	0.14	-0.68
Bloom-Grigal	-0.05	-0.08	0.07	0.33
Δ_Soil pH (50 years)				
Reuss	-0.09	-0.17	0.19	-0.88
Bloom-Grigal	-0.12	-0.16	0.12	-0.45
Δ_Soil pH (100 years)				
Reuss	-0.27	-0.36	0.28	-1.10
Bloom-Grigal	-0.21	0.22	0.15	-0.55

[a] Standard deviations are reported as absolute values.
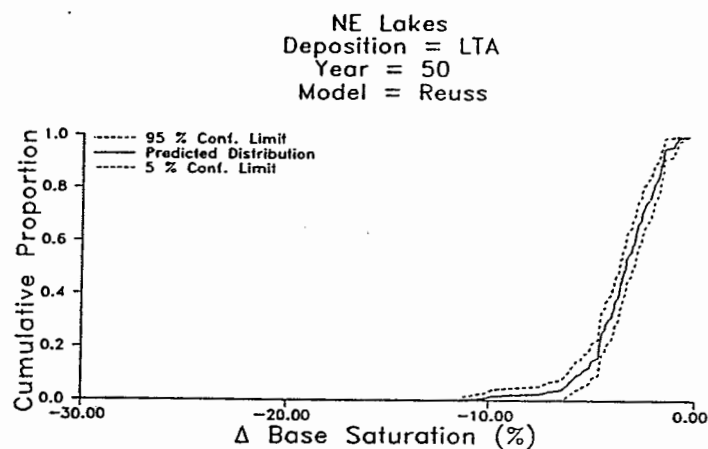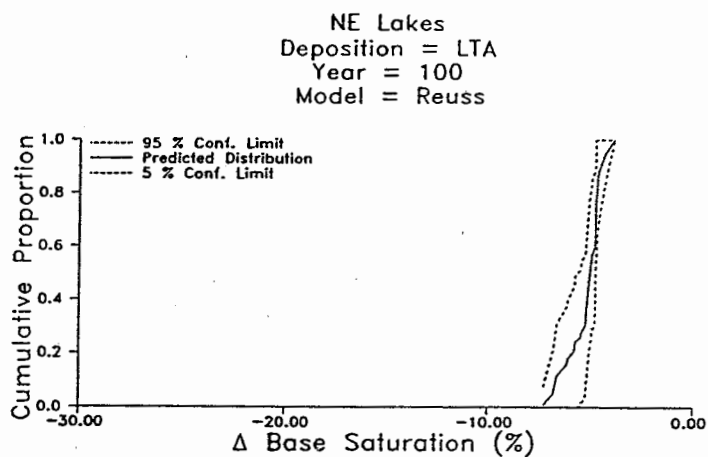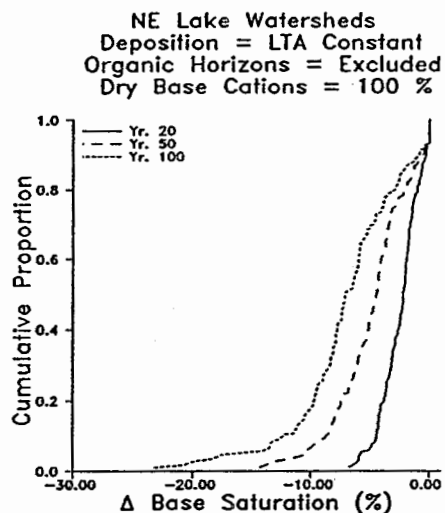
Figure 9-53. Cumulative distributions of changes in soil base saturation for the population of watersheds