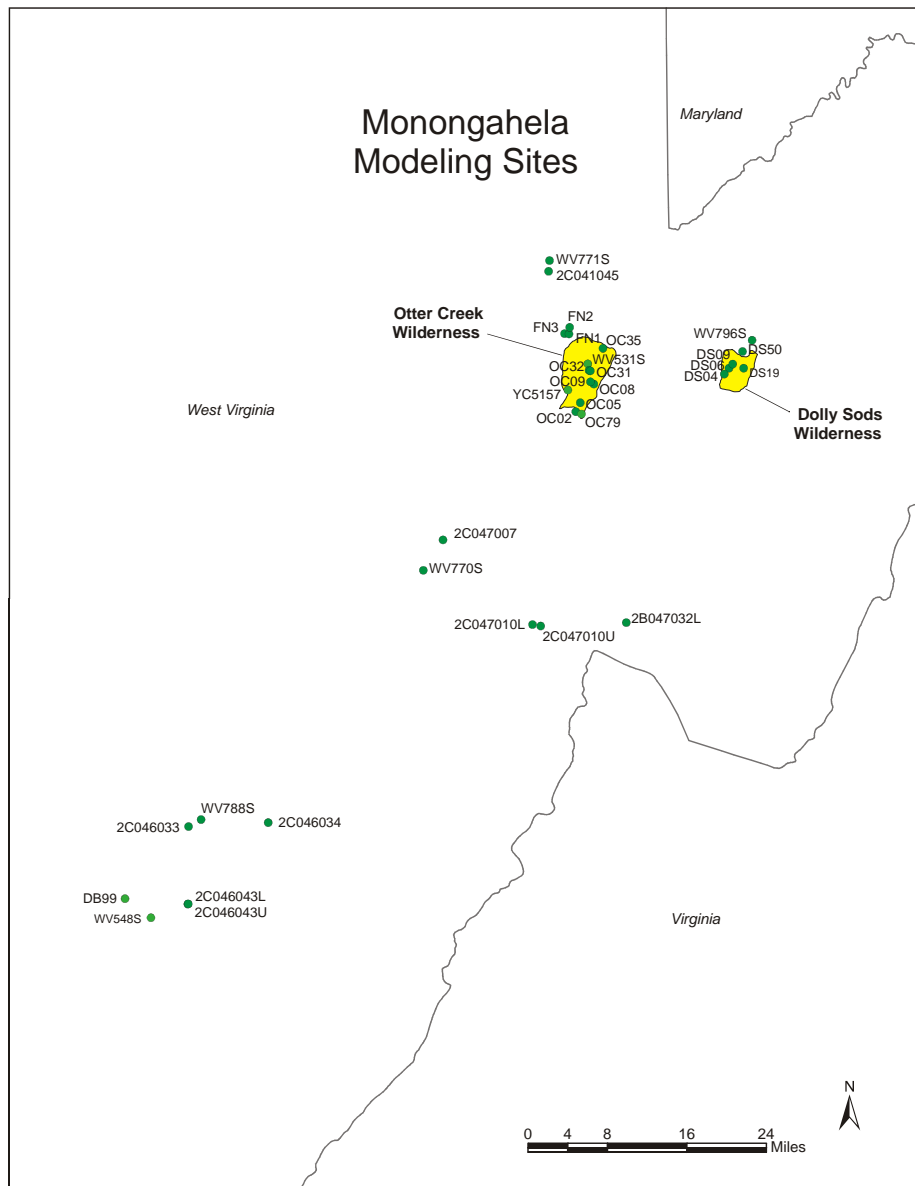


# AQUATIC CRITICAL LOAD DEVELOPMENT FOR THE MONONGAHELA NATIONAL FOREST, WEST VIRGINIA

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December, 2004

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## **ABSTRACT**

The Model of Acidification of Groundwater in Catchments (MAGIC) was used to estimate the critical loads of atmospheric sulfur deposition required to protect 33 streams in Monongahela National Forest from the adverse effects of acidification. The model was applied to each of the study streams in an iterative fashion to determine the sulfur deposition values that would cause the acid neutralizing capacity (ANC) of each modeled stream to increase or decrease to reach specified critical levels within specified periods of time. The selected critical levels of ANC were 0, 20, 50, and 100  $\mu\text{eq/L}$ . The specified endpoints were 2020, 2040, and 2100. Simulations showed that all of the modeled streams had positive ANC pre-1900. However, many had estimated pre-1900 ANC below 50  $\mu\text{eq/L}$  (27% of modeled sites) or below 100  $\mu\text{eq/L}$  (67% of modeled sites). Therefore, future “recovery” to higher ANC criteria values may not be reasonable for such streams.

The estimated amount of historical acidification of individual modeled streams ranged from a loss of ANC that was less than 50  $\mu\text{eq/L}$  to more than 100  $\mu\text{eq/L}$ . For many of the modeled streams, simulations showed that various ANC endpoints could not be achieved by 2100, even if S deposition was reduced to zero. About one-third of modeled sites were simulated to be able to attain above zero ANC by 2020, and nearly two-thirds by 2100, but many would require quite low levels of S deposition (less than 4 kg S/ha/yr) to achieve that endpoint.

## **BACKGROUND AND OBJECTIVES**

The potential effects of sulfur deposition on surface water quality have been well-studied in the eastern United States, particularly within the National Acid Precipitation Assessment Program (NAPAP), the Fish in Sensitive Habitats (FISH) project, and the Southern Appalachian Mountains Initiative (SAMI). Major findings were summarized in a series of State of Science and Technology Reports (e.g., Sullivan 1990, Baker et al. 1990), NAPAP Integrated Assessment (NAPAP 1991), the SAMI effects reports (Sullivan et al. 2002a,b), and the FISH report (Bulger et al. 1999). Although aquatic effects from nitrogen deposition have not been studied as thoroughly as those from sulfur deposition, concern has been expressed regarding the role of  $\text{NO}_3^-$  in acidification of surface waters, particularly during hydrologic episodes (e.g., Sullivan 1993, 2000; Sullivan et al. 1997; Wigington et al. 1993).

Wildernesses and other national forest lands include areas of exceptional ecological significance. However, anthropogenic atmospheric emissions of sulfur and nitrogen outside wilderness boundaries potentially threaten the ecological integrity of highly sensitive systems. Sensitive aquatic and terrestrial systems, particularly those at high elevations, can be degraded by previous, existing, or future pollution. According to the Clean Air Act and subsequent amendments (Public Laws 95-95, 101-549), Federal land managers have, "... an affirmative responsibility to protect the air quality related values (AQRVs)...within a Class I area." The USDA Forest Service manages potentially sensitive (to acidic deposition) aquatic resources in two wildernesses on the Monongahela National Forest: Otter Creek and Dolly Sods Wildernesses. In order to maintain healthy ecosystems, it is increasingly imperative that land managers be able to determine the levels of air pollution that are likely to cause unacceptable damage to ecosystems in these wildernesses and in surrounding national forest lands. For streams that have already been damaged, it is important to know the extent to which pollution levels need to be reduced in order to allow resource recovery or whether other mitigation measures are needed to assist in the recovery. This information can then be used to aid in management decisions and to set public policy.

Computer models can be used to predict pollution effects on ecosystems and to perform simulations of future ecosystem response (Cosby et al. 1985a,b,c; Agren and Bosatta 1988). The MAGIC Model, a lumped-parameter, mechanistic model, has been widely used throughout North America and Europe to project streamwater response and has been extensively tested against the results of diatom reconstructions and ecosystem manipulation experiments (e.g., Wright et al.

1986; Sullivan et al. 1992, 1996; Sullivan and Cosby 1995; Cosby et al. 1995, 1996). It has been used in the western United States and Europe to determine the deposition levels at which unacceptable environmental damage would be expected to occur (c.f., Skeffington 1999, Cosby and Sullivan 2001).

The need for emissions controls to protect resources has given rise to the concepts of critical levels of pollutants and critical loads of deposition. Critical levels and loads can be defined as "quantitative estimates of exposure to one or more pollutants below which significant harmful effects on specified sensitive elements of the environment do not occur according to present knowledge." The basic concept of critical load is relatively simple, as the threshold concentration of pollutants at which harmful effects on sensitive receptors begin to occur. Implementation of the concept is, however, not at all simple or straight-forward. Practical definitions for particular receptors (soils, fresh waters, forests) have not been agreed to easily. Different research groups have employed different definitions and different levels of complexity. Constraints on the availability of suitable, high-quality, regional data have been considerable.

Target load is somewhat different. It is based on both science, including in particular quantitative estimates of critical load, and also on policy. A target load is set on the basis of, in addition to model-based estimates of critical loads, such considerations as:

- desire to protect the ecosystem against chronic critical load exceedence
- consideration of the temporal components of acidification/recovery processes, so that, for example, resources could be protected only for a specified period of time or allowed to recover within a designated window
- seasonal and episodic variability, and probable associated biological responses
- model, data, and knowledge uncertainty and any desire to err on the side of resource protection

A critical load is objectively determined, based on specific chemical criteria that are known or believed to be associated with adverse biological impacts. A target load is subjectively determined, but it is rooted in science and incorporates allowances for uncertainty and ecosystem variability.

The principal objective of the work reported here was to determine threshold levels of sustained atmospheric deposition of S to achieve specific ANC levels at various years in the future for streams on the Monongahela National Forest. This evaluation of critical loads is accomplished using the MAGIC model (Cosby et al. 1985 a,b,c), a process-based dynamic modeling approach. MAGIC has been the principal model used thus far throughout North

America and Europe for streamwater acid-base chemistry assessment purposes (Cosby et al. 1995, 1996; Church et al. 1989; NAPAP 1991; Turner et al. 1992; Sullivan and Cosby 1995; Ferrier et al. 1995; Sullivan et al. 2002a, 2003).

## **METHODS**

Critical loads for sulfur deposition were calculated using the MAGIC model for 33 streams in the Monongahela National Forest. Streamwater and soils model input data and model calibration files were taken from the SAMI effort for 31 of these streams (Table 1). New input data were provided by the Forest Service for model calibration of two streams, Yellow Creek and Desert Branch. Model calibration protocols were selected to conform with the approach followed in the SAMI assessment (Sullivan et al. 2002a). Site locations are shown in Figure 1.

### **A. Modeling Methods for Aquatic Effects**

#### *Application of MAGIC for Aquatic Assessment*

The MAGIC modeling conducted for SAMI provided the basis for modeling in this project. MAGIC was previously successfully calibrated to 130 watersheds throughout the SAMI geographic domain for the SAMI regional assessment and an additional 34 Special Interest watersheds, mainly located in Class I areas (Sullivan et al. 2002a). Thirty-one of those sites were located in Monongahela National Forest. The input data required for aquatic resource modeling with the MAGIC model (stream water, catchment, soils, and deposition data) were assembled and maintained in data bases (electronic spreadsheets) for each landscape unit. The initial parameter files contain observed (or estimated) soils, deposition and catchment data for each site. The optimization files contain the observed soil and streamwater data that were the targets for the calibration at each site, and the ranges of uncertainty in each of the observed values.

For the sites modeled for SAMI, soils chemistry data were assembled from existing databases. For some sites (designated Tier I), soils chemistry data were available from within the watershed to be modeled. For other sites (Tier II), soils data were borrowed from a nearby watershed underlain by similar geology. Missing MAGIC model input data were generated for Tier III (no soils data from the watershed or from a nearby watershed on similar geology) sites using a surrogate approach, whereby a watershed that lacked one or more input parameters was paired

Table 1. Streams modeled in Monongahela National Forest using model calibrations from the SAMI study.			
Site ID	Stream Name	Tier	Class I Area
DS04	L Stonecoal Run	1	Dolly Sods
DS06	Stonecoal Run Left	2	Dolly Sods
DS09	Stonecoal Run Right	2	Dolly Sods
DS19	Fisher Spring Run	2	Dolly Sods
DS50	Unnamed in Dolly Sods	2	Dolly Sods
WV796S	Red Creek	3	Dolly Sods
OC31	Possession Camp Run	2	Otter Creek
OC32	Moores Run	2	Otter Creek
OC35	Coal Run	2	Otter Creek
OC79	Otter Creek Upper	2	Otter Creek
OC02	Condon Run	1	Otter Creek
OC05	Yellow Creek	2	Otter Creek
OC08	Unnamed in Otter Creek	2	Otter Creek
OC09	Devils Gulch	1	Otter Creek
WV531S	Otter Creek	3	Otter Creek
2B047032	Elk Run	1	
2C041045	R Fork Clover	1	
2C046033	Johnson Run	1	
2C046034	Hateful Run	1	
2C046043L	N Fork Cherry – Lower	3	
2C046043U	N Fork Cherry – Upper	3	
2C047007	Crawford Run	1	
2C047010L	Clubhouse Run – Lower	3	
2C047010U	Clubhouse Run – Upper	3	
FN1	Fernow WS10	2	
FN2	Fernow WS13	2	
FN3	Fernow WS4	1	
WV548S	Noname Trib S Fork Cherry	3	
WV770S	Moss Run	3	
WV771S	Left Fork Clover Run	3	
WV788S	White Oak Fork	3	



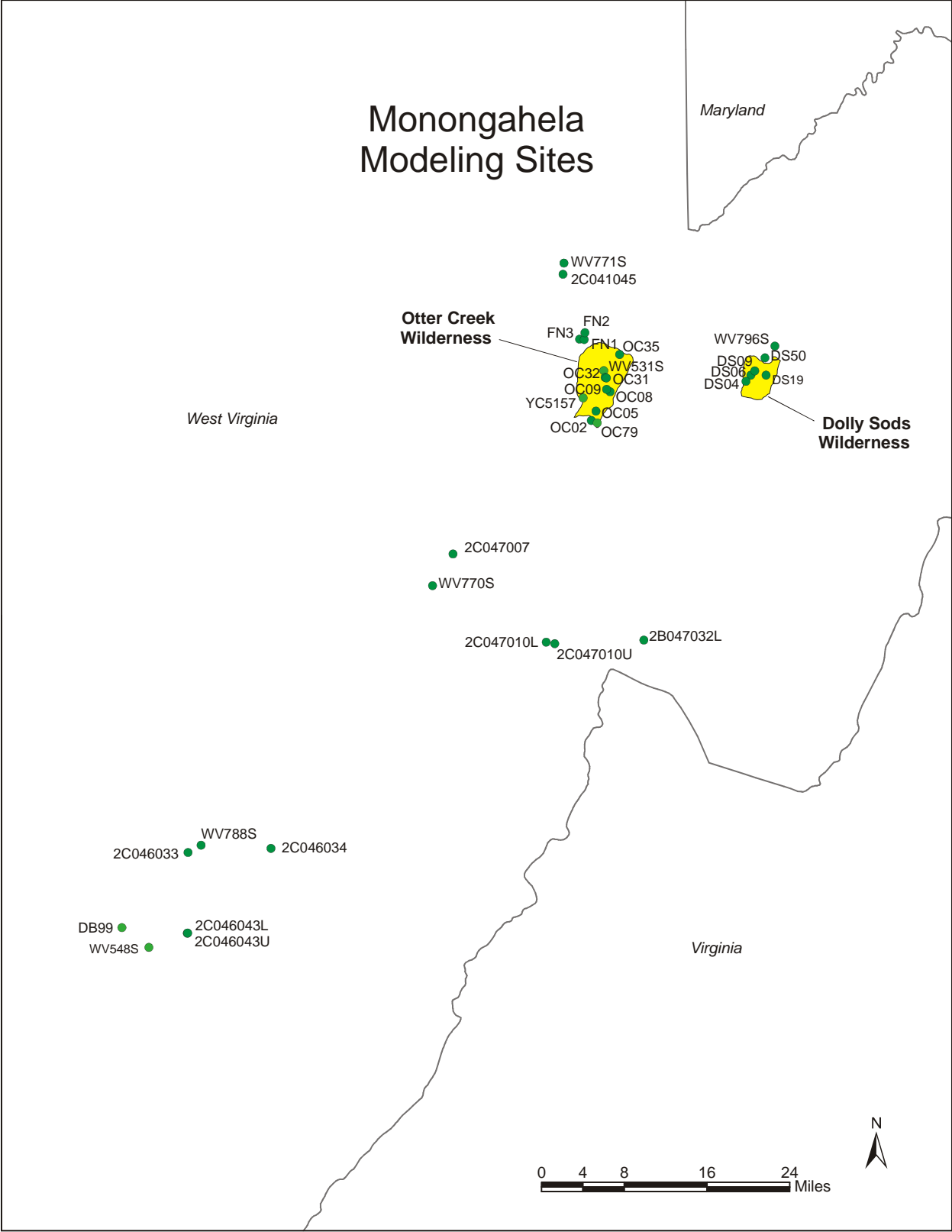


Figure 1. Modeling site locations.

with a watershed for which all input data were available. This pairing was accomplished by comparing watershed similarity on the basis of streamwater characteristics (ANC, sulfate, and base cation concentrations), physical characterization (location, elevation), and bedrock geology data. The missing data were then “borrowed” from the data-rich paired watershed judged to be most similar. The error associated with this surrogate data assignment step was quantified by applying the same approach to a suite of data-rich watersheds (i.e., borrowing data from a different data-rich watershed) and quantifying the average deviation between the projected streamwater ANC values obtained using measured data versus surrogate data (Sullivan et al. 2002a).

#### *Representation of Deposition and Meteorology Data for MAGIC*

MAGIC requires, as atmospheric inputs for each site, estimates of the total annual deposition (eq/ha/yr) of eight ions, and the annual precipitation volume (m/yr). The eight ions are: Ca, Mg, Na, K, NH<sub>4</sub>, SO<sub>4</sub>, Cl, and NO<sub>3</sub>. These total deposition data are required at each site for each year of the calibration period (the years for which observed streamwater data are used for calibrating the model to each site). Estimated total deposition data are also required for the 140 years preceding the calibration period as part of the calibration protocol for MAGIC. This section discusses the procedures used for generating these required long-term sequences of total ionic deposition for each SAMI site.

Total deposition of an ion at a particular SAMI site for any year can be represented as combined wet, dry, and occult (cloud and fog) deposition:

$$\text{TotDep} = \text{WetDep} + \text{DryDep} + \text{OccDep}.$$

Inputs to the model are specified as wet deposition (the annual flux in meq/m<sup>2</sup>/yr) and a dry and occult deposition factor (DDF, unitless) used to multiply the wet deposition in order to get total deposition:

$$\text{TotDep} = \text{WetDep} * \text{DDF},$$

where

$$\text{DDF} = 1 + \text{DryDep} / \text{WetDep} + \text{OccDep} / \text{WetDep}.$$

Thus, given an annual wet deposition flux (WetDep), the ratio of dry deposition to wet deposition (DryDep / WetDep), and the ratio of occult deposition to wet deposition (OccDep/WetDep) for a given year at a site, the total deposition for that site and year is uniquely determined.

In order to calibrate MAGIC, time-series of the total deposition at each site are needed for each year of: a) the calibration period and b) the historical reconstructions. The long-term historical observations do not exist and these sequences must be estimated. The procedure used to provide these input data was as follows. The absolute values of wet deposition and DDF (calculated from the DryDep/WetDep and OccDep/WetDep ratios) for each ion were averaged over the period 1991-1995. The averages at a site were used as Reference Year deposition values for the site (the Reference Year was designated as 1995). These absolute values for the Reference Year were derived from observed data as described below.

Given the Reference Year deposition values, the deposition data for historical and calibration periods can be calculated using the Reference Year absolute values and scaled time series of wet deposition and DDF that give the values for a given year as a fraction of the Reference Year value. For instance, to calculate the total deposition of a particular ion in some historical year j:

$$\text{TotDep}(j) = [\text{WetDep}(0) * \text{WetDepScale}(j) ] * [ \text{DDF}(0) * \text{DDF Scale}(j)] ,$$

where WetDep(0) is the Reference Year wet deposition (meq/m<sup>2</sup>/yr) of the ion, WetDepScale(j) is the scaled value of wet deposition in year j (expressed as a fraction of the wet deposition in the Reference Year), DDF(0) is the dry and occult deposition factor for the ion for the Reference Year, and DDFScale(j) is the scaled value of the dry and occult deposition factor in year j (expressed as a fraction of the DDF in the Reference Year). In constructing the historical deposition data, the scaled sequences of wet deposition and DDF were derived from simulations using the ASTRAP model as described in Appendix N of the SAMI aquatics report (Sullivan et al. 2002a).

The *absolute* value of wet deposition is time and space specific - varying geographically within the SAMI region, varying locally with elevation, and varying from year to year. It is desirable to have the estimates of wet deposition take into account the geographic location and elevation of the site as well as the year for which calibration data are available. Therefore,

estimates of wet deposition used for the SAMI Reference Year should be derived from a procedure (model) that has a high spatial resolution and considers elevation effects.

The *absolute* value of the DDF specifies the ratio between the absolute amounts of wet and total deposition. This ratio is less variable in time and space than is the estimate of total deposition. That is, if in a given year the wet deposition goes up, then the total deposition usually goes up also (and conversely); and if the elevation or aspect of a given site results in lower wet deposition, the total deposition will be lower also (and conversely). Estimates of DDF used for MAGIC calibrations may, therefore, be derived from a procedure (model) that has a lower spatial resolution and/or temporally smoothes the data.

Similarly, the *long-term sequences* used for MAGIC simulations do not require detailed spatial or temporal resolution. That is, if for any given year the deposition goes up at one site, it also goes up at neighboring sites. Thus, *scaled sequences* of deposition (normalized to the same year) at neighboring sites will be similar, even if the absolute deposition at the sites is different due to local aspect, elevation, etc. MAGIC requires scaled long-term sequences of wet deposition, DDF, and total deposition. Therefore, if the scaled long-term patterns of *any of these* do not vary much from place to place or year to year, estimates of the *scaled sequences* may be derived from a procedure (model) that has a relatively low spatial resolution and/or temporally smoothes the data.

#### *Wet Deposition Data (Reference Year and Calibration values)*

The absolute values of wet deposition used for defining the SAMI Reference Year and for the MAGIC calibrations must be highly site specific. We used estimated wet deposition data for each site derived from the spatial extrapolation model of Grimm and Lynch (1997) referred to here as the Lynch model. The Lynch model is based on observed wet deposition at NADP monitoring stations, and provides a spatially interpolated value of wet deposition of each of the eight ions needed for MAGIC. The model also makes a correction for changes in precipitation volume (and thus wet deposition) based on the elevation at a given site. This correction arises from a model of orographic effects on precipitation volumes derived from regional climatological data.

The latitude, longitude, and elevation of the MAGIC modeling sites were provided as inputs to the Lynch model. The model outputs were quarterly and annual wet deposition estimates for each modeling site. The annual data were used for definition of the SAMI Reference Year and for MAGIC calibration and simulation. The NADP data (and thus the

estimates provided by Lynch's model) cover the period 1983 to 1998. This period includes the SAMI reference period and the calibration periods for modeling sites.

#### *Dry and Occult Deposition Data and Historical Deposition Sequences*

The ASTRAP model was used to provide estimates of historical wet, dry, and occult deposition of sulfur and oxidized nitrogen at 33 sites in and around the SAMI region (Shannon 1998). The ASTRAP sites included 21 existing NADP deposition monitoring stations, 7 sites in Class I areas, and 5 sites that were neither NADP nor Class I. A number of these sites were outside the boundaries of SAMI and at much lower elevation than the sites modeled by MAGIC. A subset of the ASTRAP sites was used to set deposition input ratios for MAGIC. For each of the sites, ASTRAP produced wet, dry, and occult deposition estimates of sulfur and oxidized nitrogen every ten years starting in 1900 and ending in 1990. The model outputs are smoothed estimates of deposition roughly equivalent to a ten-year moving average centered on each of the output years.

Given the limited spatial and temporal resolution of the outputs from ASTRAP, these data were not sufficient for specification of the absolute wet deposition values needed for calibration of MAGIC. The outputs of ASTRAP were used, however, to estimate the absolute DDF for each site (using the DryDep/WetDep and OccDep/WetDep ratios from the ASTRAP output), and to set up the scaled sequences of past wet deposition and DDF for the calibration of each site.

The wet, dry, and occult deposition estimates provided by ASTRAP for each year (for both sulfur and oxidized nitrogen) at each ASTRAP site were used to calculate the DDF for each year and each site. This provided time series of DDF for sulfur and oxidized nitrogen for each ASTRAP site extending from 1900 to 1990. The value of DDF for 1990 was used as the absolute value of DDF for the SAMI Reference Year. MAGIC sites were assigned the DDF value of the nearest ASTRAP site, considering both distance and elevation. The time series of DDF values from 1900 to 1990 for each ASTRAP site was normalized to the 1990 value at each site to provide scaled sequences of DDF. The scaled sequence of past DDF used for each MAGIC site was taken from the nearest ASTRAP site.

At each of Shannon's sites, the time series of wet deposition were converted to scaled sequences by normalizing the values in any year to the value in 1990 at each site. The scaled

sequence of past wet deposition used for each MAGIC site was taken from the nearest ASTRAP site.

For each site, it was necessary to couple the past scaled sequences (used for the MAGIC calibration at the site) to the more recent scaled sequences. The past scaled sequences were tied to ASTRAP's past deposition estimates, which end in 1990. The more recent scaled sequences were based on the SAMI Reference Year, 1995. For each MAGIC site, it was necessary to provide estimates of the changes in deposition that occurred between 1990 and 1995. These changes were derived from the site specific deposition data provided by the Lynch model.

#### *Protocol for MAGIC Calibration and Simulation at Individual Sites in SAMI*

The aggregated nature of the MAGIC model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model that can be directly measured or observed in the system of interest (called fixed parameters). The model is then run (using observed and/or assumed atmospheric and hydrologic inputs) and the outputs (streamwater and soil chemical variables - called criterion variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called optimized parameters) are adjusted to improve the fit. After a number of iterations, the simulated-minus-observed values of the criterion variables usually converge to zero (within some specified tolerance). The model is then considered calibrated. If new assumptions (or values) for any of the fixed variables or inputs to the model are subsequently adopted, the model must be re-calibrated by re-adjusting the optimized parameters until the simulated-minus-observed values of the criterion variables again fall within the specified tolerance.

#### *Protocol and Data for Calibrating New Sites*

New model input data for soil and stream chemistry were provided by Monongahela National Forest for two streams. These new data were used to calibrate MAGIC to Yellow Creek and Desert Branch. The overall approach was similar to that employed for the SAMI calibrations, but more extensive data were available, especially for soils characterization. These new data, and the aggregation procedures employed for model calibration, are described below.

Soils data were available for six sites in the Desert Branch watershed, sampled by the Forest Service. Soil pH was measured in distilled water. Loss-on-ignition was measured at

550°C. Exchangeable acidity was extracted in NH<sub>4</sub>Cl and measured by plasma emission (ICPES). Effective cation exchange capacity (ECEC) was calculated by summation of the milliequivalent levels of Ca, K, Mg, Na, and acidity. Base saturation (BS) was calculated as the percentage of the ECEC provided by the base cations.

Of the six soil pits excavated in the Desert Branch watershed, two were within each of the Ernest and Buchanan soil types. One was excavated in Gilpin soils and one in an un-named alluvial soil that was mapped as Buchanan. These soil pits were considered to be representative of the variety of soil conditions present within the watershed. Samples from the A and B horizons were used for model calibration. Depth at these horizons ranged from 11 inches in the alluvial soil pit to 50 inches in the first Ernest soil pit (FSWV03067001). O-horizon samples were not used for model calibration. The sampled A horizon at soil pit #2 exhibited a very high loss-on-ignition (41.8%) and is more properly designated as an O horizon sample. The data for this horizon was, therefore, not averaged with other mineral soils data from that soil pit.

Raw data for the major soils data at Desert Branch are listed in Appendix A, Table A-1. These were weighted by horizon depth and averaged to yield one suite of average parameter values for each soil pit (Table A-2). There was relatively little difference in chemical characteristics among the soils types sampled within the watershed, especially in the B-horizon, which constituted the bulk of the upper mineral soil. In addition, differences between soil pits representing the same soil type were just as variable as differences between soil pits of different soil types. For example, the base saturation measured for the two Ernest soil pits (4.5% and 10.9%) differed as much as did the base saturation across all of the various types (Table A-2). All soil pits showed low average base saturation for the mineral soil, between about 4 and 11% (Table A-2). Base saturation less than about 15% suggests a potential concern for base cation loss (Reuss and Johnson 1986).

Soils data are available for four sites in the Yellow Creek watershed, sampled by the Forest Service. Soil pit #1 was situated close to the mouth of Yellow Creek. Soil pits 2, 3, and 4 were situated progressively further up into the watershed. The soils in this watershed are dominated by the Snowdog, Mandy, and Gauley series, high-elevation soils with a frigid soil temperature regime. At each site, samples were collected and analyzed from horizons designated as A, B, and C in the field, with depths of approximately 2, 10, and 18 inches, respectively. The horizon sampled as B included E and BE horizons; the horizon sampled as C was more typically

indicative of Bw horizon conditions (Mary Beth Adams, USDA Forest Service, pers. comm., August, 2004).

Raw data for the major soils variables in the four soil pits in the Yellow Creek watershed are listed in Table A-3. These were weighted by horizon depth and averaged to yield one suite of average parameter values for each soil pit (Table A-4). There was little difference in soils conditions among the various soil pits excavated within the Yellow Creek watershed. Base saturation values were extremely low, all less than 5% (Table A-4).

Bulk density data were not available for samples from the Desert Branch watershed. However, example bulk density data provided by the Forest Service (USDA Natural Resource Conservation Service, National Soil Survey Database) for the Gilpin, Ernest, and Buchanan soil types within the surrounding region indicated bulk density values that varied from about 1,300 to 1,600 mg/cm<sup>3</sup>. A value near 1400 mg/cm<sup>3</sup> was generally representative of the upper mineral soil (A and B horizons) Bulk density for Yellow Creek soils were provided by the Forest Service, ranging from 1,200 mg/cm<sup>3</sup> for the A, E, and BE horizons to 1,600 mg/cm<sup>3</sup> for the B<sub>w</sub> horizon. Again, a representative bulk density reported for the mineral soils was about 1,400 mg/cm<sup>3</sup>. This was the value selected to represent the overall mineral soil bulk density for both study watersheds for model calibration.

Stream chemistry was measured on four occasions during the Spring season in the lower reaches of Yellow Creek. Data are provided for the four sample occasions in Table 2. Although the samples were collected at two different locations, these were in close proximity and showed very consistent Spring chemistry values. All spring data for these two sites were therefore used for model calibration of Yellow Creek. Only one spring water chemistry sample was collected near the mouth of Desert Branch. It was used for model calibration. There was also one fall sample available, which as expected showed somewhat higher pH, ANC, Ca, and CALK (Table 2), where CALK is the calculated ANC from the charge balance:

$$\text{CALK} = (\text{Ca} + \text{Mg} + \text{K} + \text{Na} + \text{NH}_4) - (\text{SO}_4 + \text{NO}_3 + \text{Cl})$$

and all concentrations are in units of  $\mu\text{eq/L}$ . Desert Branch had spring ANC near zero and pH 5.4. Yellow Creek was extremely acidic, with calculated ANC about  $-135 \mu\text{eq/L}$  and pH 3.8.



Watershed	Site Location <sup>2</sup>	Sample Date	pH	ANC	Ca	Mg	Na	K	SO4	NO3	Cl	CAL K <sup>3</sup>	Al
Desert Branch	99-near mouth	11/01	5.8	6	83	46	6	7	91	6	19	26	11
		04/01	5.4	-1	54	50	9	8	90	14	14	2	37
Yellow Creek	51	05/94	3.8	-166	19	12	7	3	168	6	9	-142	-
	57	06/00	3.8	-	17	7	10	2	155	5	10	-134	-
	57	06/01	3.8	-	14	7	10	3	157	9	9	-141	-
	51	03/02	3.8	-182	16	12	9	4	142	11	13	-124	99

<sup>1</sup> Data are in units of ueq/L, except pH (standard units) and Al (ug/L)

<sup>2</sup> On Yellow Creek, site 51 is slightly upstream from site 57

<sup>3</sup>

Because there was not large variation in soil acid-base chemistry among the soil pits excavated within a given study watershed (Tables A-2 and A-4), and because variability within a given soil type was as large as variability among soil types (Table A-2), soils data were aggregated by averaging mineral soil parameter values for all soil pits within each study watershed (Table 3). These aggregated values were provided as inputs for the MAGIC model.

#### B. Critical Loads Analysis

The principal objectives of the critical loads analysis for the 33 study streams was to determine, using the MAGIC model, threshold levels of sustained atmospheric deposition of S below which harmful effects to sensitive aquatic receptors will not occur, and to evaluate interactions between the critical ANC endpoint value specified and the time period over which the critical load is examined. Critical loads for S deposition were calculated using the MAGIC model for the streams selected for modeling in this project.

The MAGIC model was used in an iterative fashion to calculate the S deposition values that would cause the chemistry of each of the modeled streams to either increase or decrease streamwater ANC (depending on the current value) to reach the specified levels. For these analyses, the critical ANC levels were set 0, 20, 50, and 100  $\mu\text{eq/L}$ , the first two of which are believed to approximately correspond with chronic and episodic damage to relatively acid-tolerant brook trout populations (Bulger et al. 2000). Other more acid-sensitive species of aquatic biota may be impacted at higher ANC values. In order to conduct this critical loads analysis for S deposition, it was necessary to specify the corresponding levels of N deposition. Nitrogen deposition accounts, however, for only a minor component of the overall acidification response of streams in the forest under study. For this analysis, future N deposition was held constant at 1990 levels.

It was also necessary to specify the times in the future at which the critical ANC values would be reached subsequent to a linear change, either up or down, in deposition to reach the various critical deposition load values. The ramped change in deposition was imposed over a ten-year period, through 2010, and then held constant thereafter in the simulations. We used the years 2020, 2040, and 2100 for evaluating water chemistry responses. It must be recognized that streamwater chemistry will continue to change in the future for many decades subsequent to stabilization of deposition levels. This is mainly because soils will continue to change in the

Table 3. Aggregated soils characteristics <sup>1</sup> provided as inputs to the MAGIC model for the Desert Branch and Yellow Creek watersheds.									
Watershed	Soil pH	Ca	K	Mg	Al	Na	Acidity	ECEC	BS (%)
		(mg/kg)					(meq/100g)		
Desert Branch	4.4	51.5	37.0	15.9	128.3	4.8	7.0	7.5	6.8
Yellow Creek	3.8	14.3	35.2	8.1	614.1	5.9	9.4	9.6	2.7

<sup>1</sup> Calculated as the average of the soil pits excavated in each watershed and given in Tables A-1 and A-3. ECEC is effective cation exchange capacity; BS is base saturation.

degree to which they adsorb incoming S and because some watersheds will have become depleted of base cations. The latter process can cause streamwater base cation concentrations and ANC to decrease over time while  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  concentrations maintain relatively constant levels.

## RESULTS AND DISCUSSION

Estimated annual average precipitation amount and total deposition of major ions at each modeling site are listed in Table 4. Estimated wet plus dry and occult S deposition in the reference year period (1991-1995) ranged at the various study sites from about 92 meq/m<sup>2</sup>/yr (15 kg S/ha/yr) to 136 meq/m<sup>2</sup>/yr (22 kg S/ha/yr).

The model was calibrated at each site to within a few  $\mu\text{eq/L}$  of observed chemistry for each major variable, except pH (Figure 2). The calibration year used for this comparison varied according to data source, ranging from 1985 for NSS data to 1994 for EMAP data and 1995 for the two new sites. Each watershed site was then modeled forward to 1995, which constituted the base year for this analysis.

Simulated stream chemistry at each of the modeled sites is given in Tables 5 through 7 for three points in time, pre-1900, 1975, and 1995, respectively. Model estimates of pre-1900 ANC in the modeled streams varied from 23  $\mu\text{eq/L}$  (site OC09, Devils Gulch) to 179  $\mu\text{eq/L}$  (site 2C041045, R. Fork Clover). Twenty-seven percent of the sites had simulated pre-industrial ANC below 50  $\mu\text{eq/L}$  (Table 5). None were simulated to have ANC below 20  $\mu\text{eq/L}$  pre-1900. Some sites showed relatively small estimates of acidification (< 50  $\mu\text{eq/L}$ ) since pre-1900. Other sites showed evidence of acidification through 1995 of more than 100  $\mu\text{eq/L}$  (Tables 5 and 7). Two sites (Crawford Run and Moss Run) were inferred to have had high  $\text{SO}_4^{2-}$  concentration (30 to 34  $\mu\text{eq/L}$ ) pre-1900. This can be attributed to probable geological sources of S in these two watersheds.

The calculated sulfur deposition critical loads for the modeled streams varied as a function of watershed sensitivity (as reflected in soils and streamwater characteristics), the selected ANC threshold, and the future year for which the evaluation was made. All of these criteria are important. For example, the modeled critical sulfur load to protect the streams from becoming acidic (ANC=0) in the year 2100 varied from less than zero (target ANC endpoint not achievable) to 19 kg S/ha/yr, slightly higher than average reference year deposition (Table 8).

Table 4. Total deposition (wet plus dry plus cloud) of ions at each modeled site in Monongahela National Forest for the reference year 1995. The reference year total deposition is defined as the average of the deposition for the period 1991-1995.

Site	Site No.	Volume (m/yr)	Total Deposition at Each Site (meq/m <sup>2</sup> /yr)										
			Ca	Mg	Na	K	NH <sub>4</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	SBC	SAA	Calc
Desert Branch	DB99	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Yellow Creek	YC5157	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Elk Run	2B047032	1.24	9.5	2.3	4.5	0.9	26.8	94.3	10.8	49.9	43.9	155.0	-111.1
R Fork Clover	2C041045	1.14	11.4	2.2	3.2	0.9	27.7	108.6	9.7	56.4	45.4	174.7	-129.2
Johnson Run	2C046033	1.29	9.4	2.2	4.1	1.0	26.8	96.9	10.1	52.6	43.4	159.6	-116.2
Hateful Run	2C046034	1.42	10.4	2.5	4.6	1.1	29.9	107.7	11.4	57.9	48.6	177.0	-128.5
N Fork Cherry-Lower	2C046043 L	1.34	9.2	2.2	4.2	1.0	27.2	97.1	10.0	52.9	43.8	160.0	-116.2
N Fork Cherry-Upper	2C046043 U	1.32	9.1	2.2	4.1	1.0	26.9	96.1	9.9	52.3	43.3	158.3	-115.0
Crawford Run	2C047007	1.23	10.4	2.2	3.7	0.9	27.1	101.8	10.0	53.6	44.4	165.3	-121.0
Clubhouse Run-Lower	2C047010 L	1.35	10.4	2.4	4.4	1.0	29.1	105.3	10.9	55.9	47.3	172.1	-124.8
Clubhouse Run-Upper	2C047010 U	1.37	10.5	2.4	4.5	1.0	29.4	106.3	11.1	56.4	47.9	173.8	-126.0
Little Stonecoal Run	DS04	1.34	7.2	1.6	2.9	0.6	30.0	106.2	4.9	56.8	42.3	167.9	-125.6
Stonecoal Run Left	DS06	1.34	7.2	1.6	2.9	0.6	30.0	106.2	4.9	56.8	42.3	167.9	-125.6
Stonecoal Run Right	DS09	1.34	7.2	1.6	2.9	0.6	30.0	106.2	4.9	56.8	42.3	167.9	-125.6
Fisher Spring Run	DS19	1.34	7.2	1.6	2.9	0.6	30.0	106.2	4.9	56.8	42.3	167.9	-125.6
Unnamed	DS50	1.34	7.2	1.6	2.9	0.6	30.0	106.2	4.9	56.8	42.3	167.9	-125.6
Fernow WS10	FN1	1.46	11.3	2.2	3.2	0.8	34.8	135.7	7.3	70.9	52.3	213.9	-161.5
Fernow WS13	FN2	1.43	11.0	2.1	3.2	0.8	33.8	132.0	7.2	69.0	50.9	208.1	-157.2
Fernow WS4	FN3	1.47	11.3	2.2	3.3	0.9	34.8	136.0	7.4	71.0	52.5	214.4	-162.0
Condon Run	OC02	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Yellow Creek	OC05	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Unnamed	OC08	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Devils Gulch	OC09	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Possession Camp Run	OC31	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Moores Run	OC32	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Coal Run	OC35	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Otter Creek Upper	OC79	1.36	8.4	1.7	2.7	0.7	31.2	118.2	4.7	62.2	44.6	185.2	-140.6
Otter Creek	WV531S	1.32	13.3	2.6	4.0	1.0	31.5	121.5	12.1	62.5	52.4	196.1	-143.7
Noname Trib S Fork Cherry	WV548S	1.28	9.5	2.3	4.3	1.0	25.9	92.4	11.0	50.4	43.1	153.8	-110.6
Moss Run	WV770S	1.23	10.9	2.4	4.0	1.0	27.1	101.5	11.2	53.2	45.4	165.8	-120.5

Left Fork Clover Run	<b>WV771S</b>	1.12	11.9	2.3	3.3	0.9	27.3	106.9	10.6	55.3	45.7	172.9	-127.2
White Oak Fork	<b>WV788S</b>	1.32	10.3	2.4	4.5	1.1	27.3	99.2	11.5	53.7	45.5	164.4	-118.9
Red Creek	<b>WV796S</b>	1.47	13.0	3.0	5.2	1.2	33.8	118.7	14.3	62.8	56.3	195.9	-139.6

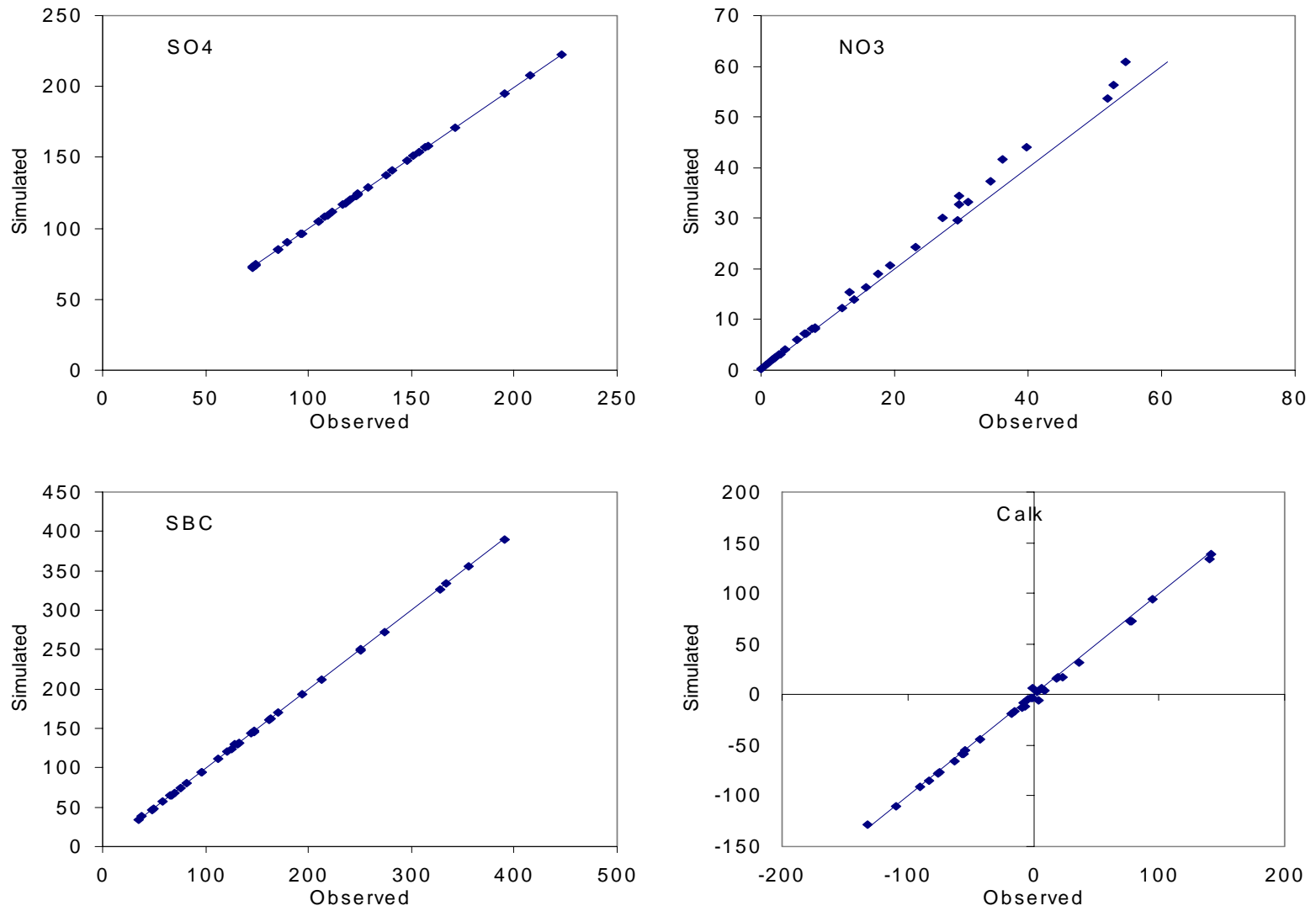


Figure 2. Simulated versus observed stream chemistry for the calibration years at each site.

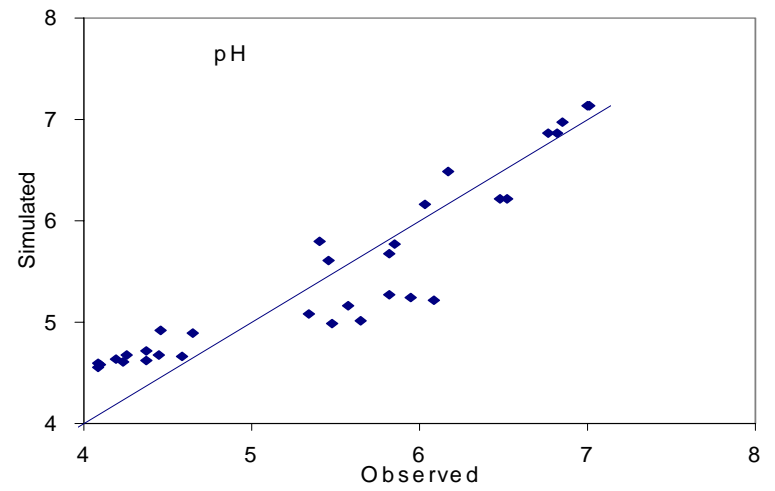
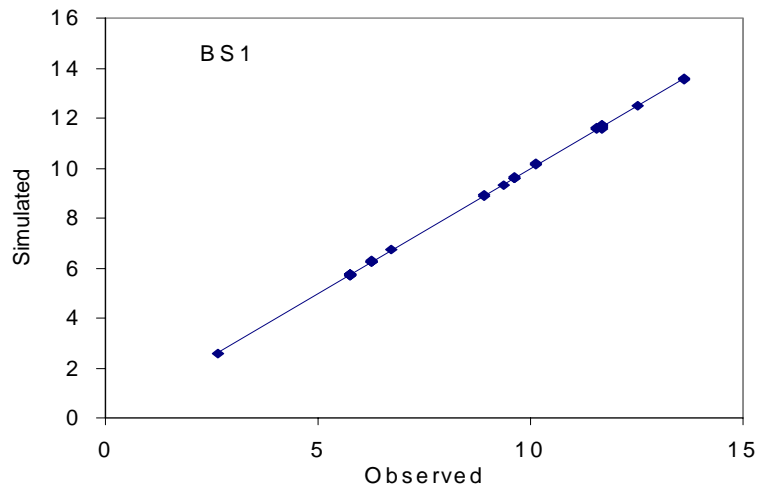
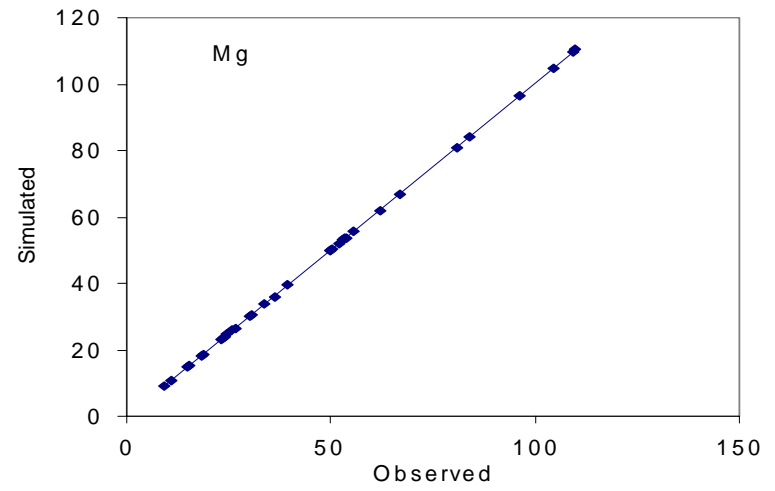
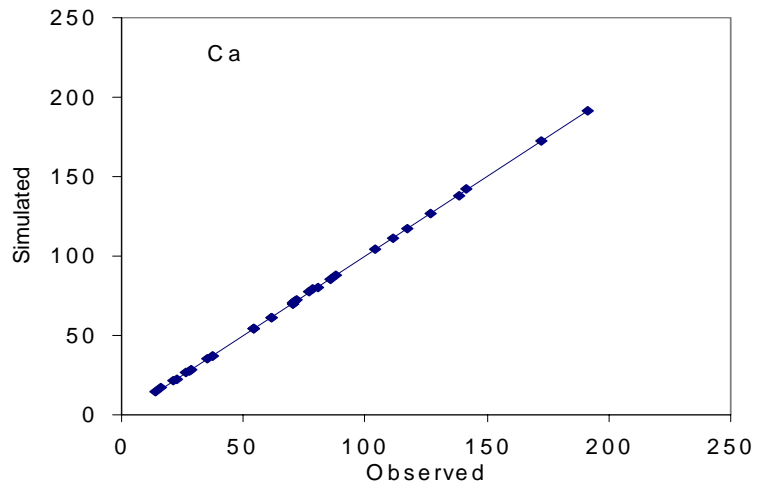


Figure 2. Continued.



Table 5. Simulated pre-1900 concentrations of a variety of ions in streamwater for the modeled streams in Monongahela National Forest.

Site	Site No.	Pre-1900 Simulated Stream Water Concentrations in $\mu\text{eq/L}$ (except pH)											
		Ca	Mg	Na	K	NH <sub>4</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	SBC	SAA	Calk	pH
Desert Branch	DB99	43.7	42.2	8.0	6.3	0.0	0.0	9.8	0.0	100.8	9.8	90.7	7.0
Yellow Creek	YC5157	13.9	6.8	8.9	2.6	0.0	0.0	7.8	0.0	32.3	7.8	24.7	6.4
Elk Run	2B047032	43.0	44.9	36.7	11.2	0.0	0.0	13.2	0.0	135.2	13.2	122.5	7.1
R Fork Clover	2C041045	84.3	59.8	90.9	13.5	0.0	0.0	70.9	0.0	246.8	70.9	179.1	7.3
Johnson Run	2C046033	18.3	18.1	7.2	5.8	0.0	0.0	13.4	0.0	47.7	13.4	35.0	6.5
Hateful Run	2C046034	51.3	36.3	6.4	5.7	0.0	0.0	12.2	0.0	100.1	12.2	88.2	7.0
N Fork Cherry-Lower	2C046043 L	87.7	35.3	81.8	5.8	0.0	0.0	94.7	0.0	211.5	94.7	109.5	7.1
N Fork Cherry-Upper	2C046043 U	70.8	32.7	69.2	6.0	0.0	0.0	81.6	0.0	178.7	81.6	96.1	7.0
Crawford Run	2C047007	47.7	49.3	46.2	16.5	0.0	30.9	16.7	0.0	159.1	47.7	108.7	7.1
Clubhouse Run-Lower	2C047010 L	52.3	40.3	21.7	15.5	0.0	0.0	14.6	0.0	130.0	14.6	115.0	7.1
Clubhouse Run-Upper	2C047010 U	19.5	18.2	20.8	11.0	0.0	0.0	13.8	0.0	69.5	13.8	55.5	6.8
Little Stonecoal Run	DS04	27.4	24.0	7.7	5.0	0.0	0.0	11.5	0.0	64.7	11.5	51.9	6.7
Stonecoal Run Left	DS06	20.9	19.8	8.2	3.9	0.0	0.0	11.5	0.0	53.5	11.5	41.5	6.6
Stonecoal Run Right	DS09	30.2	18.8	8.5	4.2	0.0	0.0	9.5	0.0	62.4	9.5	51.8	6.7
Fisher Spring Run	DS19	44.8	21.8	7.7	4.4	0.0	0.0	11.0	0.0	78.7	11.0	67.4	6.8
Unnamed	DS50	31.9	15.8	7.7	3.3	0.0	0.0	8.2	0.0	60.2	8.2	51.9	6.7
Fernow WS10	FN1	40.4	50.3	29.1	7.6	0.0	0.0	11.5	0.0	126.0	11.5	115.0	7.1
Fernow WS13	FN2	71.5	57.9	20.1	13.2	0.0	0.0	12.2	0.0	164.2	12.2	152.1	7.2
Fernow WS4	FN3	66.4	54.6	13.5	11.8	0.0	0.0	14.2	0.0	146.9	14.2	132.7	7.1
Condon Run	OC02	43.8	20.3	6.2	4.8	0.0	0.0	10.4	0.0	76.0	10.4	65.6	6.8
Yellow Creek	OC05	18.3	12.4	6.7	3.0	0.0	0.0	7.9	0.0	40.3	7.9	32.3	6.5
Unnamed	OC08	23.0	19.5	6.4	4.4	0.0	0.0	8.8	0.0	53.3	8.8	44.5	6.7
Devils Gulch	OC09	11.6	8.5	6.3	2.1	0.0	0.0	6.3	0.0	29.1	6.3	22.8	6.3

Possession Camp Run	OC31	16.3	11.4	6.2	2.4	0.0	0.0	7.8	0.0	37.1	7.8	29.4	6.5
Moores Run	OC32	21.8	14.2	6.2	3.2	0.0	0.0	7.8	0.0	46.0	7.8	37.8	6.6
Coal Run	OC35	40.2	17.7	11.1	2.8	0.0	0.0	8.1	0.0	71.8	8.1	64.8	6.8
Otter Creek Upper	OC79	62.2	30.6	8.3	6.7	0.0	0.0	9.9	0.0	108.8	9.9	99.3	7.0
Otter Creek	WV531S	47.6	9.8	8.2	4.3	0.0	0.0	13.2	0.0	71.0	13.2	58.4	6.8
Noname Trib S Fork Cherry	WV548S	54.4	43.2	9.8	10.0	0.0	0.0	15.4	0.0	118.4	15.4	102.8	7.0
Moss Run	WV770S	55.1	56.6	55.2	21.0	0.0	33.5	18.5	0.0	184.4	51.4	132.9	7.1
Left Fork Clover Run	WV771S	88.8	49.0	47.3	12.8	0.0	0.0	26.8	0.0	198.2	26.8	173.5	7.3
White Oak Fork	WV788S	25.7	13.4	8.2	6.5	0.0	0.0	12.0	0.0	53.0	12.0	41.1	6.6
Red Creek	WV796S	37.9	16.9	9.5	3.4	0.0	0.0	13.1	0.0	67.2	13.1	53.8	6.7

Table 6. Simulated 1975 concentrations of a variety of ions in streamwater for the modeled streams in Monongahela National Forest.