in the NE: (A) illustrates changes projected by the Reuss model at 50 years; (B) indicates those changes projected after 100 years, again using the Reuss model; and (C) shows the results at 20, 50, and 100 years, as projected using the Bloom-Grigal formulation.
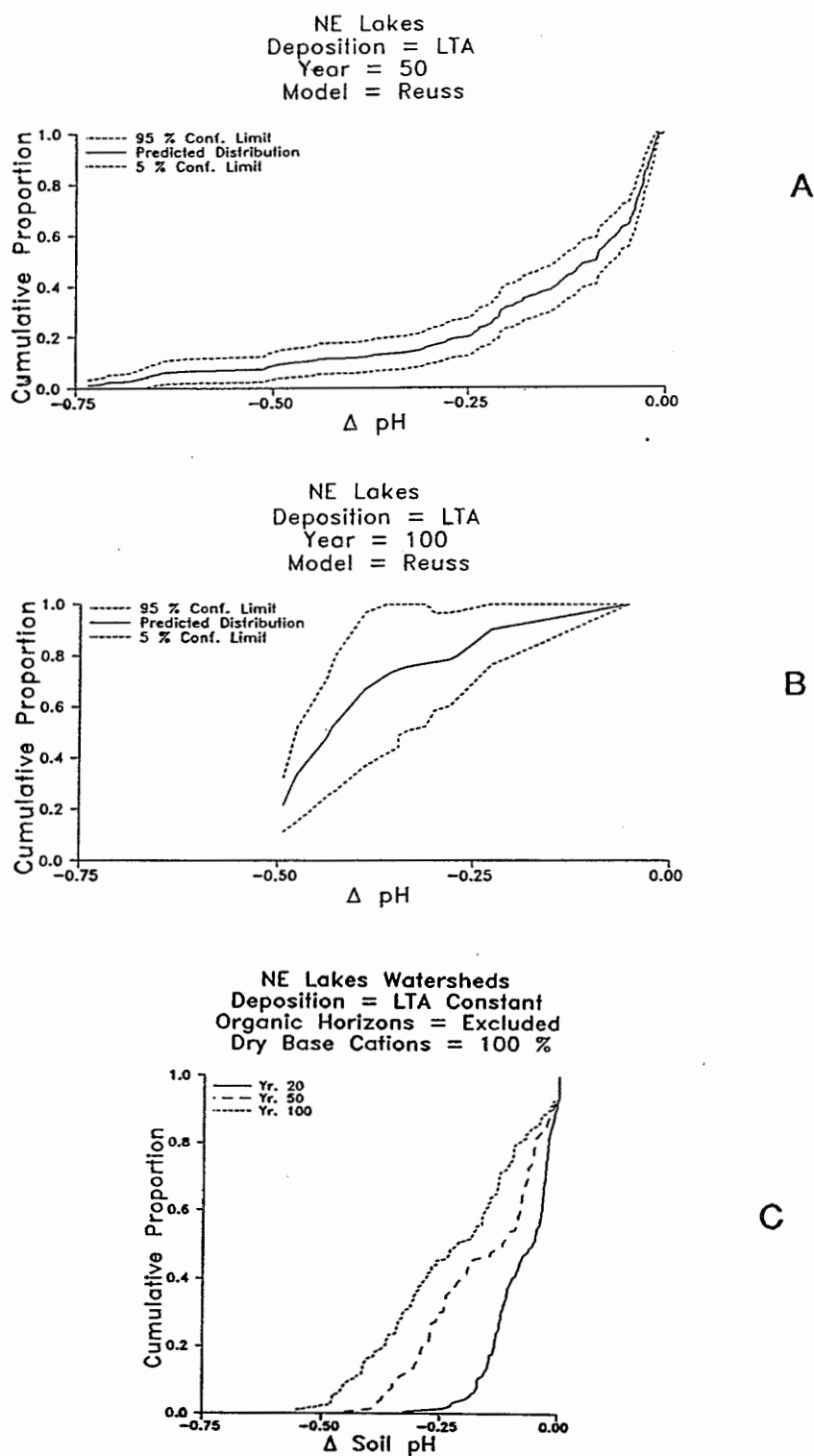
Figure 9-54. Cumulative distributions of changes In soil pH for the population of watersheds in the NE: (A) illustrates changes projected by the Reuss model at 50 years; (B) indicates those changes projected after 100 years, again using the Reuss model; and (C) shows the results at 20, 50, and 100 years, as projected using the Bloom-Grigal formulation.
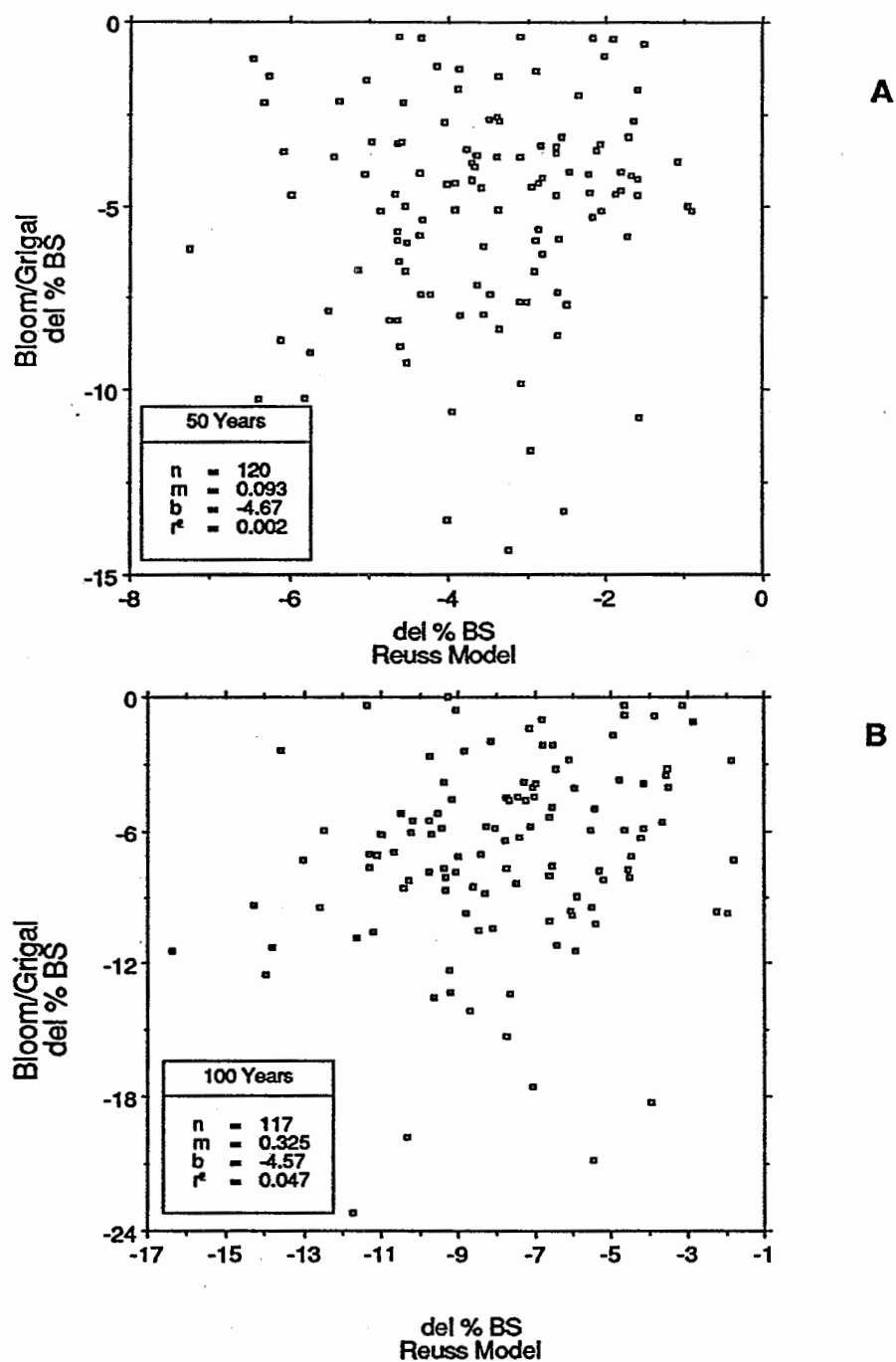
Figure 9-55. Scatter diagrams of the projected changes in base saturation for individual systems (not population weighted) in the NE obtained from the Reuss and Bloom-Grigal models: (A) compares results from the two models after a 50-year simulation and (B) illustrates the relationship observed after 100 years.