Site	1975 Simulated Stream Water Concentrations in $\mu\text{eq/L}$ (except pH)											
	Ca	Mg	Na	K	NH <sub>4</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	SBC	SAA	Calk	pH
Desert Branch	51.3	48.4	9.0	7.5	0.0	63.3	9.8	15.0	116.1	87.7	26.7	6.4
Yellow Creek	16.7	8.7	9.7	3.0	0.0	111.4	7.8	8.8	37.9	128.6	-89.8	4.6
Elk Run	105.0	85.6	37.7	17.1	0.0	110.4	13.2	41.0	247.4	163.8	82.9	6.9
R Fork Clover	160.4	101.0	93.2	18.4	0.0	130.5	70.9	29.7	373.4	226.7	144.0	7.2
Johnson Run	57.8	50.9	7.9	9.6	0.0	73.4	13.4	43.4	126.0	131.1	-4.5	5.2
Hateful Run	77.5	53.0	7.3	7.9	0.0	96.3	12.2	36.9	146.3	145.9	0.2	5.4
N Fork Cherry-Lower	126.7	54.6	83.0	7.8	0.0	126.1	94.7	32.3	271.1	254.0	19.4	6.3
N Fork Cherry-Upper	114.9	53.1	70.9	7.6	0.0	123.9	81.6	33.9	246.2	239.4	6.8	5.8
Crawford Run	130.0	108.4	49.7	25.5	0.0	204.8	16.7	15.3	313.8	236.7	77.2	6.9
Clubhouse Run-Lower	68.8	49.9	22.7	17.7	0.0	62.2	14.6	55.6	159.0	133.1	23.7	6.4
Clubhouse Run-Upper	67.0	49.7	22.4	18.2	0.0	60.8	13.8	60.0	158.8	132.7	22.7	6.3
L. Stonecoal Run	32.9	28.8	8.7	5.7	0.0	83.2	11.5	7.5	75.6	102.7	-25.7	4.8
Stonecoal Run Left	25.4	23.3	9.2	4.3	0.0	79.5	11.5	7.5	62.2	97.5	-35.1	4.8
Stonecoal Run Right	35.2	22.0	9.2	4.8	0.0	75.6	9.5	3.3	71.9	89.1	-18.7	4.9
Fisher Spring Run	51.6	25.2	8.5	4.9	0.0	68.9	11.0	6.1	90.4	87.5	5.0	5.7
Unnamed	36.0	17.7	8.7	3.8	0.0	53.8	8.2	4.2	66.6	65.4	-0.5	5.4
Fernow WS10	81.3	85.4	31.1	12.5	0.0	145.3	11.5	8.3	214.2	165.8	48.4	6.7
Fernow WS13	90.3	69.7	21.4	16.7	0.0	116.2	12.2	30.4	199.1	155.7	42.4	6.6
Fernow WS4	80.6	63.7	14.5	14.0	0.0	72.8	14.2	55.0	172.8	139.5	30.8	6.5
Condon Run	52.7	24.9	8.1	5.6	0.0	86.4	10.4	21.0	91.0	117.8	-26.9	4.8
Yellow Creek	21.7	14.7	7.3	3.3	0.0	90.8	7.9	2.3	46.6	100.7	-53.0	4.7
Unnamed	27.5	22.8	6.9	4.9	0.0	92.6	8.8	2.5	62.2	104.3	-42.2	4.7
Devils Gulch	14.2	10.5	6.9	2.3	0.0	90.2	6.3	1.0	33.6	97.2	-63.6	4.7
Possession Camp Run	20.4	14.0	7.1	2.8	0.0	109.9	7.8	1.7	44.9	119.5	-74.2	4.6
Moore's Run	26.6	17.2	7.1	3.9	0.0	91.6	7.8	3.2	55.1	102.6	-46.4	4.7
Coal Run	60.5	28.4	13.9	4.4	0.0	119.0	8.1	2.5	108.8	129.4	-20.8	4.9
Otter Creek Upper	70.0	35.1	9.2	7.8	0.0	53.9	9.9	24.8	122.6	88.7	34.6	6.5
Otter Creek	99.1	21.7	9.3	6.2	0.0	96.3	13.2	8.7	136.6	118.7	17.0	6.2
Noname Trib S Fork Cherry	70.4	54.5	10.4	11.9	0.0	84.9	15.4	34.7	148.1	134.2	12.1	6.0
Moss Run	121.1	107.3	56.9	29.0	0.0	176.7	18.5	12.8	315.3	209.4	103.9	7.0
Left Fork Clover Run	161.0	83.5	49.4	17.4	0.0	117.0	26.8	19.2	312.7	165.7	149.9	7.2
White Oak Fork	68.3	37.0	9.6	10.5	0.0	79.1	12.0	17.1	124.6	108.0	16.6	6.2

Table 7. Simulated 1995 concentrations of a variety of ions in streamwater for the modeled streams in Monongahela National Forest.

Site	1995 Simulated Stream Water Concentrations in $\mu\text{eq/L}$ (except pH)											
	Ca	Mg	Na	K	NH <sub>4</sub>	SO <sub>4</sub>	Cl	NO <sub>3</sub>	SBC	SAA	Calk	pH
Desert Branch	54.2	49.7	9.2	7.7	0.0	89.9	9.8	14.0	120.9	114.0	6.3	5.8
Yellow Creek	17.0	9.0	9.7	3.1	0.0	151.2	7.8	8.1	39.0	166.6	-128.4	4.5
Elk Run	106.8	78.1	37.2	17.8	0.0	127.7	13.2	37.5	239.3	178.4	62.9	6.8
R Fork Clover	176.9	103.3	92.2	20.2	0.0	168.8	70.9	28.3	393.3	269.8	126.0	7.1
Johnson Run	62.6	51.4	7.8	10.0	0.0	94.1	13.4	40.1	131.6	147.7	-16.5	4.9
Hateful Run	74.8	50.8	7.0	8.2	0.0	116.4	12.2	34.0	140.4	162.4	-21.6	4.9
N Fork Cherry-Lower	123.0	54.5	81.8	8.1	0.0	146.6	94.7	29.9	267.3	272.9	-2.6	5.3
N Fork Cherry-Upper	115.2	52.8	69.6	7.8	0.0	144.3	81.6	31.4	246.2	257.5	-11.7	5.0
Crawford Run	146.0	105.0	48.3	26.6	0.0	226.1	16.7	14.3	325.6	257.2	69.8	6.8
Clubhouse Run-Lower	70.1	49.5	22.0	18.3	0.0	84.3	14.6	51.4	160.0	150.5	11.9	6.0
Clubhouse Run-Upper	73.6	48.6	21.5	18.3	0.0	81.8	13.8	55.7	161.6	150.8	13.4	6.1
L. Stonecoal Run	35.1	30.1	9.0	6.0	0.0	117.8	11.5	7.1	80.0	136.7	-56.4	4.7
Stonecoal Run Left	27.2	24.6	9.5	4.6	0.0	113.1	11.5	7.1	65.6	131.7	-66.9	4.6
Stonecoal Run Right	37.0	23.0	9.3	5.0	0.0	105.9	9.5	3.1	74.5	118.8	-44.6	4.7
Fisher Spring Run	53.9	26.6	8.7	5.3	0.0	97.6	11.0	5.7	94.7	114.5	-20.2	4.9
Unnamed	37.1	18.7	8.9	4.1	0.0	73.3	8.2	3.9	68.7	85.8	-17.3	4.9
Fernow WS10	84.7	79.9	30.6	15.0	0.0	196.1	11.5	8.0	210.4	215.3	-5.6	5.2
Fernow WS13	87.4	66.5	21.0	18.1	0.0	158.2	12.2	29.1	193.2	199.4	-6.3	5.2
Fernow WS4	78.7	61.7	14.3	14.6	0.0	105.9	14.2	52.5	169.0	172.4	-3.9	5.2
Condon Run	54.3	25.8	8.2	6.1	0.0	124.4	10.4	20.2	94.5	154.6	-59.4	4.7
Yellow Creek	22.5	15.1	7.4	3.4	0.0	123.9	7.9	2.2	48.5	133.8	-85.5	4.6
Unnamed	28.5	23.6	7.1	5.1	0.0	129.9	8.8	2.4	64.5	141.0	-77.2	4.6
Devils Gulch	14.6	10.8	6.9	2.4	0.0	118.5	6.3	0.9	34.5	126.0	-91.2	4.6
Possession Camp Run	21.5	14.8	7.3	3.0	0.0	149.0	7.8	1.6	46.6	158.5	-111.8	4.6
Moore's Run	27.8	18.0	7.3	4.1	0.0	124.9	7.8	3.0	57.4	135.6	-78.3	4.6
Coal Run	61.0	30.6	14.2	5.2	0.0	159.4	8.1	2.4	110.8	169.7	-59.3	4.7
Otter Creek Upper	70.1	35.7	9.5	8.0	0.0	75.2	9.9	23.7	123.7	109.5	15.2	6.2
Otter Creek	104.2	24.2	9.1	6.6	0.0	120.1	13.2	8.3	143.7	141.6	2.8	5.6
Noname Trib S Fork Cherry	70.2	53.2	10.2	12.4	0.0	108.3	15.4	32.2	145.9	155.9	-8.4	5.1
Moss Run	137.7	109.2	56.1	29.8	0.0	208.0	18.5	12.0	333.4	238.7	93.7	7.0
Left Fork Clover Run	192.1	96.9	49.0	18.9	0.0	172.7	26.8	18.6	355.8	217.1	137.7	7.1
White Oak Fork	71.2	39.3	9.1	10.6	0.0	96.2	12.0	15.8	129.8	124.4	5.8	5.8
Red Creek	80.5	33.6	10.1	4.9	0.0	85.3	13.1	0.2	129.6	98.9	31.1	6.5
Red Creek	71.2	30.8	10.2	4.5	0.0	66.3	13.1	0.2	117.2	79.6	38.3	6.6

Table 8. Estimated critical load (kg/ha/yr) of sulfur\* to achieve a variety of ANC ( $\mu\text{eq/L}$ ) endpoints in a variety of future years for modeled streams in Monongahela National Forest.\*\*

Site	Simulated Calc ( $\mu\text{eq/L}$ )			Critical Load of S deposition to achieve ANC value***											
				Endpoint ANC = 0			Endpoint ANC =20			Endpoint ANC =50			Endpoint ANC =100		
	pre-1900	1975	1995	2020	2040	2100	2020	2040	2100	2020	2040	2100	2020	2040	2100
Desert Branch	91	27	6			2.0									
Yellow Creek	25	-90	-128												
Elk Run	123	83	63	32.5	15.0	12.9	25.8	11.1	9.9	10.1	3.1	4.8			
R Fork Clover	179	144	126	77.1	39.8	18.3	73.2	37.6	16.8	65.8	33.5	14.4	45.3	22.2	8.7
Johnson Run	35	-5	-17												
Hateful Run	88	0	-22			4.3									
N Fork Cherry-Lower	109	19	-3	0.4	5.7	7.8			3.9						
N Fork Cherry-Upper	96	7	-12	0.3	5.8	7.6			3.6						
Crawford Run	109	77	70	67.7	32.6	13.7	60.5	29.7	12.6	39.3	20.4	9.2			
Clubhouse Run-Lower	115	24	12		0.4	3.5									
Clubhouse Run-Upper	56	23	13			1.3									
L. Stonecoal Run	52	-26	-56												
Stonecoal Run Left	42	-35	-67												
Stonecoal Run Right	52	-19	-45												
Fisher Spring Run	67	5	-20			0.4									
Unnamed	52	-1	-17												
Fernow WS10	115	48	-6		5.5	10.3			7.3			1.9			
Fernow WS13	152	42	-6		1.8	7.6			4.3						
Fernow WS4	133	31	-4			2.2									
Condon Run	66	-27	-59												
Yellow Creek	32	-53	-86												
Unnamed	45	-42	-77												
Devils Gulch	23	-64	-91												
Possession Camp Run	29	-74	-112												
Moore's Run	38	-46	-78												
Coal Run	65	-21	-59			0.9									
Otter Creek Upper	99	35	15	3.4	2.9	3.4									
Otter Creek	58	17	3	0.1	6.6	8.8			3.0						
Noname Trib S Fork Cherry	103	12	-8			4.0									
Moss Run	133	104	94	58.7	31.9	17.0	53.2	28.7	15.1	42.4	22.7	11.9	8.0	5.1	3.7

Table 8. Continued.															
Site	Simulated Calc ( $\mu\text{eq/L}$ )			Critical Load of S deposition to achieve ANC value***											
				Endpoint ANC = 0			Endpoint ANC =20			Endpoint ANC =50			Endpoint ANC =100		
	pre-1900	1975	1995	2020	2040	2100	2020	2040	2100	2020	2040	2100	2020	2040	2100
L Fork Clover Run	173	150	138	89.3	46.5	18.9	85.5	44.5	18.0	78.5	40.7	16.4	58.5	29.6	11.6
White Oak Fork	41	17	6		2.4	5.8									
Red Creek	54	38	31	38.3	22.9	14.8	9.8	9.0	8.1						

\* Current deposition of sulfur is about 18 kg/ha/yr  
\*\* All simulations based on straight-line ramp changes in deposition from 2000 to 2010, followed by constant deposition thereafter.  
\*\*\* Blank entries indicate that ecological endpoint could not be achieved (no recovery) even if S deposition was reduced to zero.

For example, for site FN1 (Fernow watershed 10) in the year 2100, the critical load to protect against ANC=0 was 10 kg S/ha/yr, but this watershed could tolerate only 2 kg S/ha/yr to protect against acidification to ANC of 50  $\mu\text{eq/L}$  within the same time period. The model suggested that it would not be possible to achieve ANC=100  $\mu\text{eq/L}$  at this site by 2100, even if sulfur deposition was reduced to zero (Table 8). The estimated pre-1900 ANC of this stream was 115  $\mu\text{eq/L}$ , which had declined to -6  $\mu\text{eq/L}$  by 1995.

The relationships between critical load, selection of ANC criterion value, and selection of evaluation year were investigated. For some streams, the simulations suggested that higher critical loads can be tolerated if one is willing to wait a longer period of time to allow chemical recovery to occur (Table 8). These tend to be the streams that had low ANC (below or near zero) in 1995. Streams that had higher ANC in 1995 ( $> 50 \mu\text{eq/L}$ ) showed lower critical load estimates further into the future. This is the result of continued reduction in S adsorption capacity of watershed soils. Higher critical loads are allowable if one wishes to prevent acidification to ANC = 0 (chronic acidification) than if one wishes to prevent acidification to ANC below 20  $\mu\text{eq/L}$  (possible episodic acidification) or some higher ANC endpoint.

For many of the modeled streams, the various ecological endpoints (ANC=0, 20, 50, 100  $\mu\text{eq/L}$ ) were simulated to not be achievable even if S deposition was reduced to zero. For example, only one-third of the modeled sites were projected to be able to recover to ANC=0 by 2020, and several of those (e.g., North Fork Cherry, Otter Creek) could only do so if S deposition was reduced to below 4 kg/ha/yr (Table 8). If the endpoint year is pushed back to 2100, instead of 2020, more of the modeled sites (64%) could achieve ANC=0 according to the simulations, but again many would require quite low levels of S deposition in order for this to occur (Table 8).

Relatively few streams were projected to be able to achieve ANC values of 50 or 100  $\mu\text{eq/L}$ , even if S deposition was reduced to zero. This result was consistent regardless of what endpoint year was used in the simulation (Table 8).

Table 9 provides estimates of the percent change in sulfur deposition required to achieve ANC values of 0, 20, 50, or 100  $\mu\text{eq/L}$  by the years 2020, 2040, and 2100. Most of the streams modeled would either require decreased deposition to protect against acidification to ANC=0 in 2100, or could not get there at all.

Table 9. Estimated percent change in current (1991-1995) sulfur deposition\* required to produce a variety of ANC ( $\mu\text{eq/L}$ ) endpoints in a variety of future years for modeled streams in Monongahela National Forest.\*\*

Site	Simulated Calc ( $\mu\text{eq/L}$ )			Critical Load of S deposition to achieve ANC value***											
				Endpoint ANC = 0			Endpoint ANC =20			Endpoint ANC =50			Endpoint ANC =100		
	pre-1900	1975	1995	2020	2040	2100	2020	2040	2100	2020	2040	2100	2020	2040	2100
Desert Branch	91	27	6			-90									
Yellow Creek	25	-90	-128												
Elk Run	123	83	63	116	0	-15	71	-26	-34	-33	-80	-68			
R Fork Clover	179	144	126	341	127	5	318	115	-4	276	91	-18	159	27	-50
Johnson Run	35	-5	-17												
Hateful Run	88	0	-22			-75									
N Fork Cherry-Lower	109	19	-3	-98	-63	-50			-75						
N Fork Cherry-Upper	96	7	-12	-98	-62	-50			-77						
Crawford Run	109	77	70	299	92	-19	257	75	-26	132	20	-46			
Clubhouse Run-Lower	115	24	12		-98	-79									
Clubhouse Run-Upper	56	23	13			-93									
L. Stonecoal Run	52	-26	-56												
Stonecoal Run Left	42	-35	-67												
Stonecoal Run Right	52	-19	-45												
Fisher Spring Run	67	5	-20			-98									
Unnamed	52	-1	-17												
Fernow WS10	115	48	-6		-74	-52			-66			-91			
Fernow WS13	152	42	-6		-91	-64			-80						
Fernow WS4	133	31	-4			-90									
Condon Run	66	-27	-59												
Yellow Creek	32	-53	-86												
Unnamed	45	-42	-77												
Devils Gulch	23	-64	-91												
Possession Camp Run	29	-74	-112												
Moore's Run	38	-46	-78												



Coal Run	65	-21	-59			-95									
Otter Creek Upper	99	35	15	-82	-85	-82									
Otter Creek	58	17	3	-99	-66	-54				-84					

Table 9. Continued.

Site	Simulated Calc ( $\mu\text{eq/L}$ )			Critical Load of S deposition to achieve ANC value***											
				Endpoint ANC = 0			Endpoint ANC =20			Endpoint ANC =50			Endpoint ANC =100		
	pre-1900	1975	1995	2020	2040	2100	2020	2040	2100	2020	2040	2100	2020	2040	2100
Noname Trib S Fork Cherry	103	12	-8			-73									
Moss Run	133	104	94	261	96	4	227	76	-7	160	39	-27	-51	-68	-77
L Fork Clover Run	173	150	138	415	168	9	393	157	4	352	135	-6	238	71	-33
White Oak Fork	41	17	6		-85	-64									
Red Creek	54	38	31	102	21	-22	-49	-53	-57						

\* Current deposition of sulfur is about 18 kg/ha/yr

\*\* All simulations based on straight-line ramp changes in deposition from 2000 to 2010, followed by constant deposition thereafter.

\*\*\* Blank entries indicate that ecological endpoint could not be achieved (no recovery) even if S deposition was reduced to zero.

Site	1975 Calc ( $\mu\text{eq/L}$ )	1995 Calc ( $\mu\text{eq/L}$ )	Evaluation Year		
			2020	2040	2100
Desert Branch	27	6			
Yellow Creek	-90	-128		5.9	9.8
Elk Run	83	63			
R Fork Clover	144	126			
Johnson Run	-5	-17			
Hateful Run	0	-22			4.3
N Fork Cherry-Lower	19	-3			4.1
N Fork Cherry-Upper	7	-12		3.5	6.3
Crawford Run	77	70			0.8
Clubhouse Run-Lower	24	12			
Clubhouse Run-Upper	23	13			
L. Stonecoal Run	-26	-56			1.1
Stonecoal Run Left	-35	-67			1.6
Stonecoal Run Right	-19	-45			2.2
Fisher Spring Run	5	-20			
Unnamed	-1	-17			
Fernow WS10	48	-6			2.3
Fernow WS13	42	-6			0.0
Fernow WS4	31	-4			
Condon Run	-27	-59			0.1
Yellow Creek	-53	-86		0.6	6.1
Unnamed	-42	-77			4.8
Devils Gulch	-64	-91		4.9	9.0
Possession Camp Run	-74	-112		4.5	8.7
Moore's Run	-46	-78			5.4
Coal Run	-21	-59			4.8
Otter Creek Upper	35	15			
Otter Creek	17	3			4.0
Noname Trib S Fork Cherry	12	-8			1.2
Moss Run	104	94	3.3	2.9	2.7
Left Fork Clover Run	150	138			
White Oak Fork	17	6			0.5
Red Creek	38	31			0.0
* Current deposition of sulfur is about 18 kg/ha/yr					
** Blank entries indicate that ecological endpoint could not be achieved (no recovery) even if S deposition was reduced to zero.					

Only one site (WV770S) was simulated to be able to regain its 1975 ANC value by the year 2020, and this would require a sustained S deposition load of 3.3 kg S/ha/yr (Table 10). If

one was willing to wait until 2040, then six modeled sites might regain 1975 ANC; in all cases, this would require S deposition to be below 6 kg S/ha/yr. Two-thirds of the modeled sites were estimated to be able to regain 1975 ANC by 2100, but in all cases this would require a reduction in S deposition of 50% or more from 1995 levels (Table 10).

A time trace of simulated water chemistry from 1900 to 1995 is shown for the stream site at Desert Branch in Figure 3. The modeled response is fairly typical for very acid-sensitive streams in the southeastern United States, showing large increase in  $\text{SO}_4^{2-}$  concentration, increase in base cation concentrations, and decreases in ANC, pH, and soil base saturation. These simulated responses are due largely to depletion over time in the amount of S adsorption on watershed soils. Soil base cation depletion is also important. Time traces for the other modeled sites are presented in Appendix B. Patterns of response are generally similar, but differ in degree. In particular, changes over time in the concentration of  $\text{SO}_4^{2-}$  in streamwater is important in determining changes in other ionic constituents.

The data presented in Tables 6 through 9 illustrate that how you phrase the critical load question is extremely important. The estimated deposition change required to achieve certain benchmark streamwater chemistry endpoints can be highly variable depending on how and for what time period the endpoint is defined, and on the starting point chemistry of the watersheds that are modeled.

It is important to consider the level of uncertainty associated with model projections when interpreting the results. The uncertainties of the model projections that formed the basis for this evaluation were discussed in detail by Sullivan et al. (2002a). The data that formed the basis of the model calibrations were internally consistent. Many sites were sampled within large synoptic water chemistry surveys that had substantial Quality Assurance/Quality Control (QA/QC) programs in place. Although the input data appear to be of high quality, the laboratory analytical error for calculated ANC is on the order of 13  $\mu\text{eq/L}$ , based on previous unpublished analyses of National Surface Water Survey data.

Streamwater chemistry is temporally variable, especially in response to hydrological conditions and seasonality. Data used for model calibration generally represented spring baseflow periods. Most streams would be expected to show lower ANC during rainfall events.