Figure 9-56. Scatter diagrams of the projected changes in soil pH for individual systems (not population weighted) in the NE obtained from the Reuss and Bloom-Grigal models: (A)compares results from the two models after a 50-year simulation and (B) illustrates the relationship observed after 100 years.
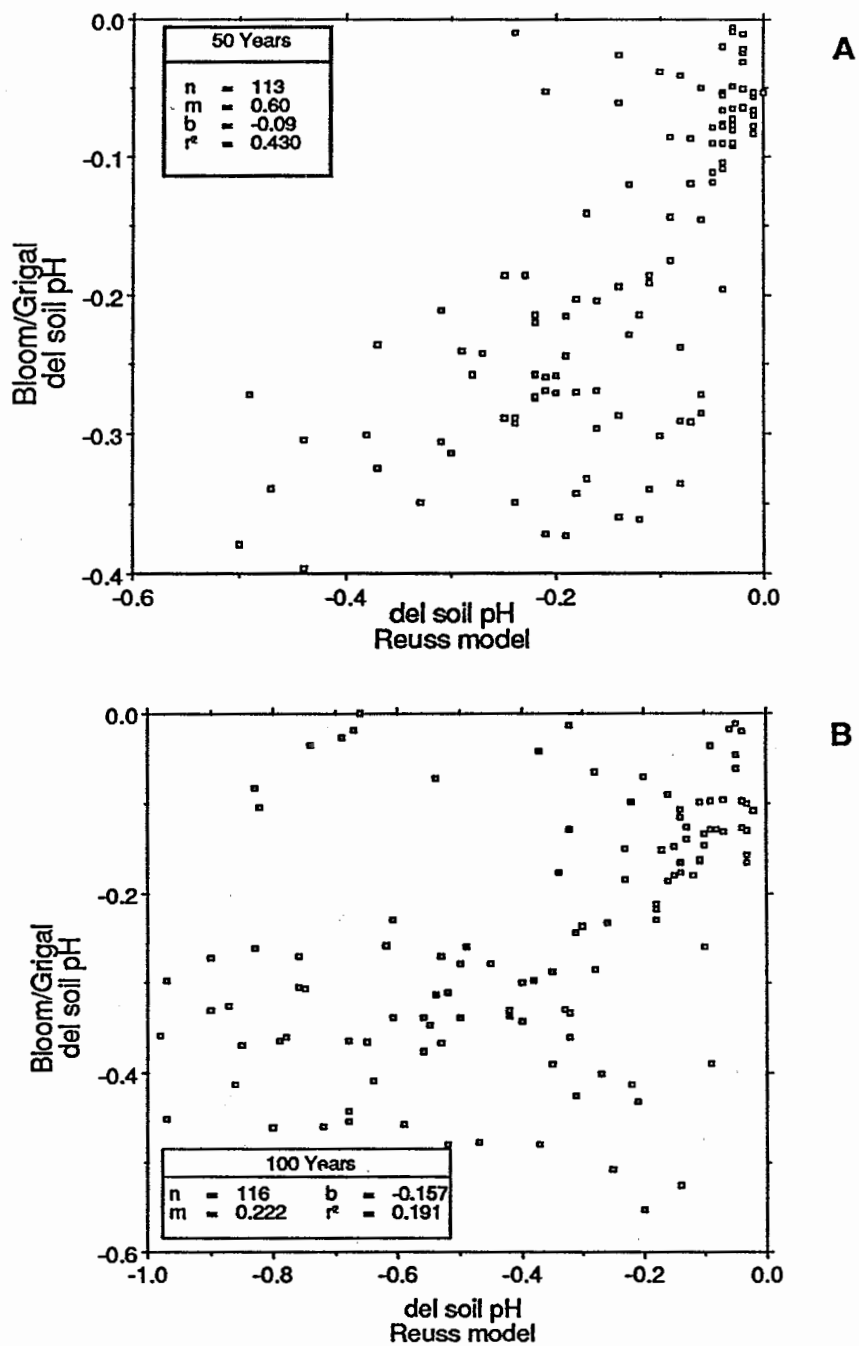
base saturation obtained with the two models for this region. In the SBRP, the Bloom-Grigal model initially projects larger changes in both soil pH and percent base saturation than does the Reuss model. As the simulations progress, however, the changes projected by the Reuss model increase more rapidly, so that by 200 years, substantially larger changes for both percent base saturation and soil pH are projected. Figures 9-57 and 9-58 illustrate the changes projected for the population of soils in the SBRP at 50 and 100 years.

In summary, soil cation exchange models were used to explore possible changes in soil chemical properties potentially occurring as a result of acidic deposition. Overall, the two models yield similar results with regard to projected changes for the NE and the SBRP. The major differences between the models appear to be that the Bloom-Grigal model projects more rapid initial changes to the soil chemical environment, whereas results obtained using the Reuss model indicate that changes should occur more rapidly as the soil exchange pool becomes depleted. Information needed for more critical evaluation of the two models currently is not available.

9.3.5 Summary and Conclusions

Results from two soil cation exchange models have been presented. These models focus on the role of cation exchange processes in regulating pH and percent base saturation in soils. The models do not consider processes such as primary mineral weathering, uptake of cations by vegetation, sulfate dynamics, or detailed hydrologic flow regimes; nor do they address the deep regolith (e.g., soil depths $> \sim 2$ m). Consequently, these model results are not directly comparable to the integrated watershed process models presented in Section 10. The models do, however, provide considerable information concerning how base cation pools may respond to continued acidic deposition.

The two models provide slightly different types of information about the soils and their associated surface waters. The Reuss model projects changes in both surface water chemistry and soil chemistry. In contrast, the Bloom-Grigal model provides information about the magnitude of projected changes only in soil chemical properties. The models employ markedly different algorithms in making these projections. The Reuss formulation uses a mass action approach. This approach allows each of the soil reactions to proceed independently, while simultaneously allowing individual soil properties to vary in an internally consistent manner. The Bloom-Grigal model relies on empirically derived relationships to define time-varying behavior of individual soil parameters. Each approach has certain advantages, making it important to determine how the two models differ in projected changes to the population of systems in the NE and SBRP regions.

While these models do not explicitly consider many processes, it is possible to understand qualitatively how non-modelled processes would affect the projections presented here. For example, cation accretion in biomass is a net base cation sink, and thus has an acidifying effect on the soils. Conversely, mineral weathering is a net source for base cations. Incorporation of a weathering term in these models would delay the projected response times of individual systems. Unfortunately, regionally based estimates of the magnitude of these processes is unavailable. Despite these limitations, model results do provide information to possible watershed responses. For systems with long projected response times, future changes in the quality of surface waters likely will not be large. However, for those

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Table 9-34. Comparison of the Results from the Reuss and Bloom-Grigal Models with Regard to the Magnitude of Changes in Soil pH and Base Saturation Projected in Soils of the SBRP. Results Are Shown for 50 and 100 Years

	Median	Mean	s.d.	Maximum
Δ_% BS (50 years)				
Reuss	-1.9	-1.9	0.4	-2.8
Bloom-Grigal	-3.1	-3.1	0.8	-5.1
Δ_% BS (100 years)				
Reuss	-5.1	-5.2	0.8	-7.2
Bloom-Grigal	-3.9	-4.4	1.3	-7.9
Δ_% BS (200 years)				
Reuss	-8.8	-8.8	1.0	-12.4
Bloom-Grigal	-4.4	-5.1	2.2	-11.7
Δ_Soil pH (50 years)				
Reuss	-0.10	-0.10	0.03	-0.19
Bloom-Grigal	0.23	-0.23	0.07	-0.40
Δ_Soil pH (100 years)				
Reuss	-0.35	-0.34	0.09	-0.49
Bloom-Grigal	-0.35	-0.35	0.10	-0.67
Δ_Soil pH (200 years)				
Reuss	-0.67	-0.66	0.15	-0.82
Bloom-Grigal	-0.38	-0.39	0.10	-0.75