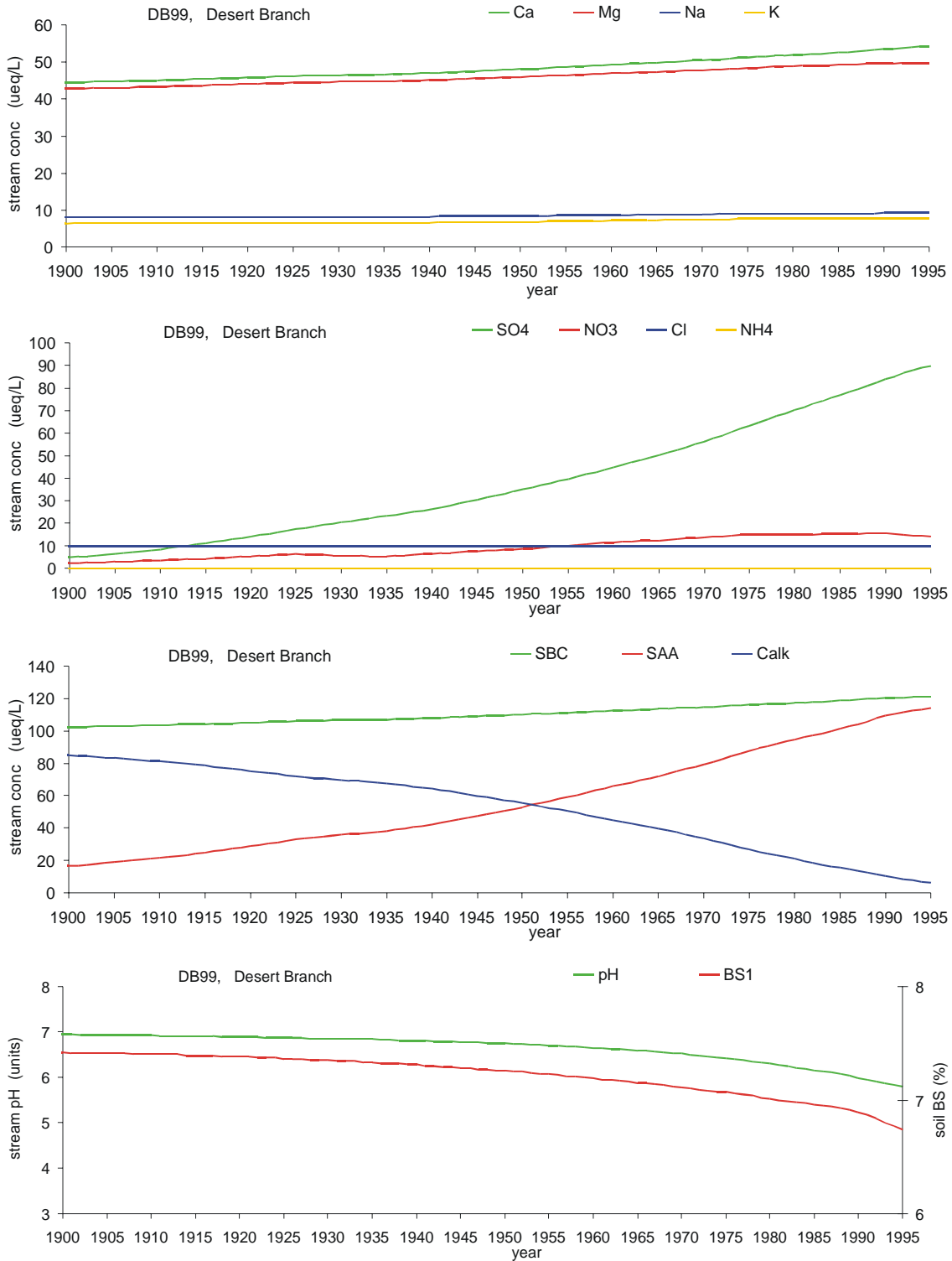


Figure 3. Time series of major variables at Desert Branch between 1900 and 1995. See Appendix B for data for other modeling sites.

This uncertainty was considered in the selection of ANC classes used for stratifying modeling sites and for presentation of the results according to different ANC criteria values. In other words, interpretation of the model projections of chronic chemistry allows for the likelihood of additional episodic acidification. Although the extent and magnitude of episodic acidification varies from site to site and with meteorological conditions, some generalities are possible. For example, Webb et al. (1994) developed an empirical approach to quantify streamwater ANC of extreme events in the Virginia Trout Stream Sensitivity Study (VTSSS) long-term monitoring streams in western Virginia, based on the model of Eshleman (1988). Minimum measured episodic ANC values were about 20% lower than the median spring ANC. Further discussion of uncertainty can be found in Appendix C.

### **WHAT ARE THE NEXT STEPS?**

Calculating, with a model such as MAGIC, the critical loads for protecting sensitive resources against acidification to specified criteria values is only part of the overall effort of setting target loads for atmospheric deposition. The next logical steps in this effort could include development of an approach for recommending target loads on the basis of identified critical loads thresholds. The development of an approach for recommending target loads will require, in addition to critical loads estimates at a broad range of sites, assessment of additional factors, including episodic variability, biological dose-response functions, and model uncertainty. Subsequent work might develop an analysis approach that could provide the USDA Forest Service with the technical foundation for setting target loads. There are many pieces of the puzzle that may ultimately contribute to developing target loads for resource protection. It is our opinion that the following steps could be helpful:

1. Interpret the MAGIC output described in this report within context of what is known about model uncertainty, model accuracy, regional representativeness of modeled systems, etc. This is a purely scientific exercise.
2. Add quantitative allowance for variability, to incorporate, at a minimum, allowance for known (or suspected, based on similar systems) episodic variability in chemistry. Each allowance should be clearly stated, with justification for selection, and acknowledgment of possibility that the choice will change in the future. Scientists should make recommendations; USDA-FS should make ultimate choices. This is part science and part policy.

3. Specify biological dose-response functions to be used. These can include biological response of fish, algae, or other species to changes in acid-base status (e.g., streamwater ANC, pH) or nutrient status (e.g., streamwater  $\text{NO}_3^-$  concentration). These will be expected to change as more research is done. They will be used to help decide what critical load or critical threshold criteria will be used in setting target loads. This is mostly science, but policy perspective is also important.
4. Set target loads. These will be based on all items identified above, and will be determined solely by Federal land managers. This is a policy judgment, which should be based on, and rooted in, the best available science and appropriate allowance for variability and uncertainties. It might best be accomplished in conjunction with a target loads workshop.

## REFERENCES CITED

Agren, G.I. and E. Bosatta. 1988. Nitrogen saturation of terrestrial ecosystems. *Environ. Pollut.* 54:185-197.

Baker, J.P., Bernard, D.P., Christensen, S.W., and Sale, M.J. 1990. Biological Effects of Changes in Surface Water Acid-Base Chemistry. Report SOS/T 13. National Acid Precipitation Assessment Program, Washington, DC.

Beier, C., P. Gundersen, and L. Rasmussen. 1998. European experience of manipulation of forest ecosystems by roof cover: possibilities and limitations, pp. 397-409. In: Hultberg, H. and R. Skeffington (Eds.). *Experimental Reversal of Acid Rain Effects. The Gårdsjön Roof Project.* John Wiley and Sons, Chichester.

Bulger, A.J., B.J. Cosby and J.R. Webb. 2000. Current, reconstructed past and projected future status of brook trout (*Salvelinus fontinalis*) streams in Virginia. *Can. J. Fish. Aq. Sci.* 57:1515-1523.

Bulger, A. J., B. J. Cosby, C. A. Dolloff, K. N. Eshleman, J. R. Webb, and J. N. Galloway. 1999. The "Shenandoah National Park: Fish in Sensitive Habitats (SNP: FISH)" Project Final Report. An Integrated Assessment of Fish Community Responses to Stream Acidification. National Park Service. 570 pages plus interactive computer model.

Church, M.R., K.W. Thorton, P.W. Shaffer, D.L. Stevens, B.P. Rochelle, R.G. Holdren, M.G. Johnson, J.J. Lee, R.S. Turner, D.L. Cassell, D.A. Lammers, W.G. Campbell, C.I. Liff, C.C. Brandt, L.H. Liegel, G.D. Bishop, D.C. Mortenson, and S.M. Pierson. 1989. Future Effects of Long-Term Sulfur Deposition on Surface Water Chemistry in the Northeast and Southern Blue Ridge Province (Results of the Direct/Delayed Response Project). U.S. Environmental Protection Agency Environmental Research Laboratory, Corvallis, OR.

Cosby, B.J. and T.J. Sullivan. 2001. Quantification of dose-response relationships and critical loads of sulfur and nitrogen for six headwater catchments in Rocky Mountain, Grand Teton, Sequoia, and Mount Rainier National Parks. Report 97-15-01. E&S Environmental Chemistry, Inc., Corvallis, OR.

Cosby, B.J., S.A. Norton, and J.S. Kahl. 1996. Using a paired-catchment manipulation experiment to evaluate a catchment-scale biogeochemical model. *Sci. Tot. Environ.* 183:49-66.

Cosby, B.J., R.F. Wright, and E. Gjessing. 1995. An acidification model (MAGIC) with organic acids evaluated using whole-catchment manipulations in Norway. *J. Hydrol.* 170:101-122.

Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway. 1985a. Modelling the effects of acid deposition: assessment of a lumped parameter model of soil water and streamwater chemistry. *Water Resour. Res.* 21:51\_63.

- Cosby, B.J., R.F. Wright, G.M. Hornberger, and J.N. Galloway. 1985b. Modelling the effects of acid deposition: estimation of long-term water quality responses in a small forested catchment. *Water Resour. Res.* 21:1591-1601.
- Cosby, B. J., G. M. Hornberger, J. N. Galloway, and R. F. Wright. 1985c. Time scales of catchment acidification: a quantitative model for estimating freshwater acidification. *Environmental Science and Technology* 19:1145-1149.
- Eshleman, K.N. 1988. Predicting regional episodic acidification of surface waters using empirical models. *Water Resour. Res.* 34:1118-1126.
- Ferrier, R.C., A. Jenkins, B.J. Cosby, R.C. Hall, R.F. Wright, and A.J. Bulger. 1995. Effects of future N deposition scenarios on the Galloway region of Scotland using a coupled sulphur & nitrogen model (MAGIC-WAND). *Water Air Soil Pollut.* 85:707-712.
- Grimm, J.W., and J.A. Lynch. 1997. Enhanced Wet Deposition Estimates Using Modeled Precipitation Inputs. Final Report to the USDA Forest Service, Northeast Forest Experiment Station, Northern Global Change Research Program (23-721).
- Gundersen, P., B.A. Emmett, O.J. Kjønaas, C. Koopmans, and A. Tietema. 1998. Impact of nitrogen deposition on nitrogen cycling in forests: a synthesis of NITREX data. *For. Ecol. Manage.* 101:37-56.
- NAPAP. 1991. Integrated Assessment Report. National Acid Precipitation Assessment Program, Washington, DC.
- Oreskes, N., K. Schrader-Frechette and K. Belitz. 1994. Verification, validation and confirmation of numerical models in the earth sciences. *Science* 263:641-646.
- Reuss, J.O., and D.W. Johnson. 1986. Acid deposition and the acidification of soil and water. Springer-Verlag, New York.
- Shannon, J.D. 1998. Calculation of Trends from 1900 through 1990 for Sulfur and NO<sub>x</sub>-N Deposition Concentrations of Sulfate and Nitrate in Precipitation, and Atmospheric Concentrations of SO<sub>x</sub> and NO<sub>x</sub> Species over the Southern Appalachians. Report to SAMI, April 1998.
- Sinha, R., M.J. Small, P.F. Ryan, T.J. Sullivan, and B.J. Cosby. 1998. Reduced-form modeling of surface water and soil chemistry for the Tracking and Analysis Framework. *Water Air Soil Pollut.* 105:617-642.
- Skeffington, R.A. 1999. The use of critical loads in environmental policy making: a critical appraisal. *Environ. Sci. Technol./News* June 1, 1999. pp. 245A-252A.
- Sullivan, T.J. 2000. Aquatic Effects of Acidic Deposition. Lewis Publ., Boca Raton, FL. 373 pp.



Sullivan, T.J. 1993. Whole ecosystem nitrogen effects research in Europe. *Environ. Sci. Technol.* 27(8):1482-1486.

Sullivan, T.J. 1990. Historical Changes in Surface Water Acid-Base Chemistry in Response to Acidic Deposition. State of the Science, SOS/T 11, National Acid Precipitation Assessment Program. 212 pp.

Sullivan, T.J. and B.J. Cosby. 1995. Testing, improvement, and confirmation of a watershed model of acid-base chemistry. *Water Air Soil Pollut.* 85:2607-2612.

Sullivan, T.J., B.J. Cosby, J.R. Webb, K.U. Snyder, A.T. Herlihy, A.J. Bulger, E.H. Gilbert, and D. Moore. 2002a. Assessment of the Effects of Acidic Deposition on Aquatic Resources in the Southern Appalachian Mountains. Report prepared for the Southern Appalachian Mountains Initiative (SAMI). E&S Environmental Chemistry, Inc., Corvallis, OR. (Available at [www.esenvironmental.com/sami\\_download.htm](http://www.esenvironmental.com/sami_download.htm))

Sullivan, T.J., D.W. Johnson, R. Munson, and J.D. Joslin. 2002b. Assessment of Effects of Acid Deposition On Forest Resources in the Southern Appalachian Mountains. Report prepared for the Southern Appalachian Mountains Initiative (SAMI). E&S Environmental Chemistry, Inc., Corvallis, OR.

Sullivan, T.J., D.L. Peterson, C.L. Blanchard, and S.J. Tanenbaum. 2001. Assessment of Air Quality and Air Pollutant Impacts in Class I National Parks of California. Report NPS D-1454, U.S. Dept. of Interior, National Park Service.

Sullivan, T.J., J. M. Eilers, B.J. Cosby, and K.B. Vaché. 1997. Increasing role of nitrogen in the acidification of surface waters in the Adirondack Mountains, New York. *Water, Air, Soil Pollut.* 95:313-336.

Sullivan, T.J., B.J. Cosby, C.T. Driscoll, D.F. Charles, and H.F. Hemond. 1996. Influence of organic acids on model projections of lake acidification. *Water Air Soil Pollut.* 91:271-282.

Sullivan, T.J., R.S. Turner, D.F. Charles, B.F. Cumming, J.P. Smol, C.L. Schofield, C.T. Driscoll, B.J. Cosby, H.J.B. Birks, A.J. Uutala, J.C. Kingston, S.S. Dixit, J.A. Bernert, P.F. Ryan, and D.R. Marmorek. 1992. Use of historical assessment for evaluation of process-based model projections of future environmental change: Lake acidification in the Adirondack Mountains, New York, U.S.A. *Environ. Pollut.* 77:253-262.

Tietema, A. 1998. Microbial carbon and nitrogen dynamics in coniferous forest floor material collected along a European nitrogen deposition gradient. *Forest Ecology and Management* 101:29-36.

Tietema, A. and C. Beier. 1995. A correlative evaluation of nitrogen cycling in the forest ecosystems of the EC projects NITREX and EXMAN. *For. Ecol. Mgmt.* 71: 143-151.

Turner, R.S., P.F. Ryan, D.R. Marmorek, K.W. Thornton, T.J. Sullivan, J.P. Baker, S.W. Christensen, and M.J. Sale. 1992. Sensitivity to change for low-ANC eastern US lakes and streams and brook trout populations under alternative sulfate deposition scenarios. *Environ. Pollut.* 77:269-277.

U.S. Environmental Protection Agency. 1995. Acid Deposition Standard Feasibility Study. A Report to Congress. EPA 430-R-95-001A. U.S. Environmental Protection Agency, Washington, DC.

Webb, J.R., F.A. Deviney, J.N. Galloway, C.A. Rinehart, P.A. Thompson, and S. Wilson. 1994. The acid-base status of native brook trout streams in the mountains of Virginia. A regional assessment based on the Virginia Trout Stream Sensitivity Study. Univ. of Virginia, Charlottesville, VA.

Wigington, P.J., J.P. Baker, D.R. DeWalle, W.A. Kretser, P.S. Murdoch, H.A. Simonin, J. Van Sickle, M.K. McDowell, D.V. Peck, and W.R. Barchet. 1993. Episodic acidification of streams in the northeastern United States: Chemical and biological results of the Episodic Response Project. EPA/600/R-93/190, U.S. Environmental Protection Agency, Washington, DC.

Wright, R.F., E.T. Gjessing, N. Christophersen, E. Lotse, H.M. Seip, A. Semb, B. Sletaune, R. Storhaug, and K. Wedum. 1986. Project rain: changing acid deposition to whole catchments. The first year of treatment. *Water Air Soil Pollut.* 30:47-64.

## **APPENDIX A**

Soils data for Yellow Creek and Desert Branch, two sites for which model calibrations were developed for this project. Calibrations for other modeled sites were taken from the SAMI study.

Table A-1. Physical and chemical characteristics of 6 soil pits excavated in the Desert Branch watershed.\*

Soil Series	Site ID	Soil Type	Horizon	Soil Depth	Soil pH	% LOI	% TN	% TC	Ca	K	Mg	Al	Na	acidity	ECEC	BS (%)
									mg/kg				meq/100gm			
Ernest (inclusion)	FSWV03067001	Head slope downslope from a bench	A	5	4.3	14.0	0.37	5.59	58	79	22	685	7	20.0	20.7	3.37
		midslope	BA	10.5	4.7	6.3	0.11	1.47	20	32	7.4	535	4	7.6	7.9	3.32
		colluvial soil	Bt	7.5	4.7	5.5	0.08	0.73	26	31	9.2	547	6	8.0	8.3	3.76
			Btg	7	4.7	4.1	0.05	0.39	36	26	12	502	6	6.6	7.0	5.31
			Bxg	20.5	4.7	4.0	0.04	0.32	18	30	25	442	5	5.8	6.2	6.38
Buchanan-like	FSWV03067002	colluvial soil	A1	0	3.1	41.8	0.93	22.0	545	172	59	241	8	8.8	12.5	29.49
		midslope	E1	4	3.6	2.6	0.05	1.17	30	2	4.9	83	3	2.2	2.4	8.68
			E2	5	3.7	2.2	0.04	0.58	19	10	3.0	279	< 2	5.0	5.1	2.77
			Bht	4	4.0	5.7	0.10	1.84	35	49	8.4	863	5	12.0	12.4	3.17
			Bt1	12	4.7	4.2	0.05	0.85	10	18	3.1	195	5	3.6	3.7	3.77
			2Bt2	3.5	4.9	3.4	0.04	0.28	14	25	3.8	333	5	4.8	5.0	3.78
Un-named	FSWV03067003	alluvial	A1	3	4.3	10.5	0.28	4.04	105	66	28	293	6	5.6	6.6	14.46
*mapped as			A2	8	4.4	6.5	0.17	2.31	43	35	16	230	4	4.6	5.1	8.94
Buchanan																
mesic soil temp																
Buchanan-like	FSWV03067004	colluvial soil	A	5	4.0	16.7	0.38	6.99	150	101	40	650	7	9.8	11.2	12.27
		toeslope	BA	7	4.3	8.2	0.19	2.55	38	58	14	629	4	9.4	9.9	4.76
			Bt1	9.5	4.6	6.1	0.09	0.97	39	46	10	593	4	8.4	8.8	4.68
			Bt2	12.5	4.6	4.9	0.06	0.70	32	35	11	514	4	7.6	8.0	4.50
			Btg	6	4.5	5.4	0.06	0.80	28	26	12	451	2	6.6	6.9	4.49
Gilpin	FSWV03067005	bench	A	4	3.8	17.0	0.50	7.83	254	83	44	890	10	22.8	24.7	7.635
		located at midslope	BA	6	4.6	8.3	0.16	2.93	31	26	8.2	514	4	6.8	7.1	4.306
			Bt1	4	4.5	6.2	0.12	1.75	30	35	7.7	419	4	6.4	6.7	4.741
			Bt2	11	4.5	6.2	0.11	1.71	23	30	6.2	470	2	6.4	6.7	3.753

Table A-1. Continued.

<b>Soil Series</b>	<b>Site ID</b>	<b>Soil Type</b>	<b>Horizon</b>	<b>Soil Depth</b>	<b>Soil pH</b>	<b>% LOI</b>	<b>% TN</b>	<b>% TC</b>	<b>Ca</b>	<b>K</b>	<b>Mg</b>	<b>Al</b>	<b>Na</b>	<b>Acidity</b>	<b>ECEC</b>	<b>BS (%)</b>
Ernest-like	FSWV03067006	toeslope	A	3	3.9	14.1	0.46	5.50	370	123	88	518	6	16.0	18.9	15.36
mesic soil temp		located above bench	BA	6	4.4	7.7	0.21	2.27	65	52	16	486	5	7.2	7.8	7.87
		at midslope of mountain	Bt1	6	4.6	5.6	0.09	1.04	50	31	11	492	7	7.6	8.1	5.60
			Bt2	5	4.6	5.5	0.08	0.89	47	28	11	485	5	7.2	7.6	5.44
			Btg1	17	4.7	5.1	0.08	1.01	90	25	25	371	6	5.4	6.1	12.05
			Btg2	12	4.9	4.7	0.06	0.74	85	34	37	324	7	5.0	5.8	14.351

\* LOI, loss on ignition; TN, total nitrogen; TC, total carbon; ECEC, effective cation exchange capacity; BS, base saturation.

Table A-2. Depth-weighted average values for mineral soil horizons A and B of the major physical and chemical characteristics of 6 soil pits excavated in the Desert Branch watershed.\*

Soil Series	Site ID	Soil Type	soil pH	% LOI	% TN	% TC	Ca	K	Mg	Al	Na	Acidity	ECEC	BS
							mg/kg					meq/100g		(%)
Ernest (inclusion) mesic soil temp	FSWV03067001	Head slope downslope from a bench midslope colluvial soil	4.65	5.70	0.09	1.15	25.89	35.04	16.94	509.15	5.45	8.02	8.40	4.5
Buchanan-like mesic soil temp	FSWV03067002	colluvial soil midslope	4.28	3.74	0.05	0.92	18.23	19.63	4.17	304.66	3.81	4.98	5.17	3.7
Un-named *mapped as Buchanan mesic soil temp	FSWV03067003	alluvial	4.37	7.59	0.20	2.78	60.15	43.20	18.91	247.04	4.85	4.87	5.46	10.7
Buchanan-like mesic soil temp	FSWV03067004	colluvial soil toeslope	4.45	7.31	0.13	1.89	48.65	48.66	15.10	560.06	4.33	8.23	8.74	5.8
Gilpin mesic soil temp	FSWV03067005	bench located at midslope	4.40	8.43	0.19	2.99	62.86	38.12	12.99	539.88	4.11	9.12	9.66	5.5
Ernest-like mesic soil temp	FSWV03067006	toeslope located above bench at midslope of mountain	4.64	5.97	0.12	1.36	93.33	37.56	27.32	409.02	6.10	6.62	7.44	10.9

\* LOI, loss on ignition; TN, total nitrogen; TC, total carbon; ECEC, effective cation exchange capacity; BS, base saturation.

Table A-3. Physical and chemical characteristics of 4 soil pits <sup>1</sup> excavated in the Yellow Creek watershed.															
Location	Horizon	Depth (inches)	pH	% LOI	% TN	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Ca	K	Mg	Al	Na	Acidity	ECEC	BS(%)
						mg/kg						meq/100g			
<b>1</b>	<b>B<sup>2</sup></b>	10	3.7	6.4	0.17	0.8	7.3	11	49	9.4	1185	8	16.8	17.1	1.7
	<b>B<sub>w</sub></b>	18	3.8	4.5	0.1	0.5	3.7	7.8	34	5.2	1288	8	16.4	16.6	1.2
<b>2</b>	<b>A</b>	2	3.7	12.5	0.37	30.7	11.6	37	68	18	848	7	11.7	12.2	4.4
	<b>B</b>	10	4.6	7.2	0.16	2.7	2.5	7.8	23	4.1	278	6	4.6	4.7	3.3
	<b>B<sub>w</sub></b>	18	4.5	5.2	0.1	1.9	2.8	6.9	18	2.8	240	5	4.6	4.7	2.7
<b>3</b>	<b>A</b>	2	3	26.8	0.59	0.5	45.6	89	83	24	184	4	8.5	9.4	9.3
	<b>B</b>	10	3.3	3.9	0.08	0.5	3.5	10	16	4.2	39	3	1.7	1.8	7.7
	<b>B<sub>w</sub></b>	18	3.7	1.4	0.02	0.5	1.3	7.6	13	2.7	208	4	3.8	3.9	2.8
<b>4</b>	<b>A</b>	2	3.5	19.2	0.59	9.2	9.2	34	90	29	674	8	11.1	11.8	5.7
	<b>B</b>	10	3.7	12.6	0.4	5.5	7.2	24	73	19	778	9	12.3	12.8	3.9
	<b>B<sub>w</sub></b>	18	3.8	8.8	0.29	1.3	5.6	25	49	14	763	5	12.7	13.1	3.0

<sup>1</sup> All soil pits were situated in the DeKalb soil type, which covers 90% of the watershed.  
<sup>2</sup> B-horizon includes E and BE  
\* LOI, loss on ignition; TN, total nitrogen; ECEC, effective cation exchange capacity; BS, base saturation.

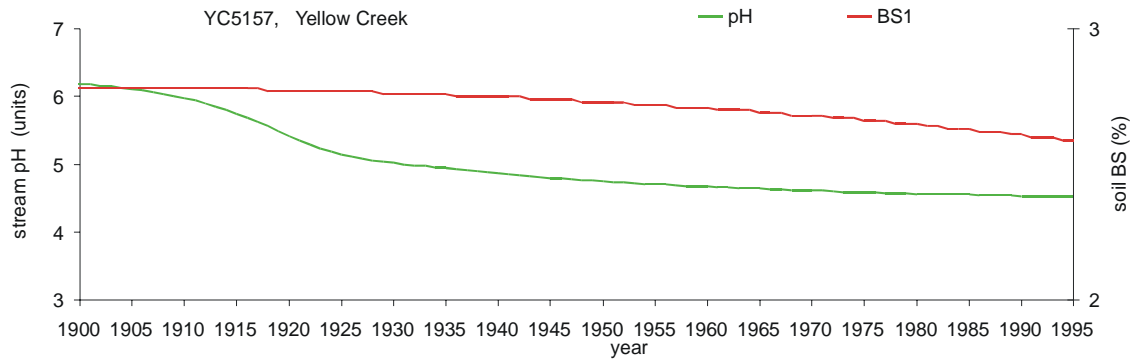
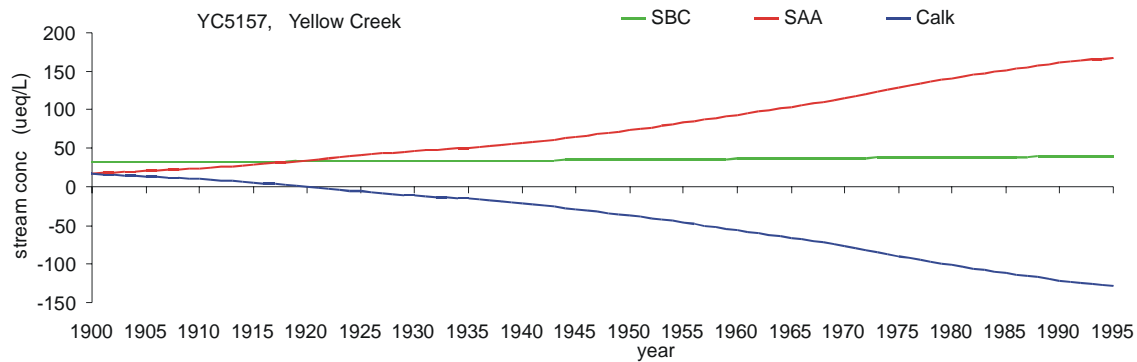
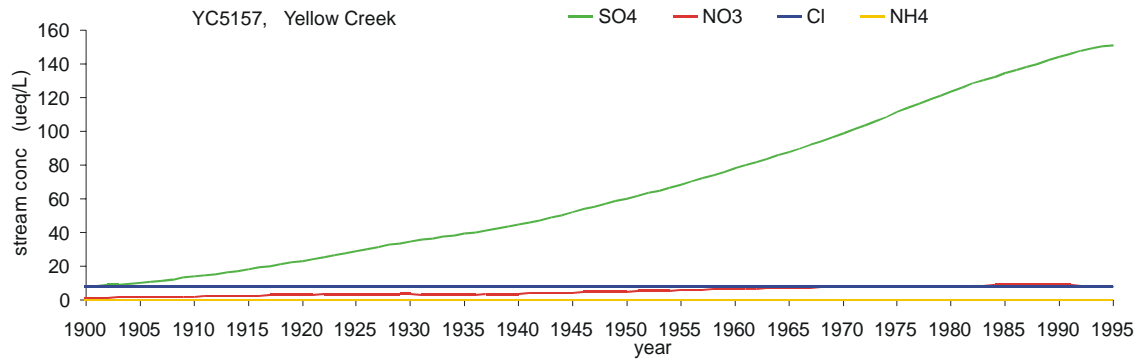
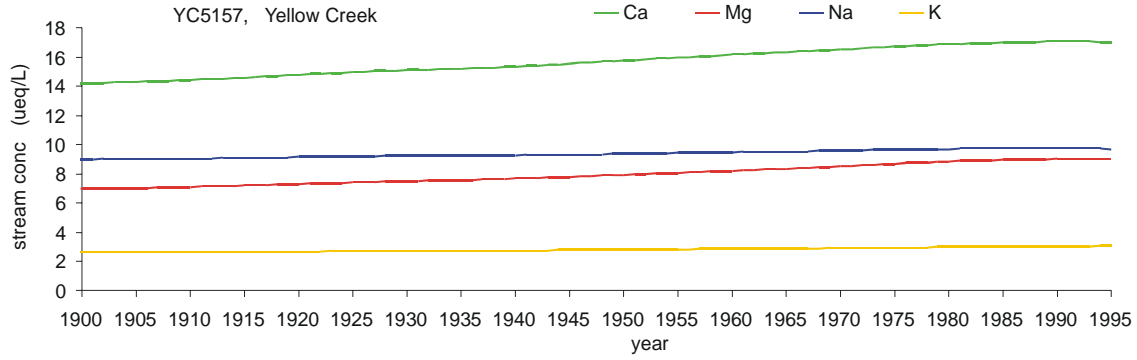
Table A-4. Depth-weighted average values for mineral soil horizons A and B of the major physical and chemical characteristics of 4 soil pits excavated in the Yellow Creek watershed.													
Location	pH	% LOI	% TN	NO <sub>3</sub> -N	NH <sub>4</sub> -N	Ca	K	Mg	Al	Na	Acidity	ECEC	BS (%)
				mg/kg								meq/100g	
1	3.76	5.18	0.13	0.61	4.99	8.94	39.36	6.70	1251.21	8.00	16.54	16.78	1.4
2	4.48	6.35	0.14	4.09	3.29	9.21	23.00	4.25	293.20	5.47	5.07	5.20	3.1
3	3.52	3.93	0.08	0.50	4.99	13.83	18.67	4.62	150.07	3.67	3.41	3.57	4.8
4	3.75	10.76	0.35	3.23	6.37	25.27	59.73	16.67	762.07	6.53	12.46	12.91	3.4

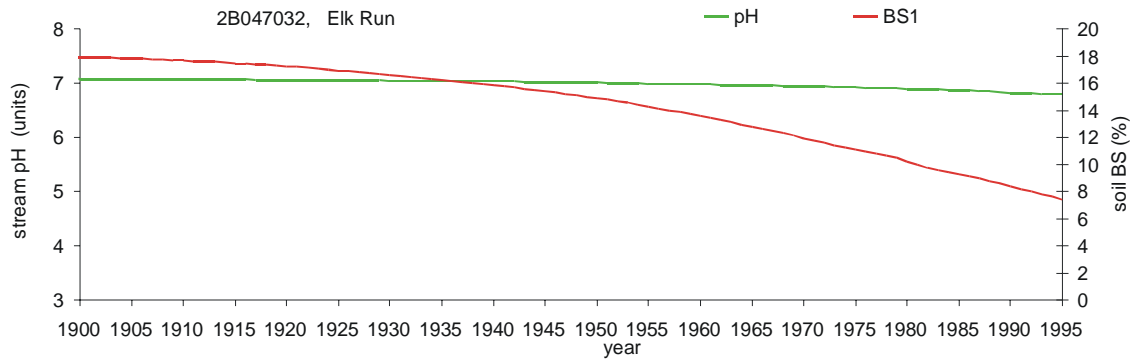
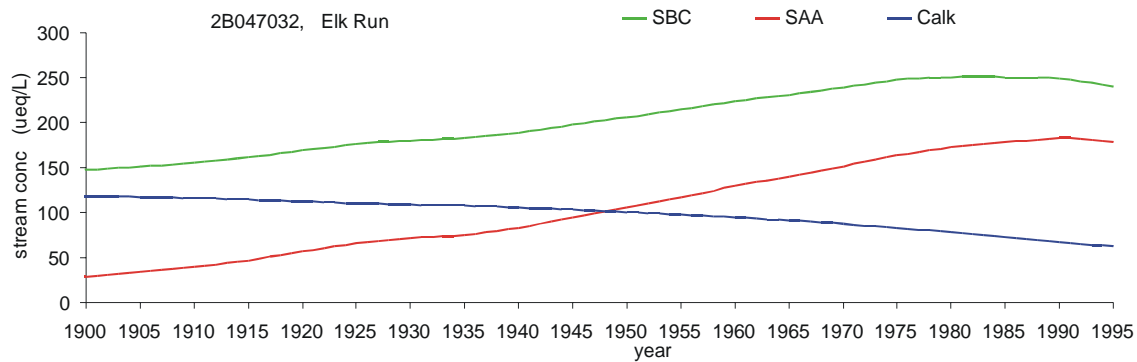
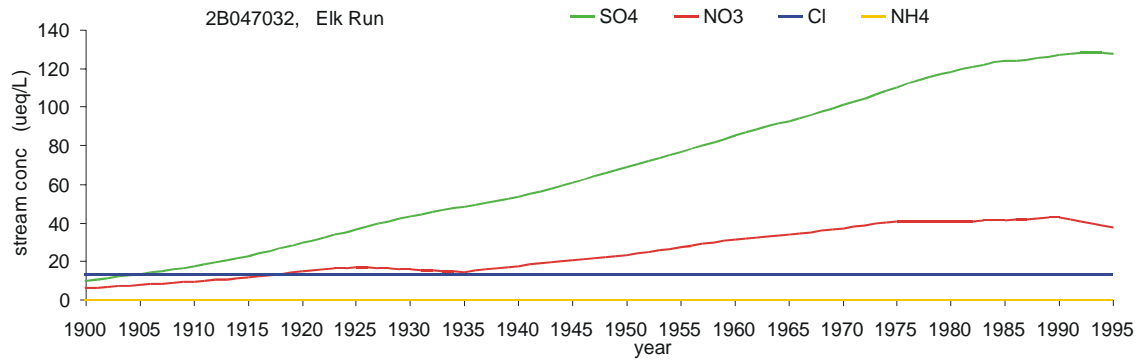
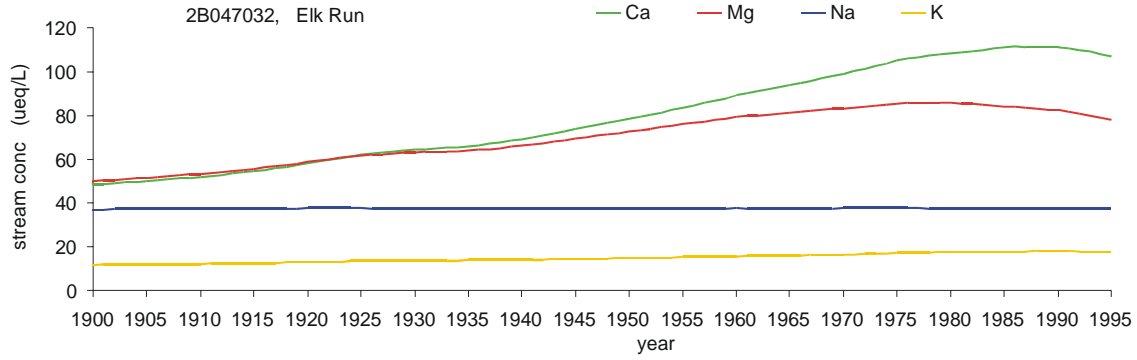
\* LOI, loss on ignition; TN, total nitrogen; ECEC, effective cation exchange capacity; BS, base saturation.

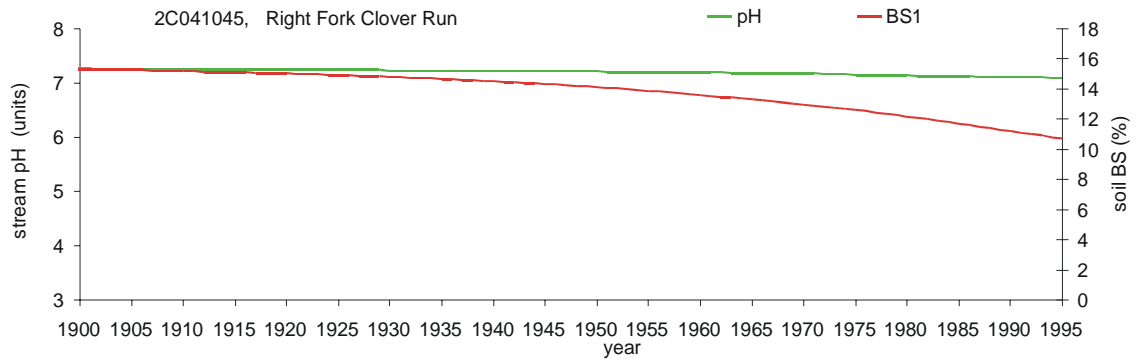
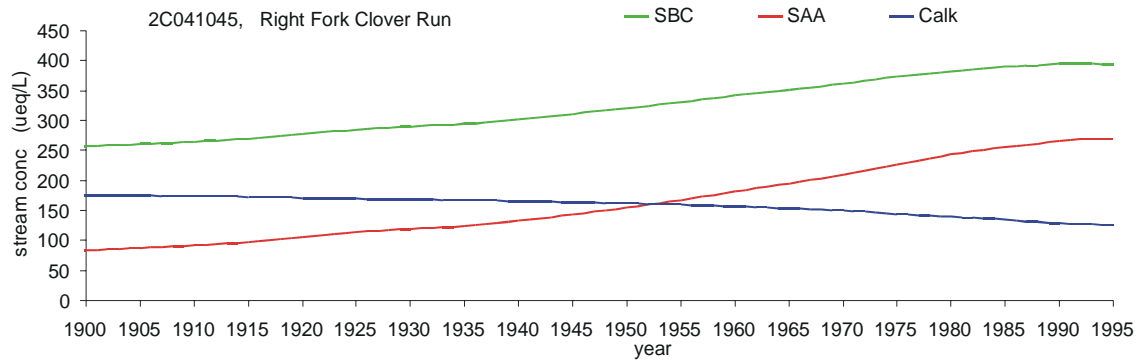
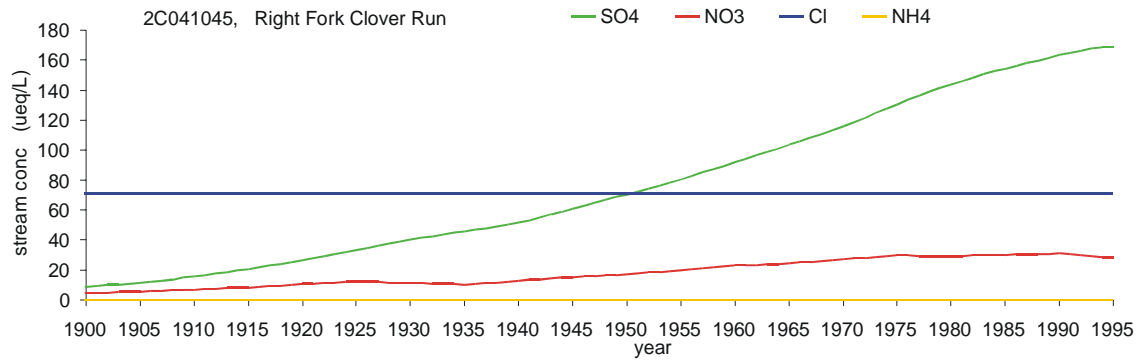
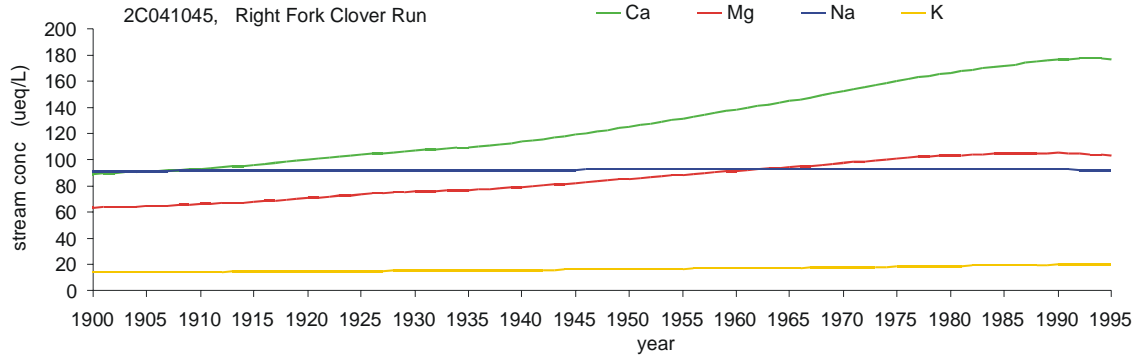


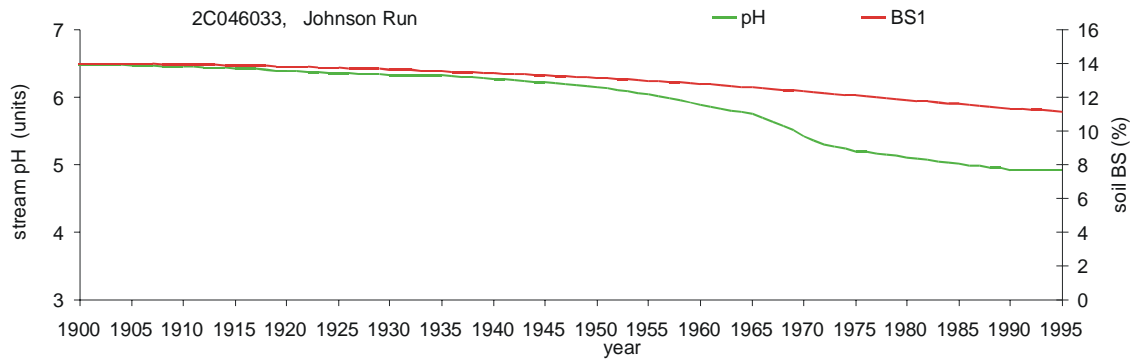
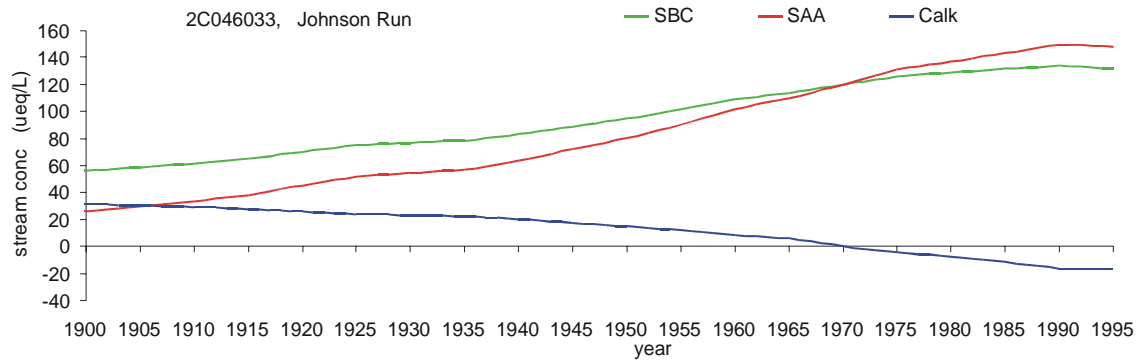
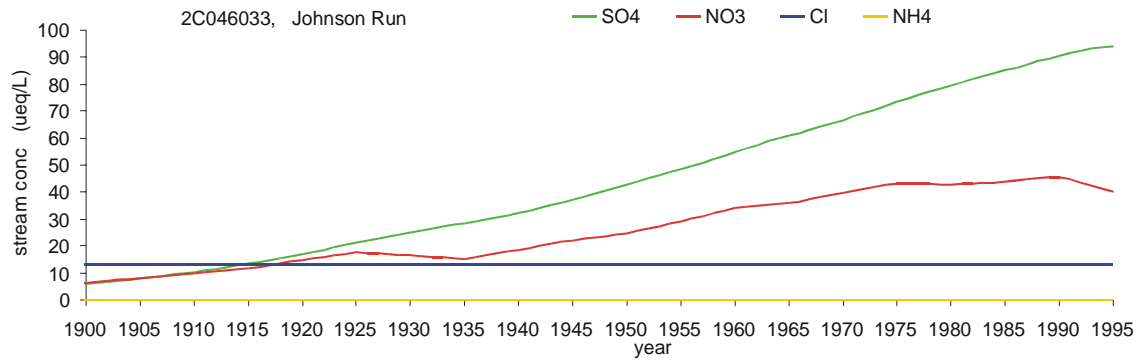
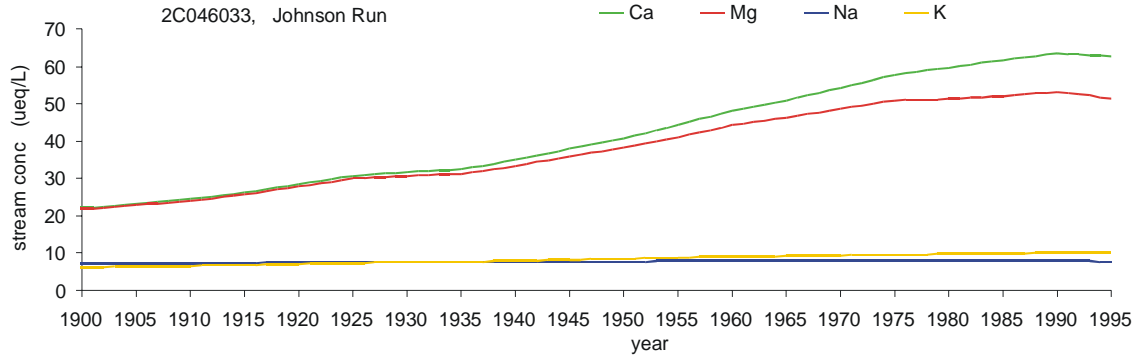
## **APPENDIX B**

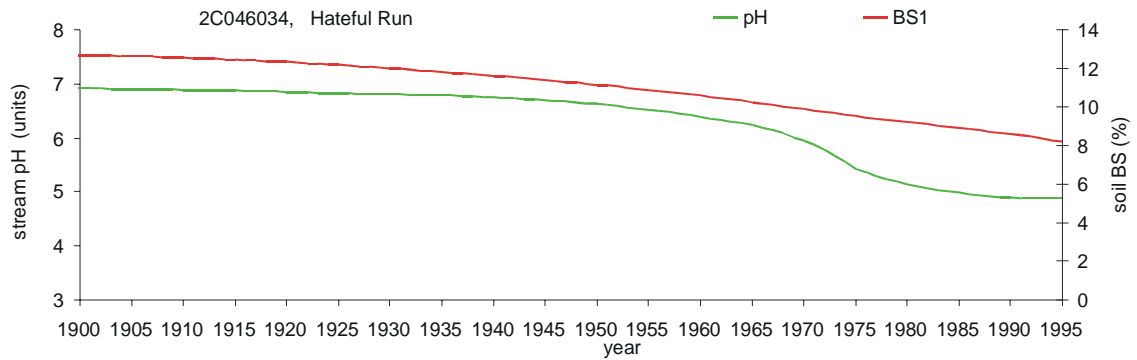
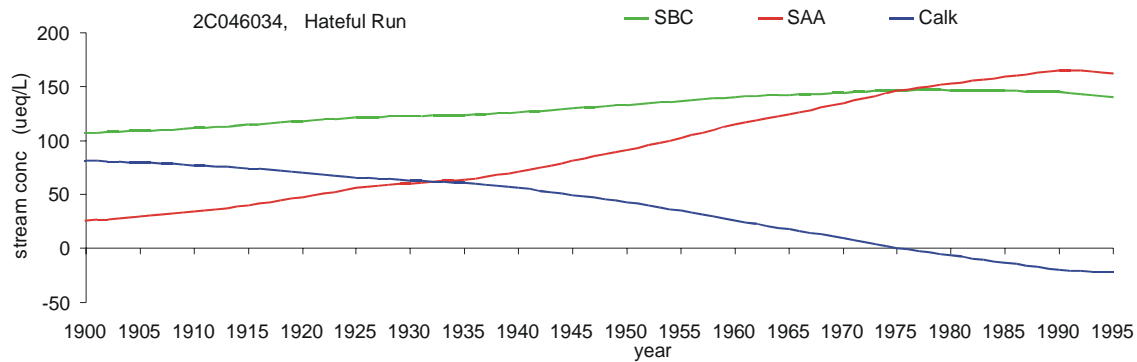
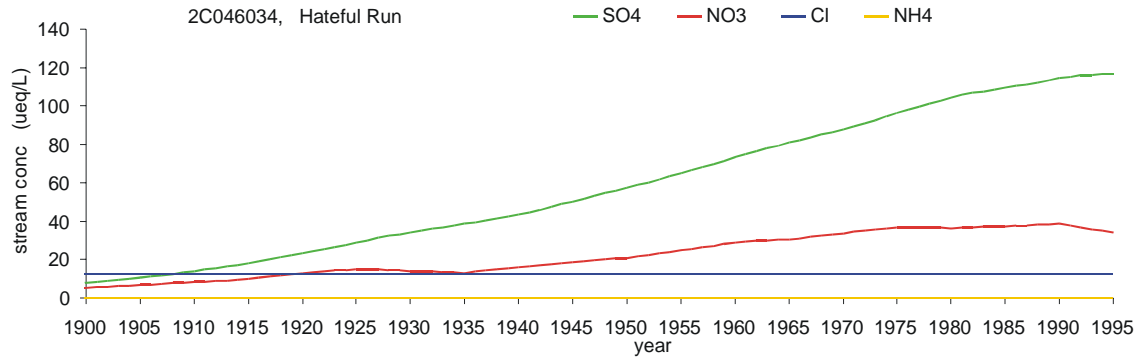
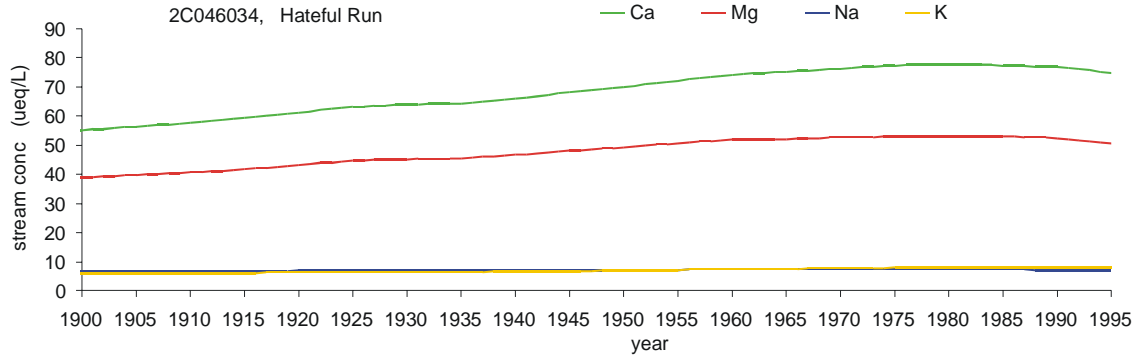
Modeled Chemical response of modeled streams over the period 1900 to 1995. The plot for one additional stream (Desert Branch) is given in Figure 3 of the report.