SBRP Stream Reaches
Deposition = LTA
Year = 50
Model = Reuss

A

SBRP Stream Reaches
Deposition = LTA
Year = 100
Model = Reuss

B

SBRP Stream Watersheds
Deposition = LTA Constant
Organic Horizons = Excluded
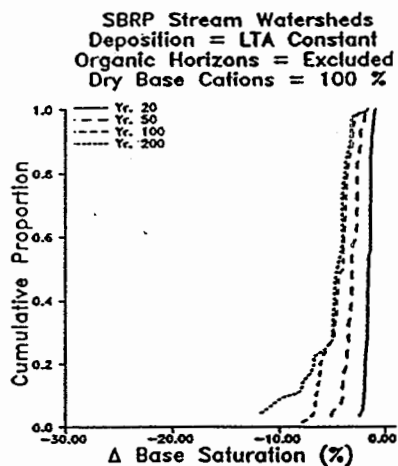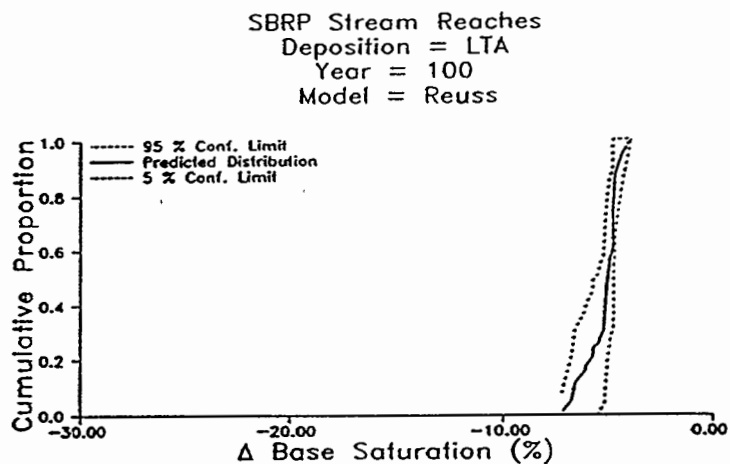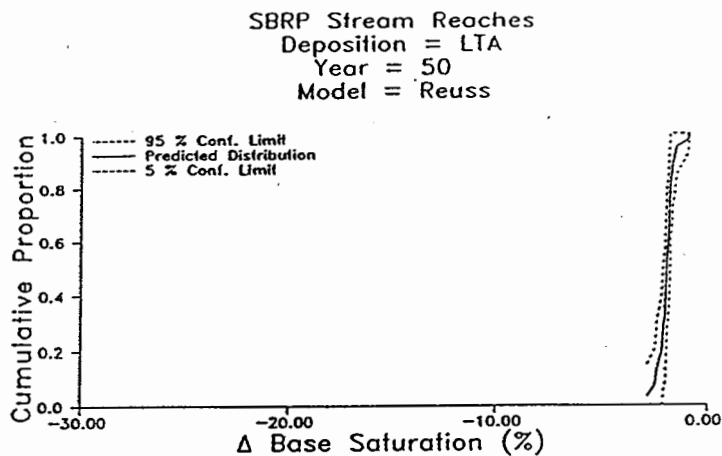Dry Base Cations = 100 %

C

Figure 9-57. Cumulative distributions of changes in soil base saturation for the population of watersheds in the SBRP: (A) illustrates changes projected by the Reuss model at 50 years; (B) indicates those changes projected after 100 years, again using the Reuss model; and (C) shows the results at 20, 50, and 100 years, as projected using the Bloom-Grigal formulation.
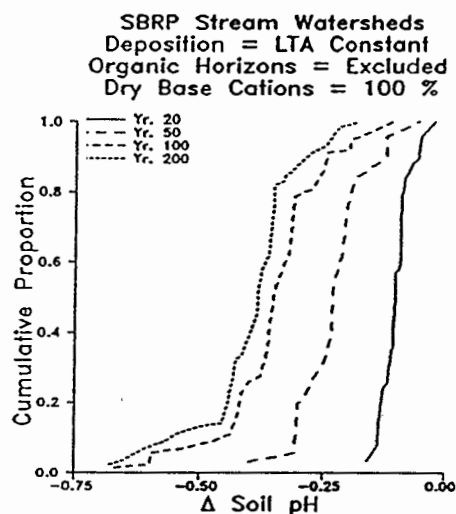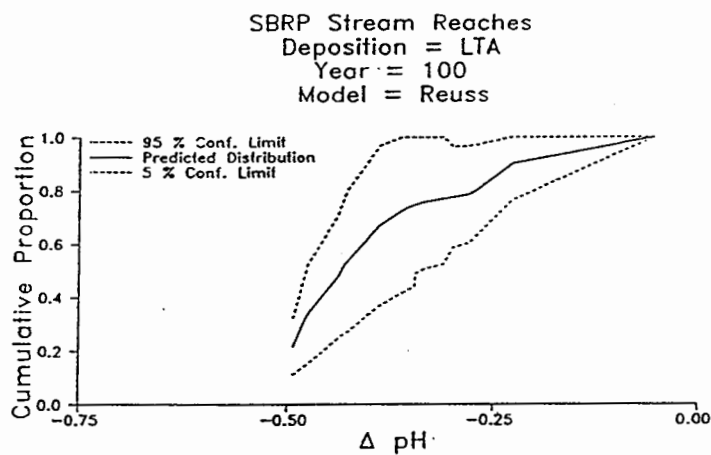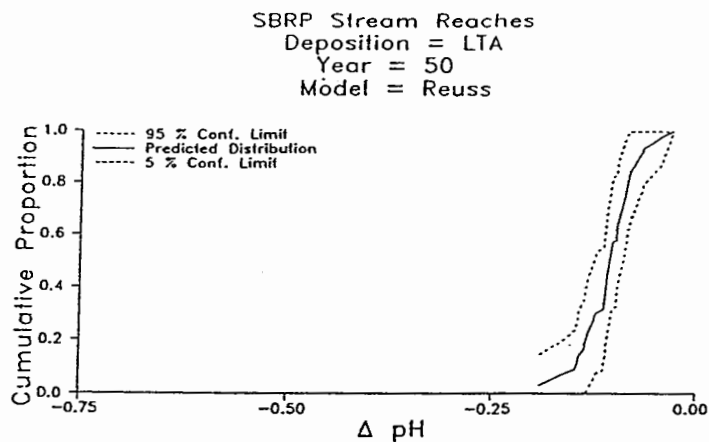
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Figure 9-58. Cumulative distributions of changes in soil pH for the population of watersheds in the SBRP: (A) illustrates changes projected by the Reuss model at 50 years; (B) indicates those changes projected after 100 years, again using the Reuss model; and (C) shows the results at 20, 50 and 100 years, as projected using the Bloom-Grigal formulation.