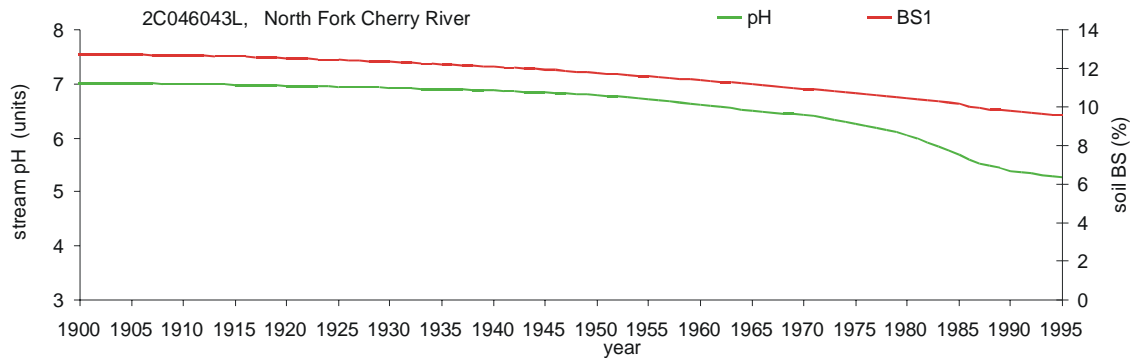
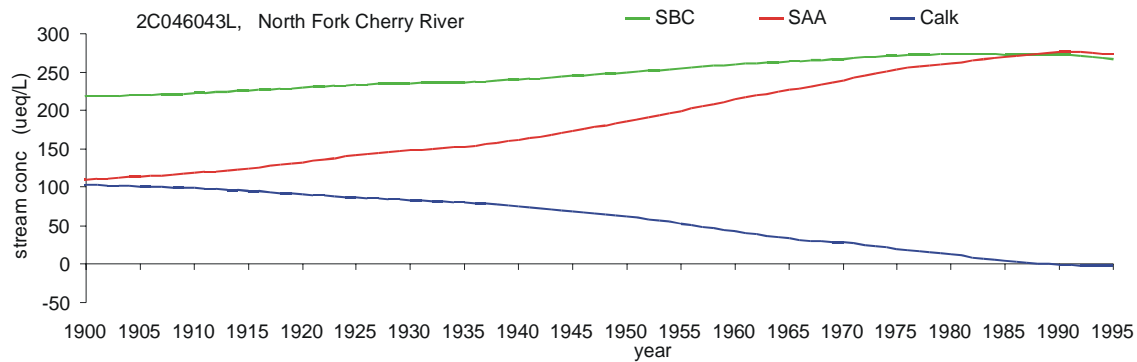
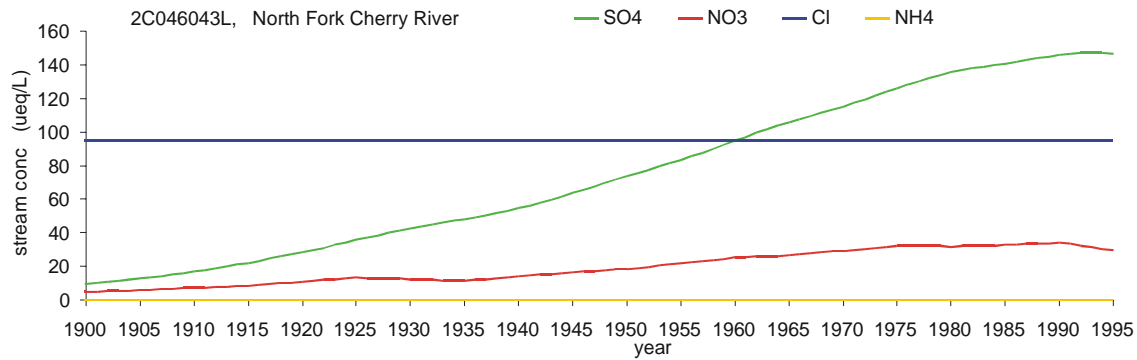
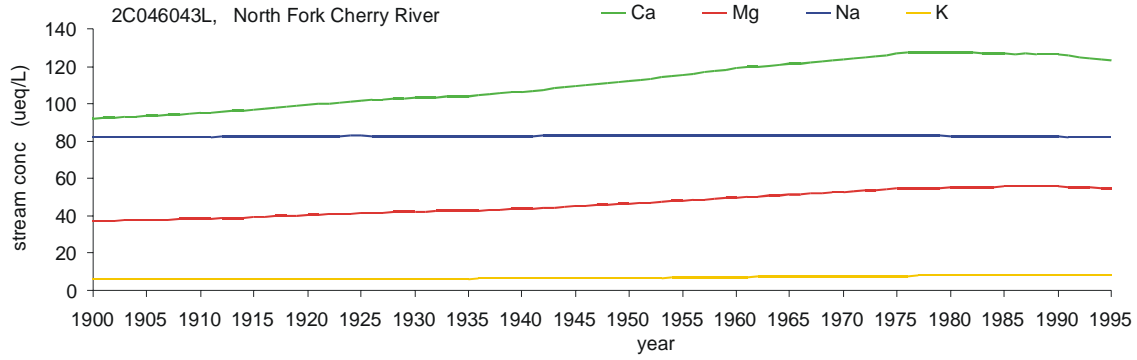


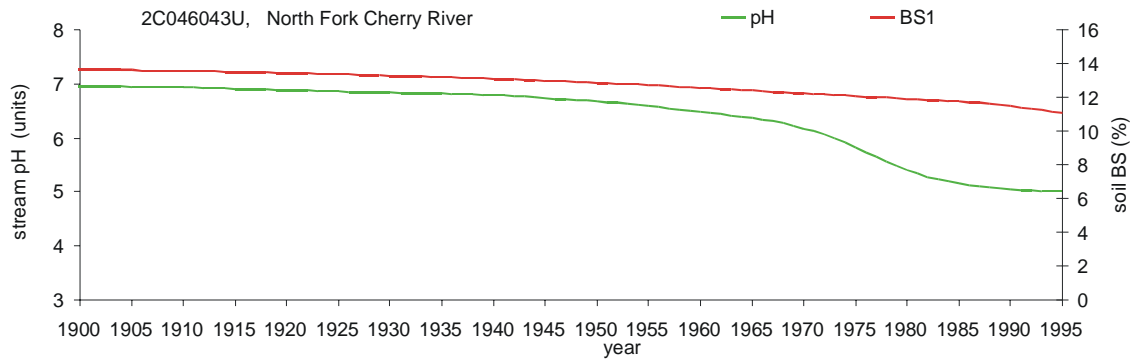
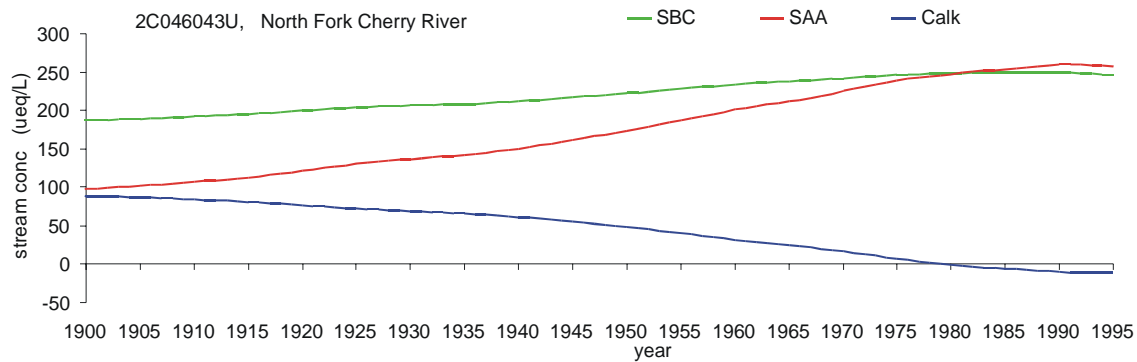
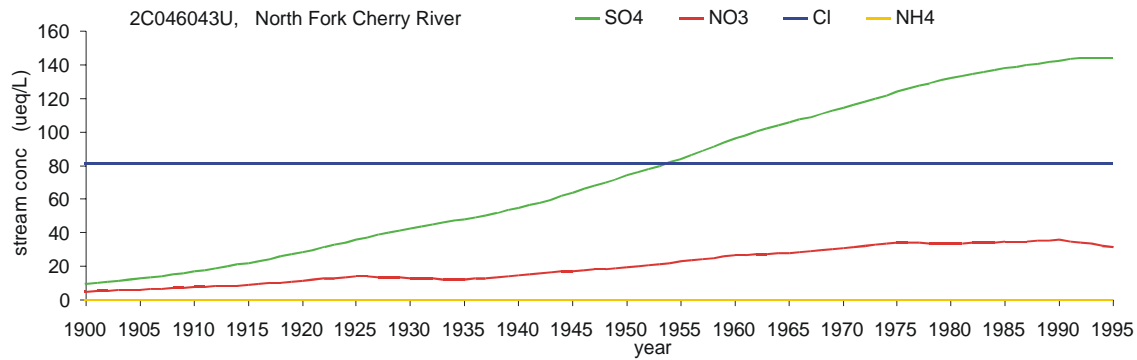
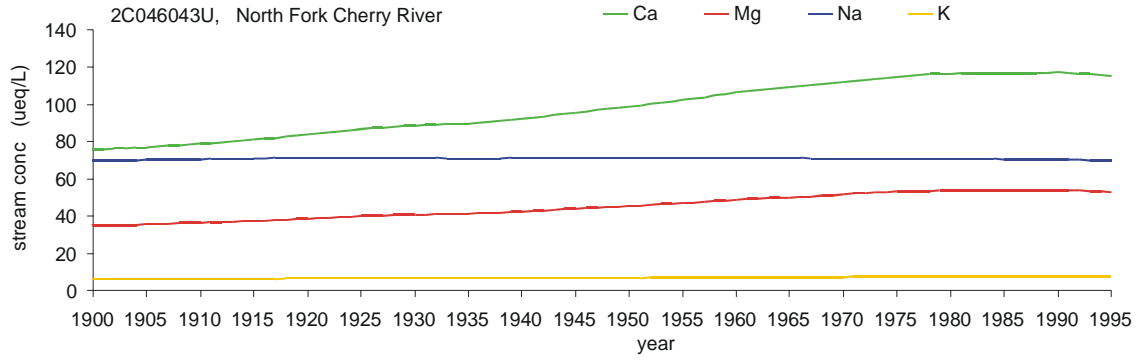




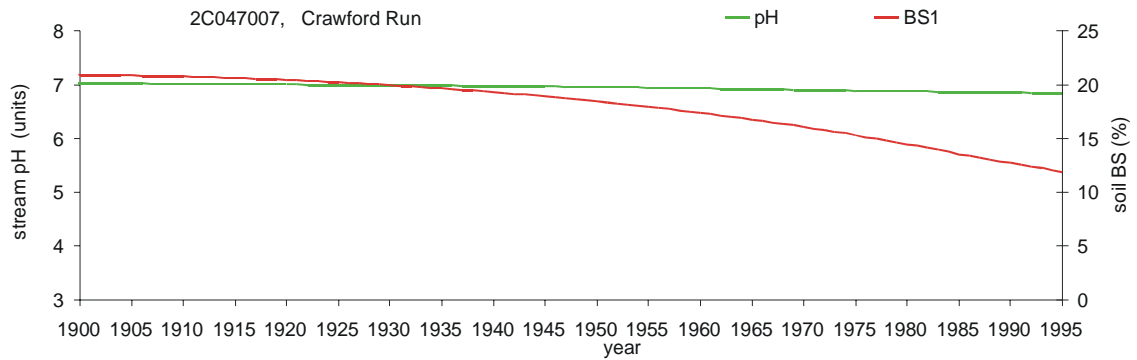
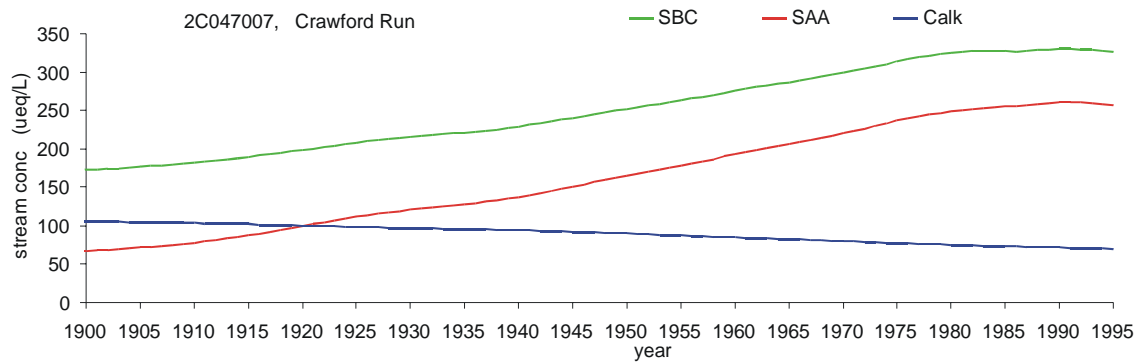
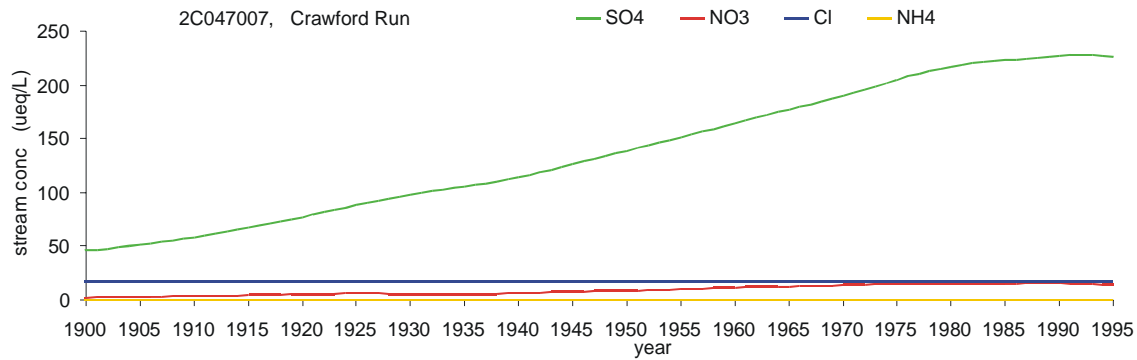
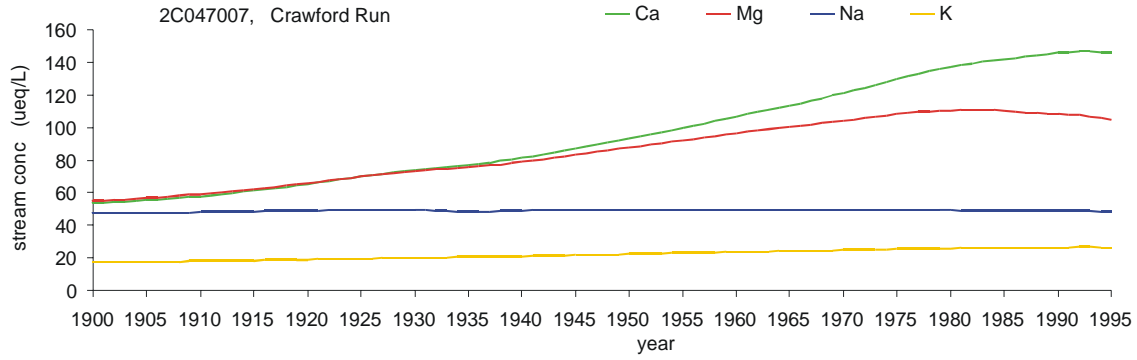


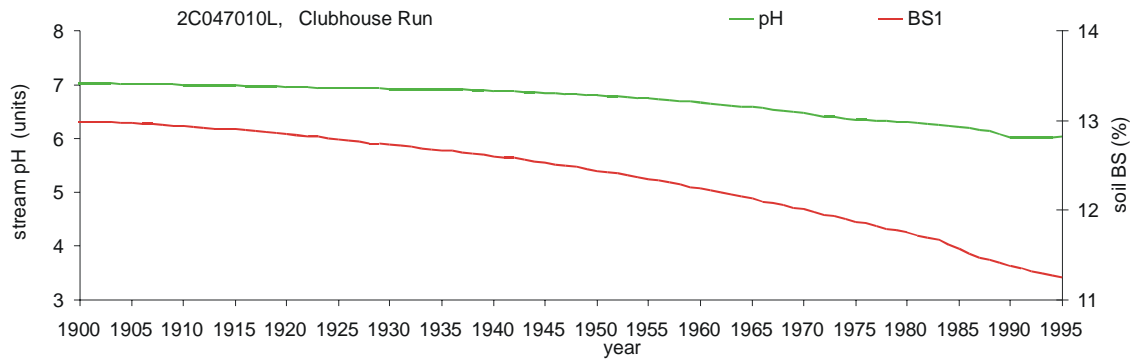
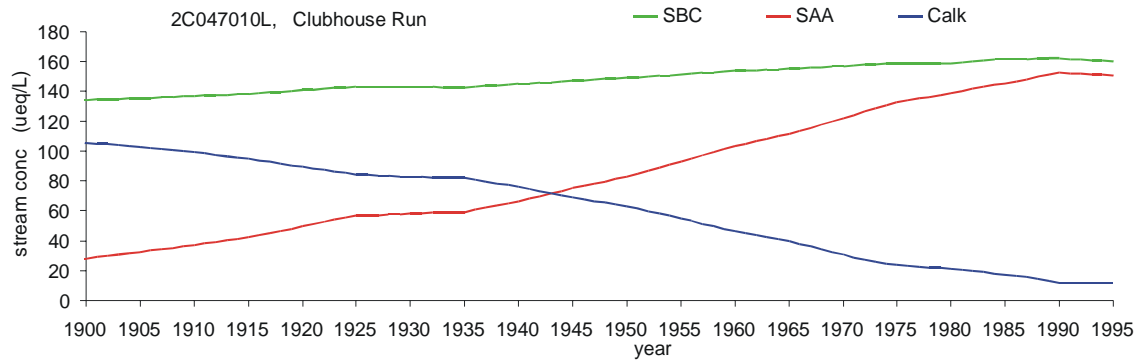
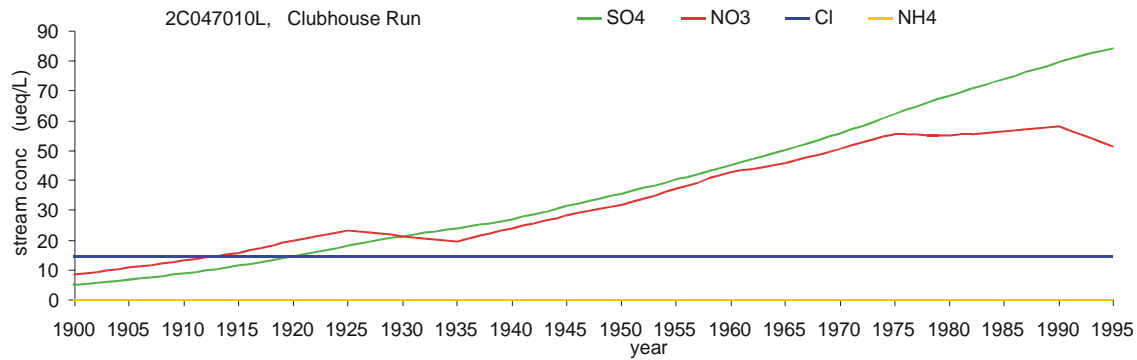
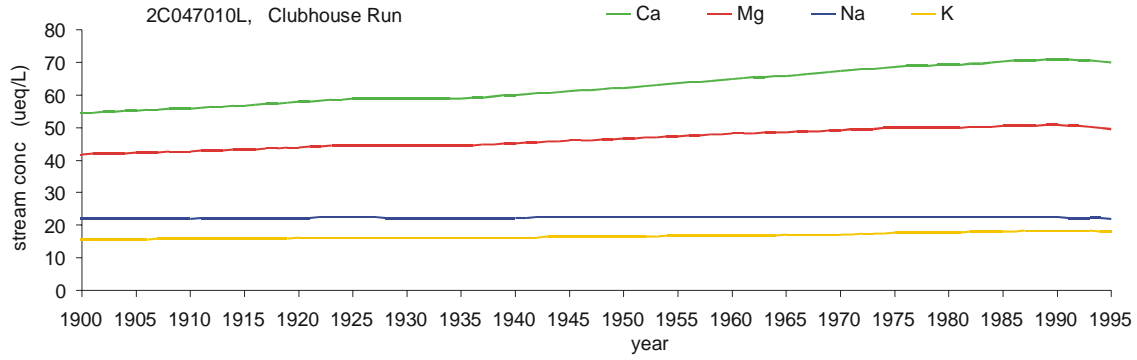


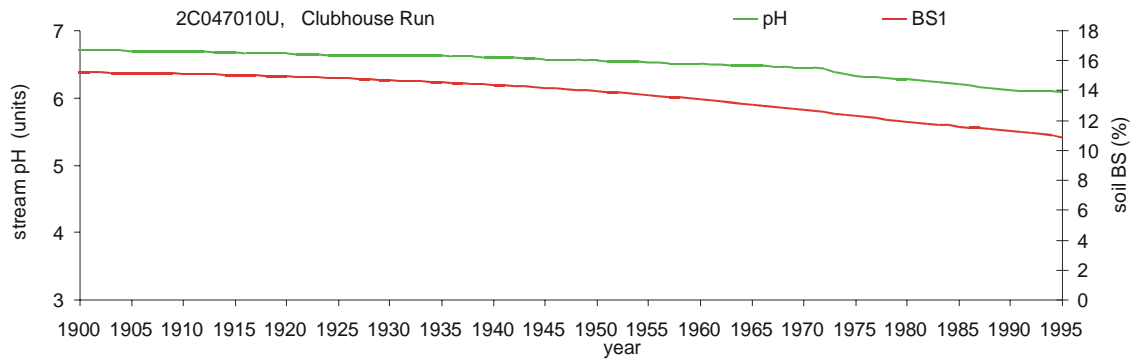
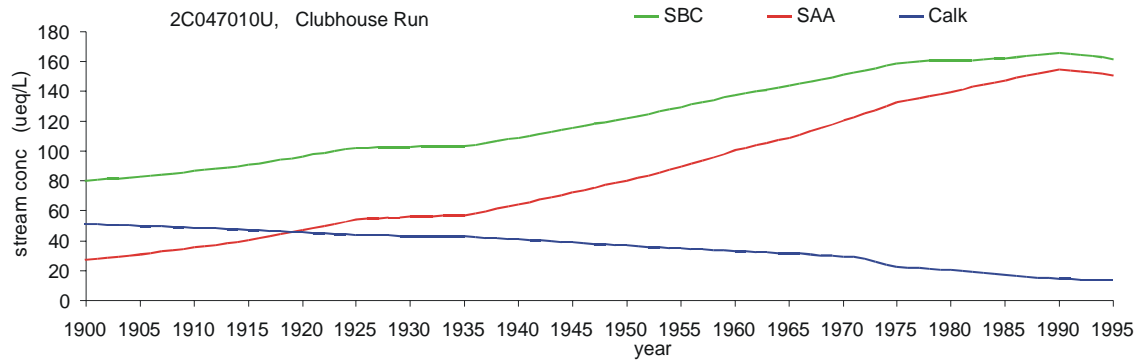
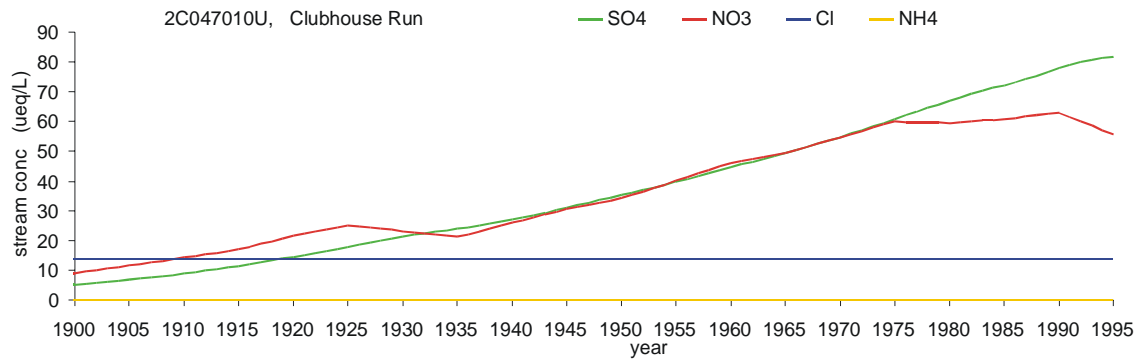
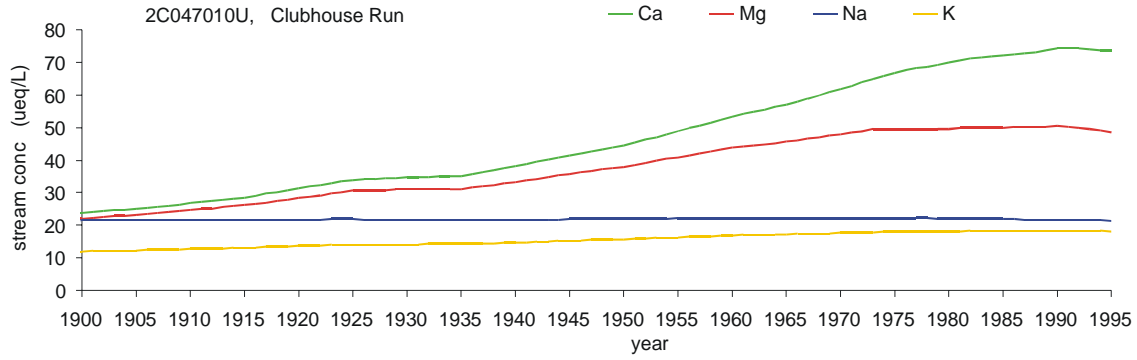