systems with short projected response times, additional information about the magnitude of other potential sources or sinks for base cations is essential for describing the responses of these systems accurately.

Detailed results from the models have been presented in Section 9.3.3. Major findings, first for surface waters and then for soils, are summarized below for both the NE and the SBRP.

- For lakes in the NE currently exhibiting ANC values in excess of 100 μeq L^{-1}, mineral weathering is probably the dominant watershed process controlling observed ANC values.

- At present levels of deposition, lakes in the NE with ANC values in excess of 100 μeq L^{-1} will probably not experience declining ANCs in the foreseeable future.

- For stream reaches in the SBRP projected to exhibit ANC values in excess of 50 μeq L^{-1} (after having attained a state of net zero sulfate retention), mineral weathering will probably be the dominant watershed process controlling ANC values for systems with chemistry currently dominated by sulfur dynamics.

- Stream reaches in the SBRP with projected ANC values in excess of 50 μeq L^{-1} (after having attained a state of net zero sulfate retention) will probably not become acidic (ANC $\leq$ 0 μeq L^{-1}) at current or slightly elevated levels of deposition. The capacity of weathering processes to mitigate the effects of acidic deposition could be overwhelmed in those systems with marginal (ANC $\leq$ 100 μeq L^{-1}) contributions from weathering, substantial increases in the levels of acidic deposition were to occur.

- For lakes in the NE exhibiting ANC values of less than 100 μeq L^{-1}, soil exchange processes may be regulating the observed ANCs, although in most systems, the ANC is probably controlled by a combination of cation exchange and mineral weathering.

- As an upper limit, approximately 15 percent or over 1000 lakes (four times the number of currently acidic lakes) in the NE with current positive ANC values could become acidic (i.e., ANC $\leq$ 0 μeq L^{-1}) within 50 to 100 years. The projection is extreme, because the contribution of weathering is not considered. However, some fraction of this number of lakes will probably become acidic during the next several decades.

- In the SBRP, changes in observed ANC values that occur because of changes in the base status of soils during the next century should be minimal.

- For systems in the NE and SBRP that have ANC values in the range of 0 to 50 μeq L^{-1}, rates of system response are projected to <u>increase</u> with continued exposure to acidic deposition. The increased rates coincide with the depletion of soil buffering capacity.

- In the absence of mineral weathering, significant depletion of base cations is projected to occur in the soils of both the NE and SBRP regions.

- The absolute magnitude of base cation depletion is greater in the NE than it is in the SBRP. The relative projected changes are, however, greater in the SBRP.

- Current percent base saturation of soils in the regions can be used as indicators of potential future change in surface water ANC. Soils with base saturation currently in excess of about 20 percent appear to undergo minimal changes on the time scale of the next 100 years. For soils with base saturation less than 20 percent, however, projected changes in surface water ANC appear to increase with decreasing aggregate percent base saturation, an effect that is more pronounced in the NE than in the SBRP.

- Current percent base saturation can be used as an indicator of the anticipated relative changes that might occur in the soil base status over the next 100 years. The relative percentage decline in percent base saturation [(current - projected)/current] x 100 increases with decreasing percent base saturation, although other factors, such as soil thickness or bulk density, probably also influence the relationship.