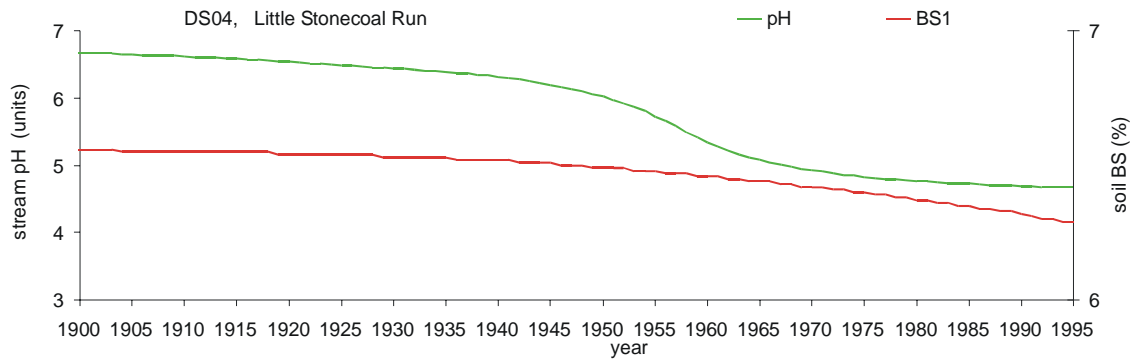
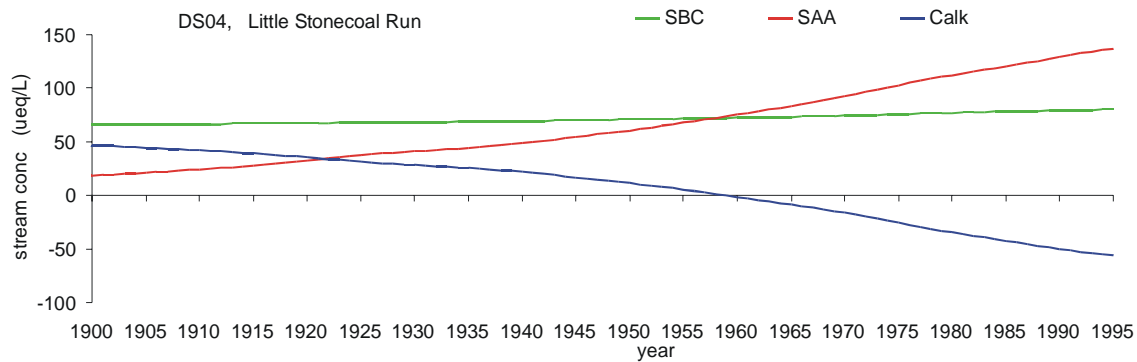
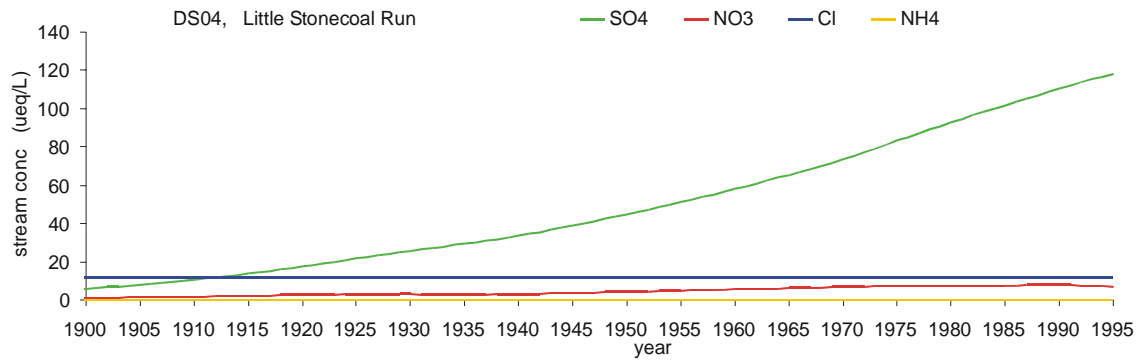
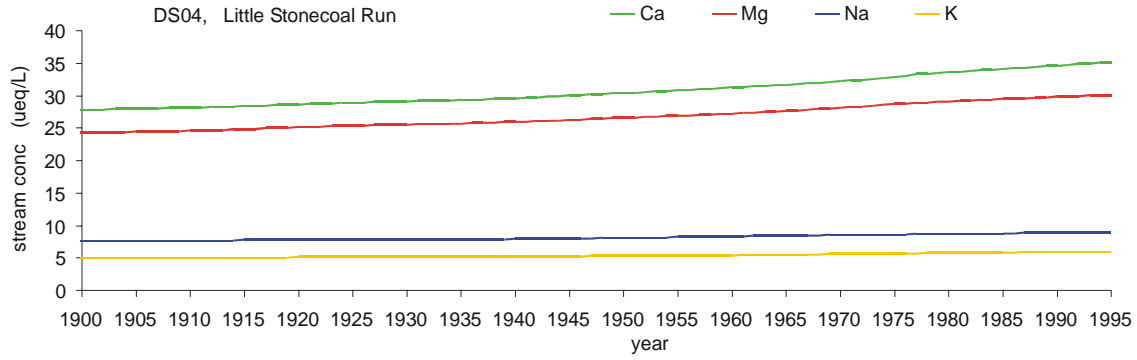


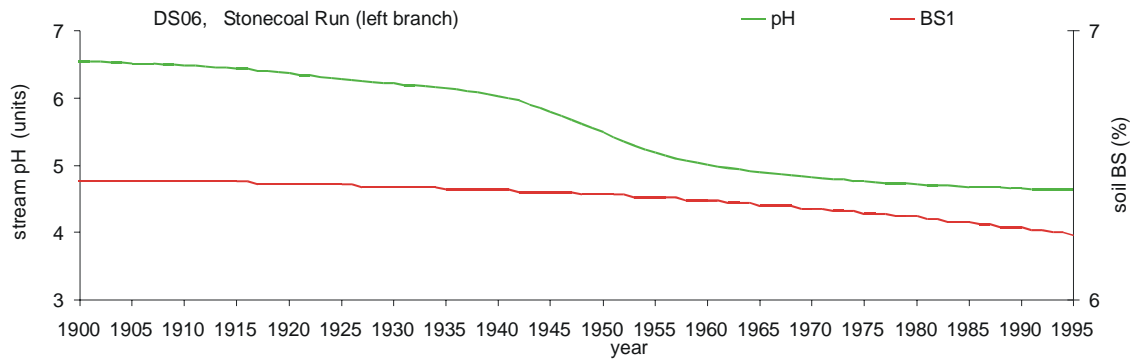
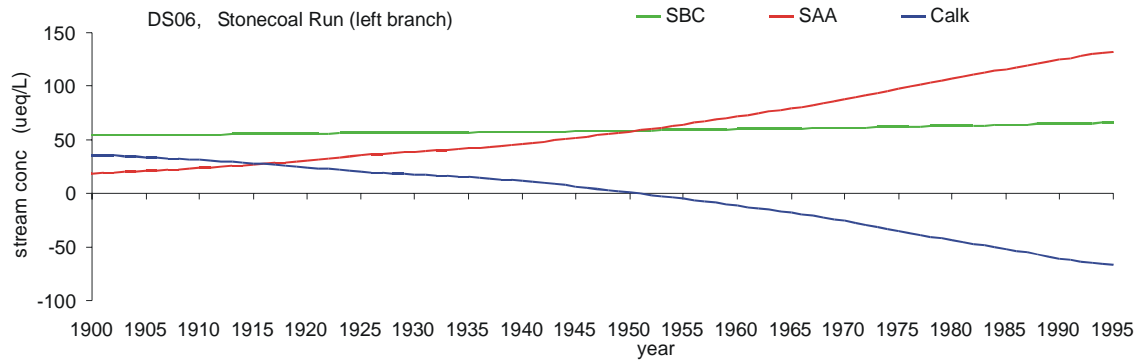
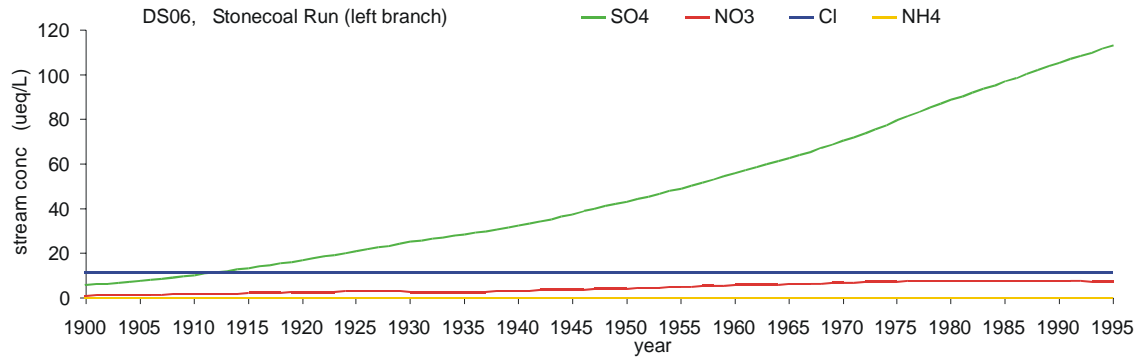
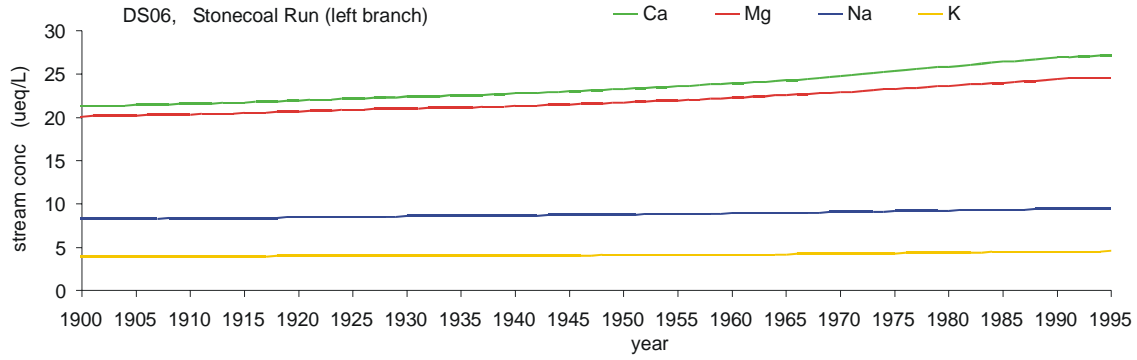


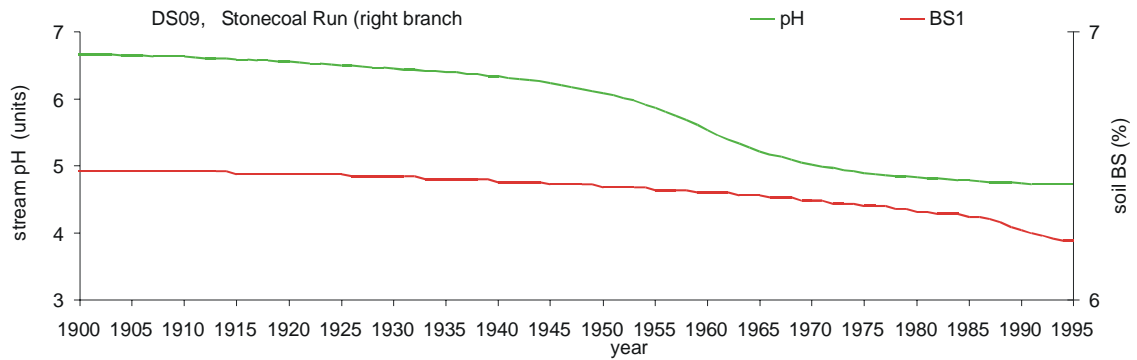
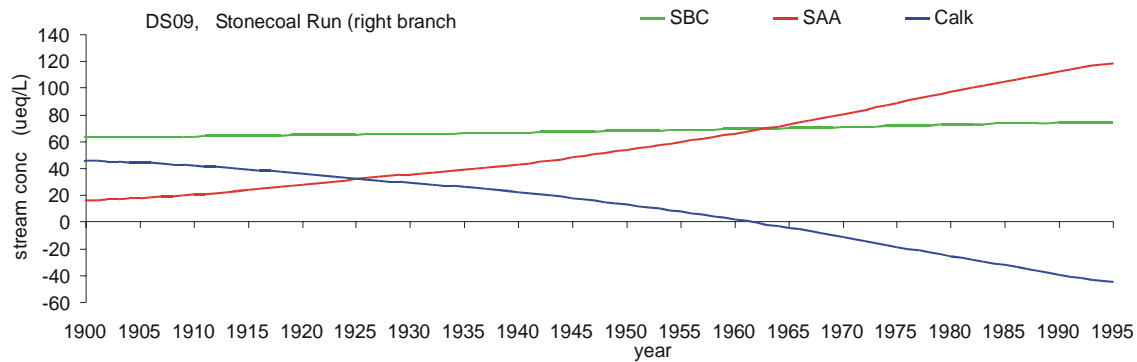
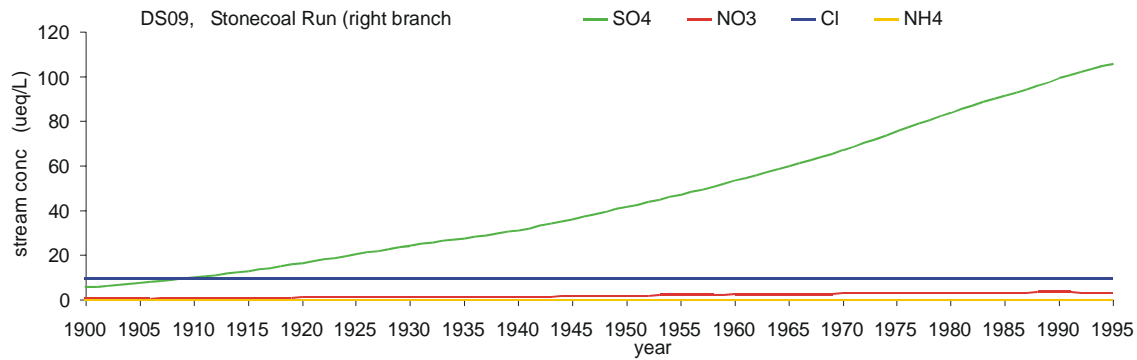
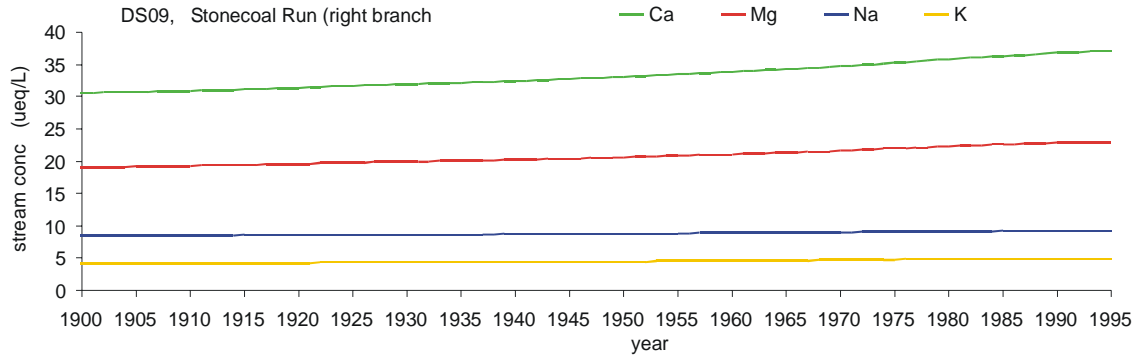


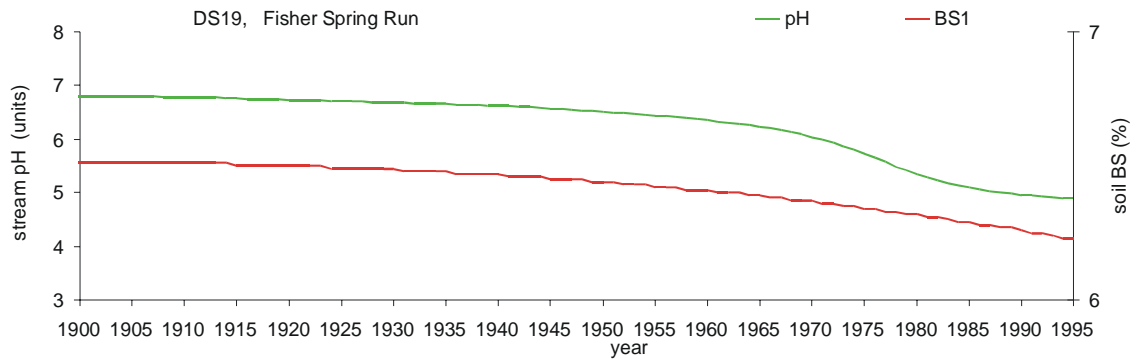
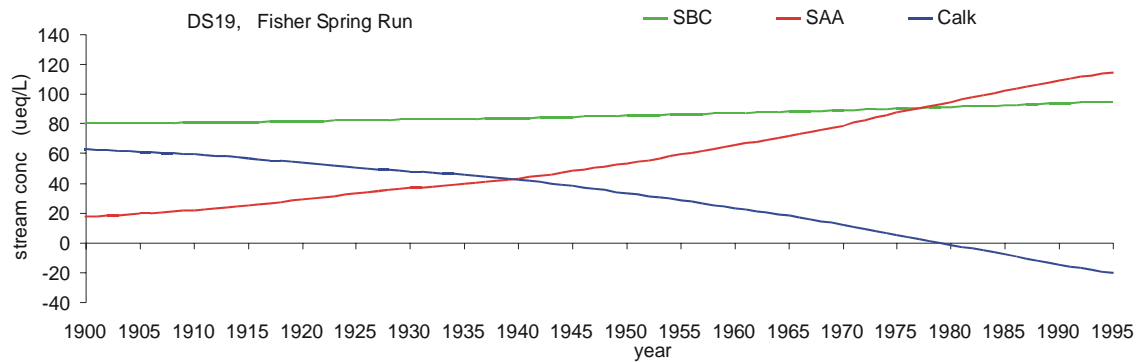
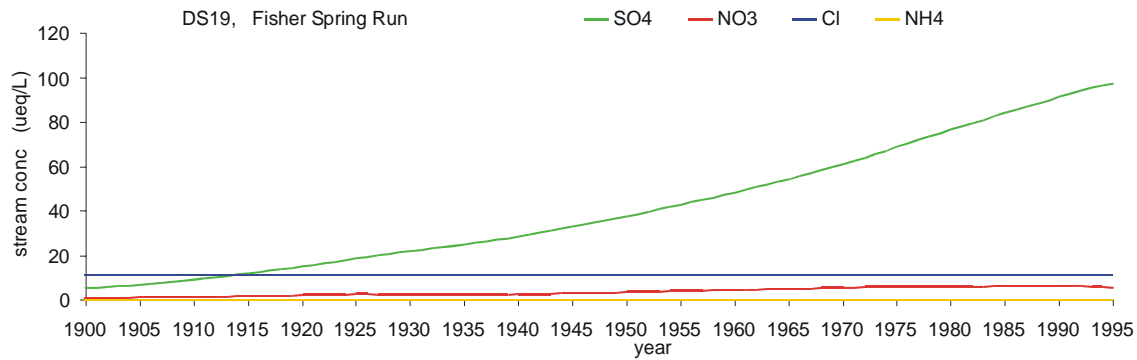
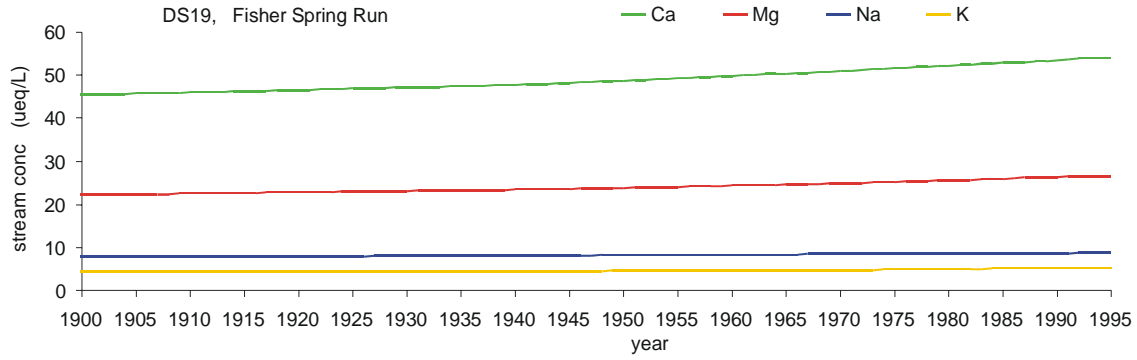


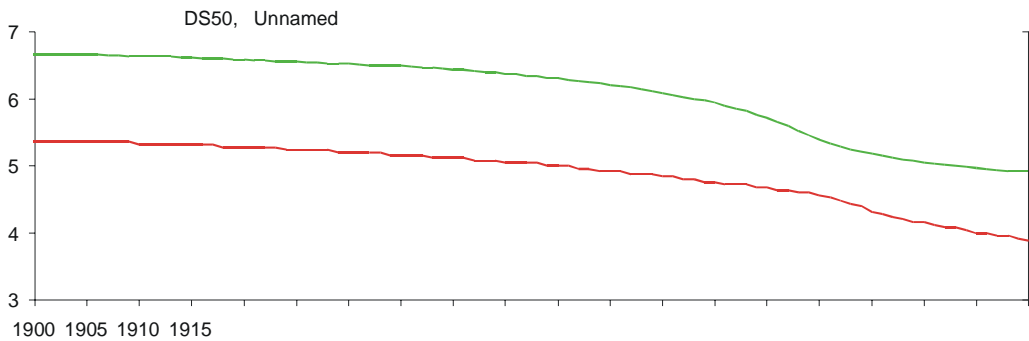
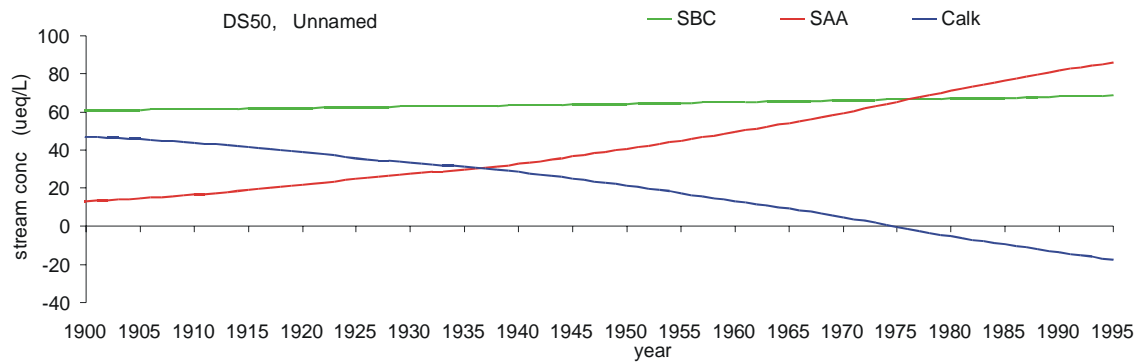
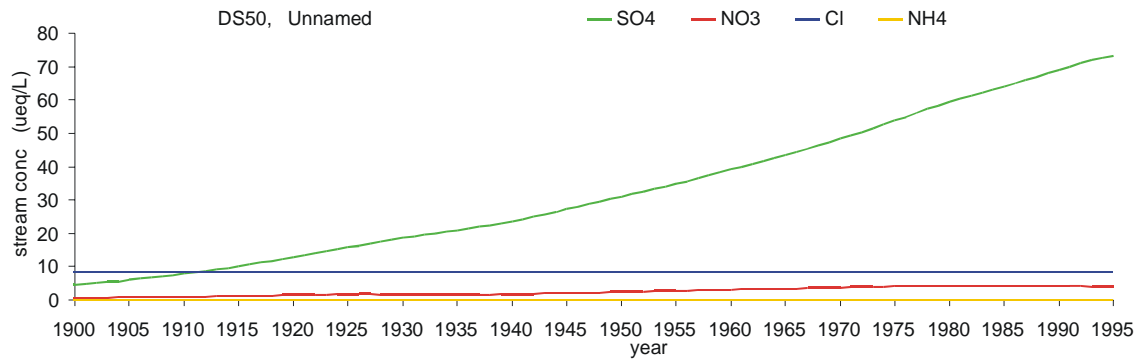
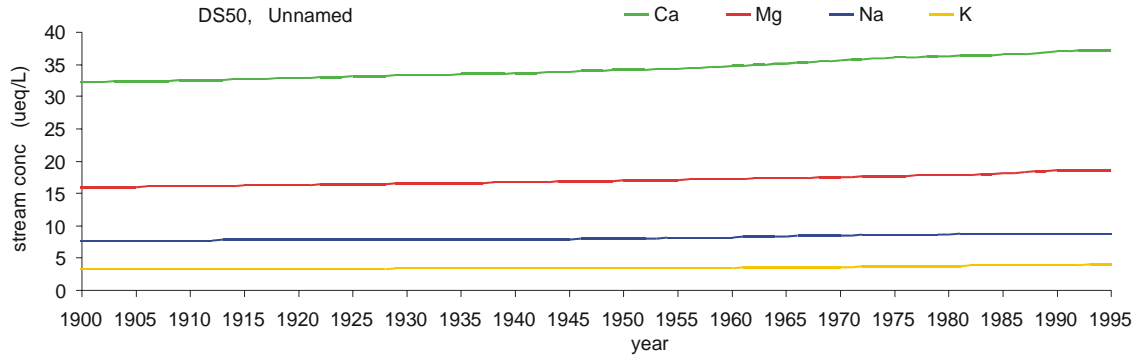




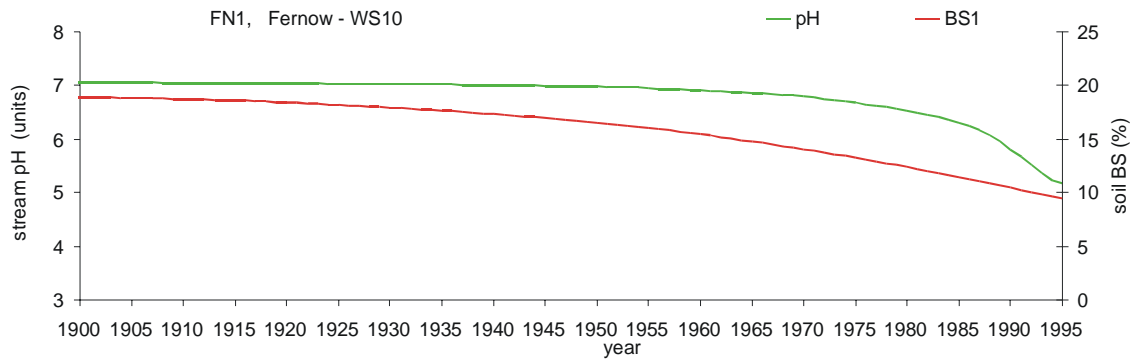
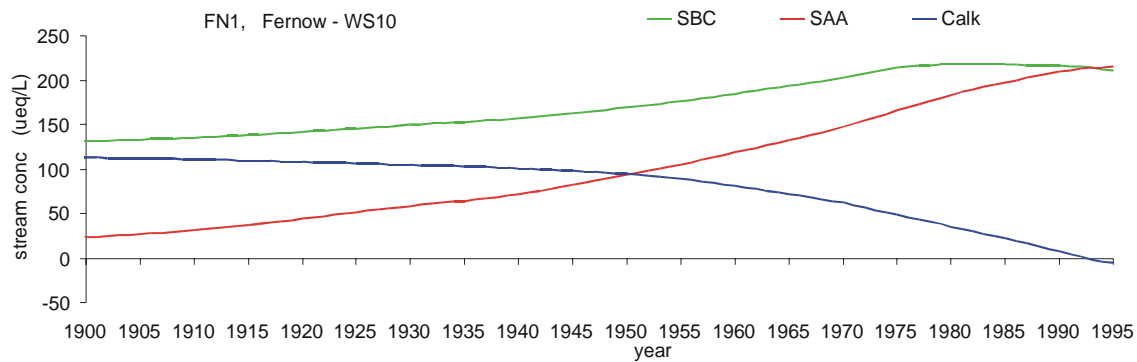
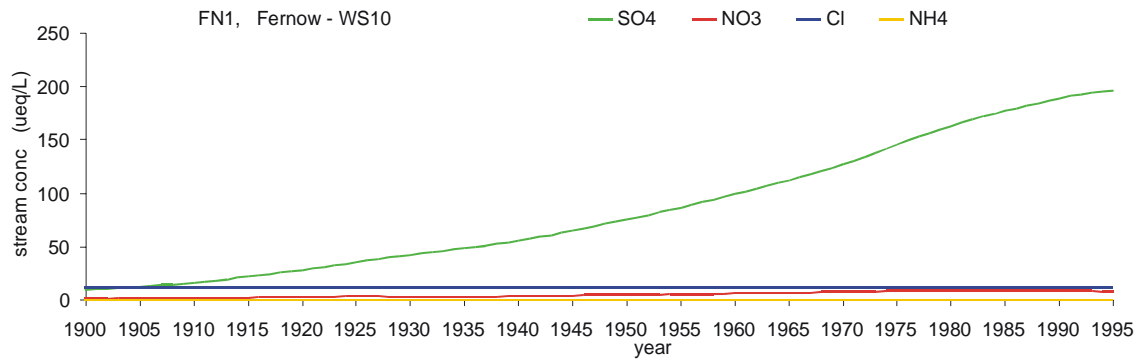
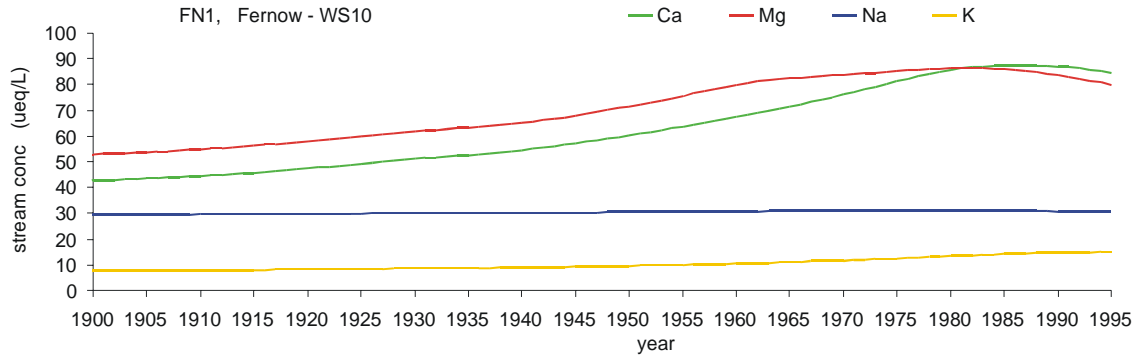


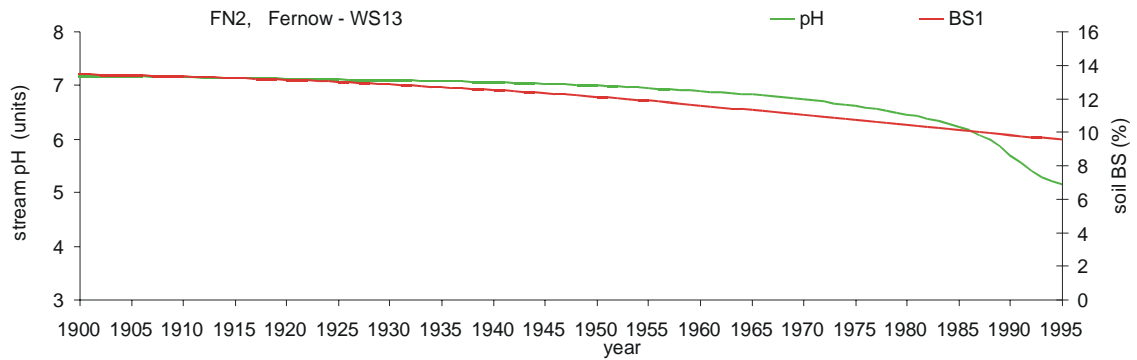
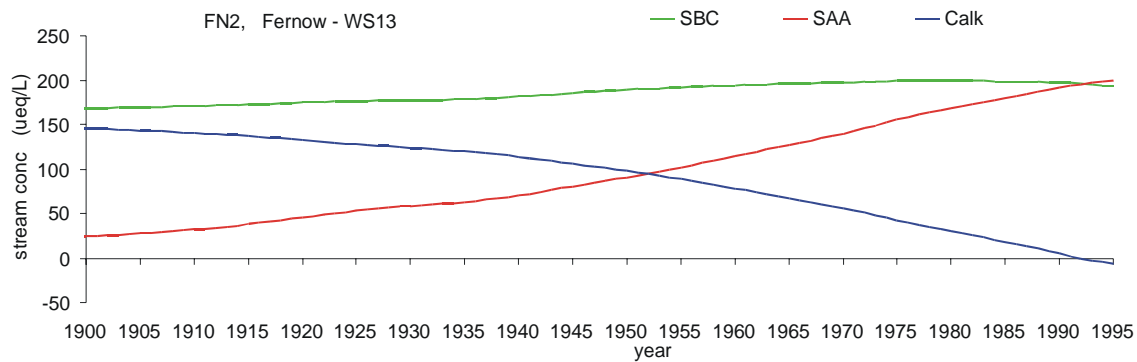
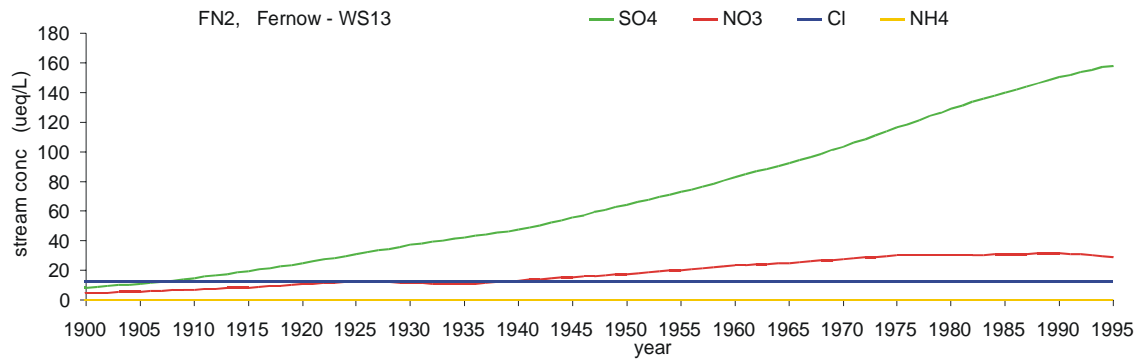
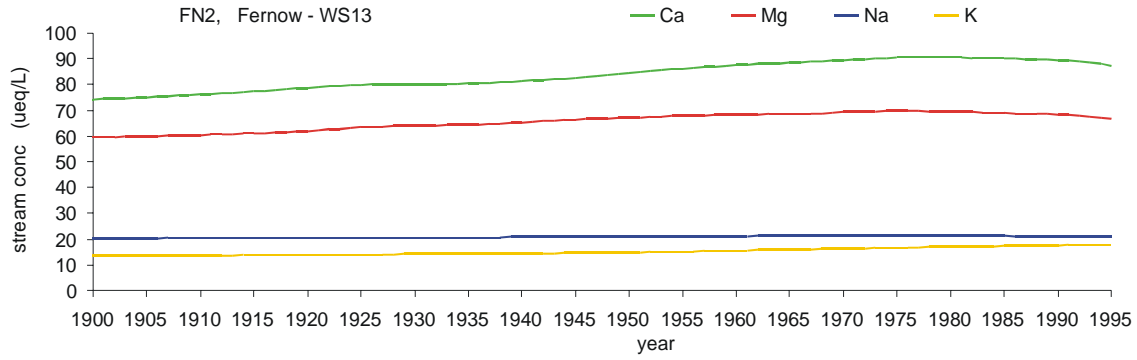


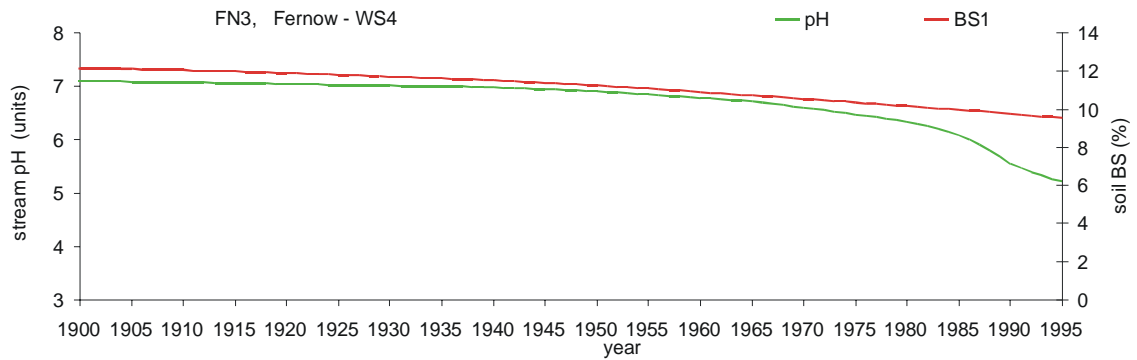
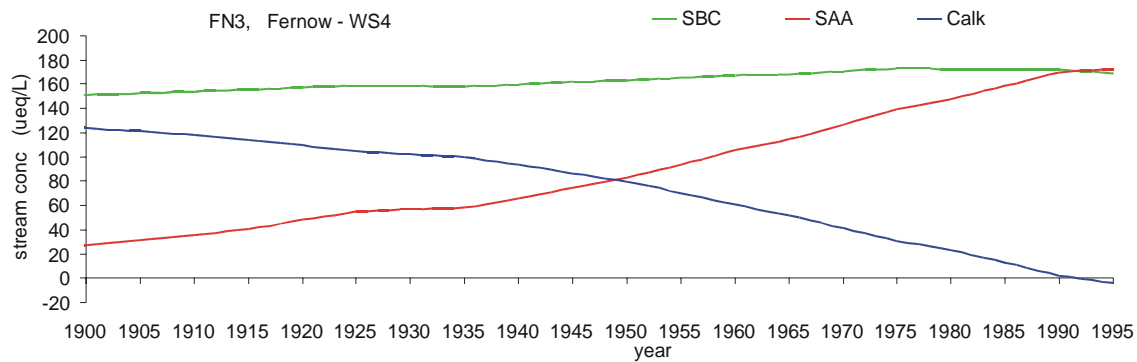
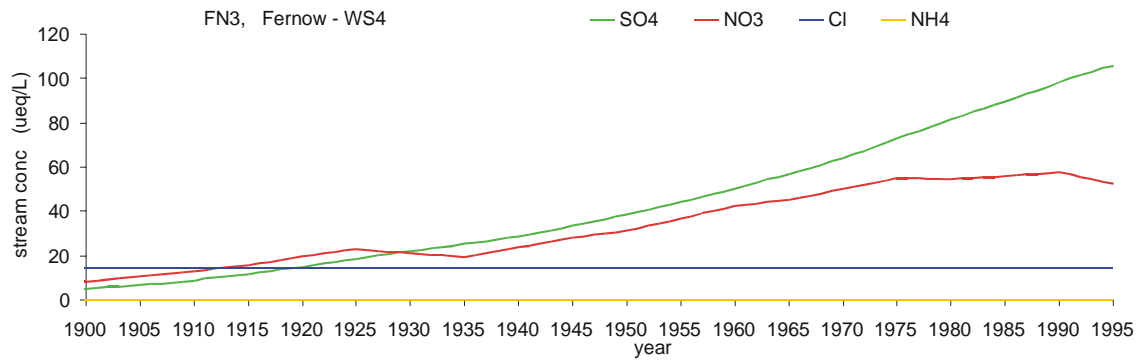
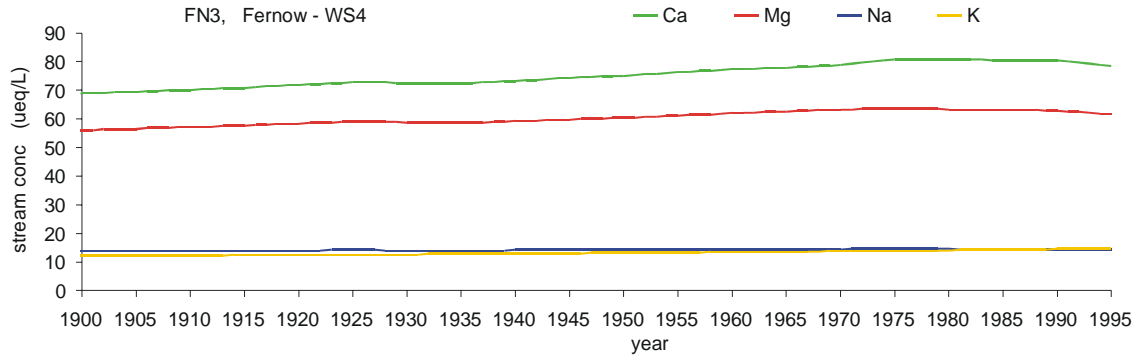


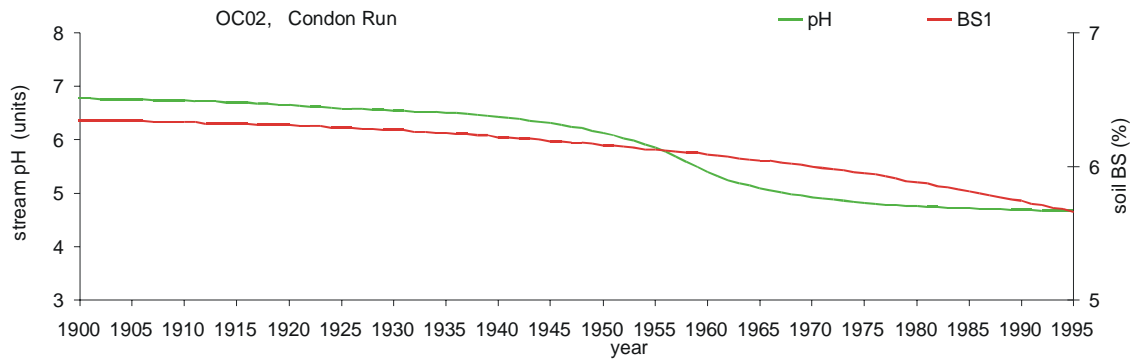
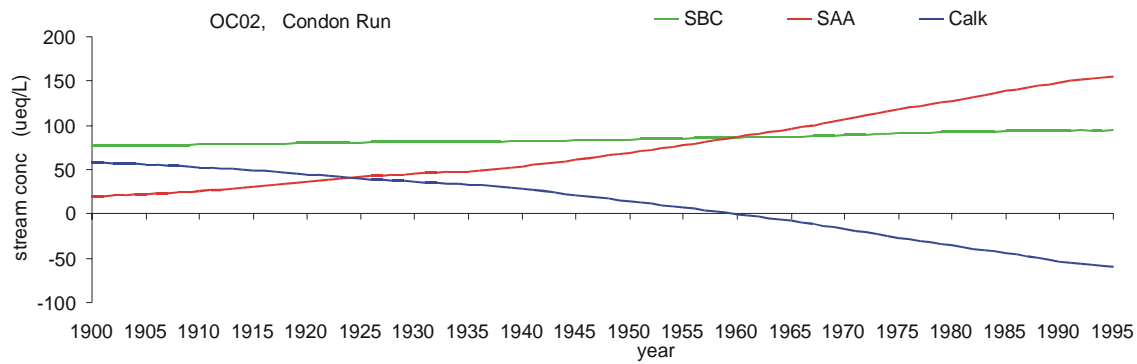
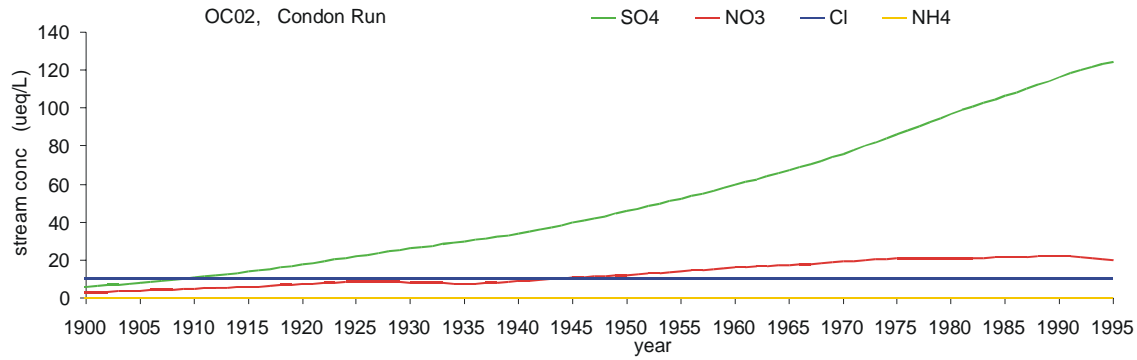
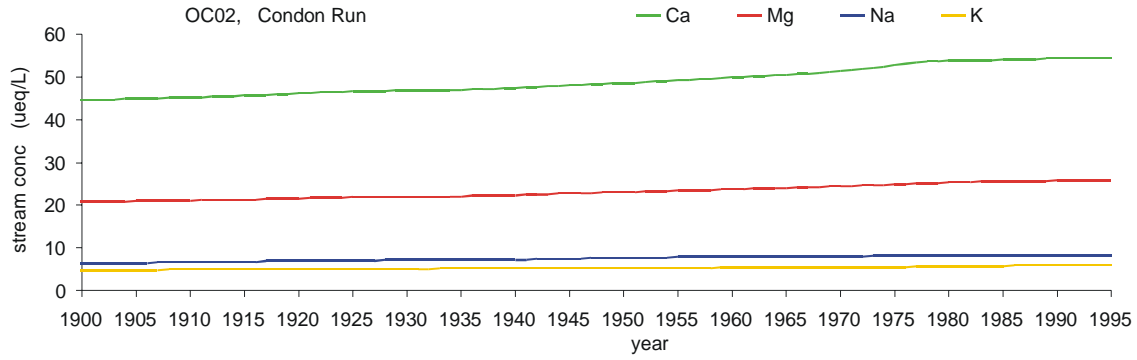


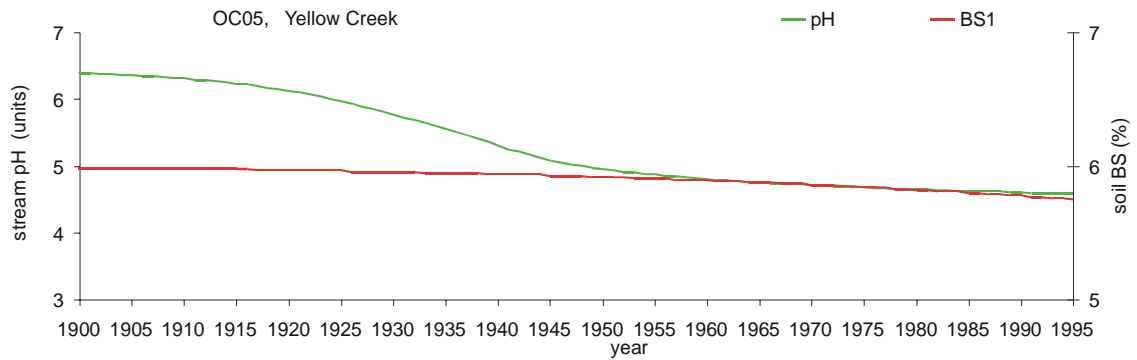
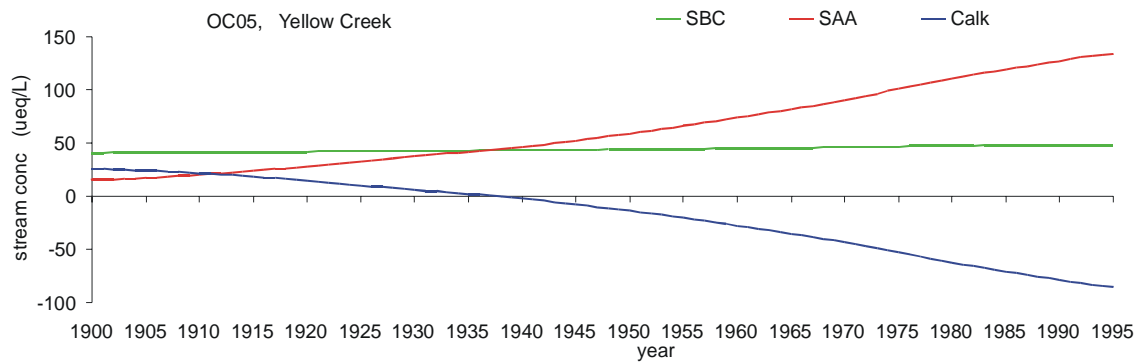
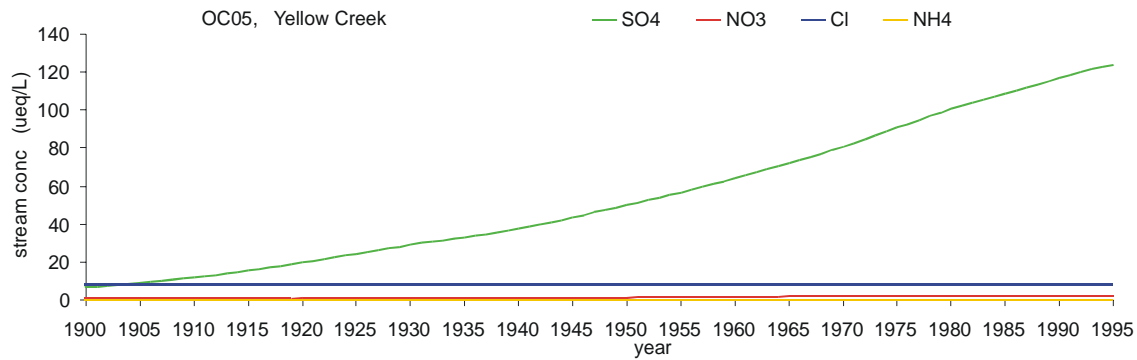
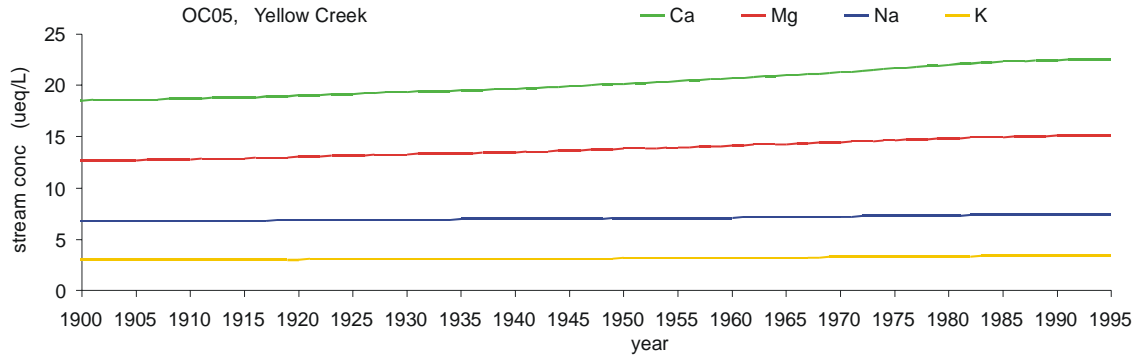


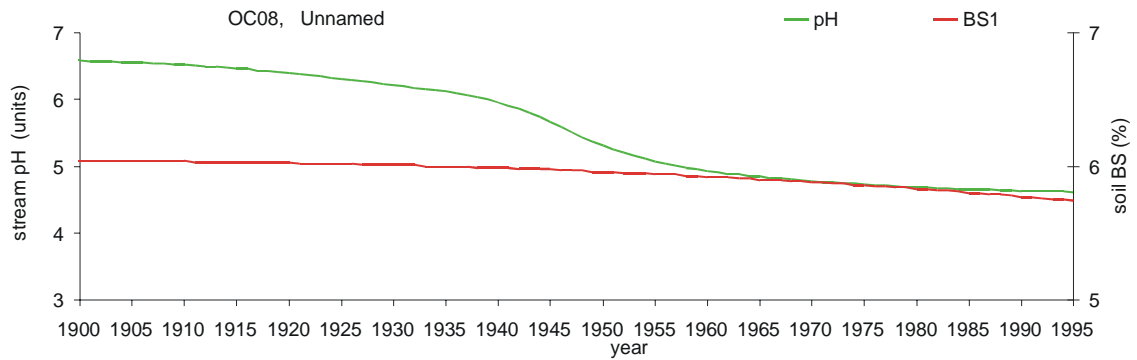
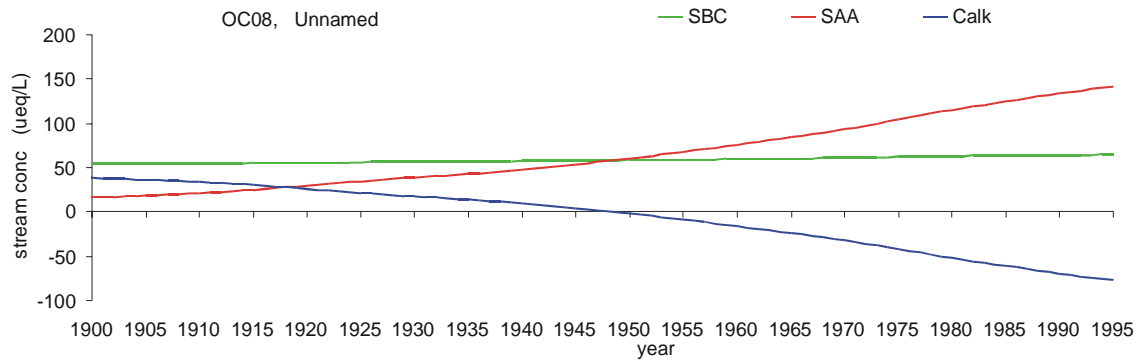
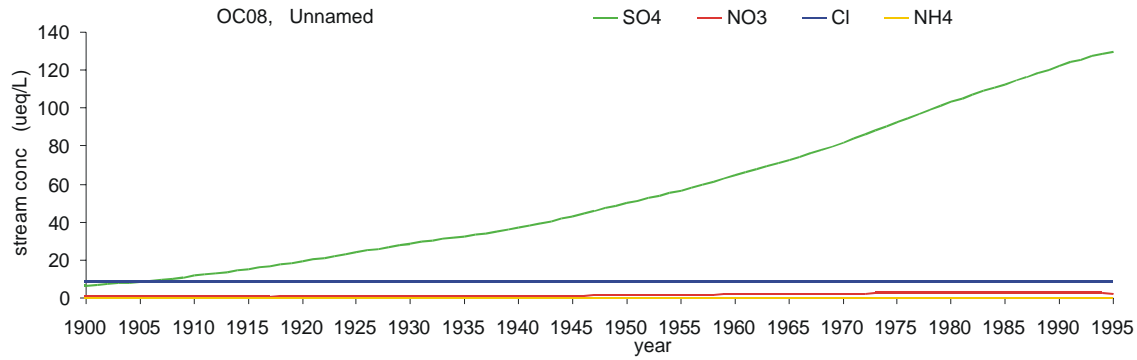
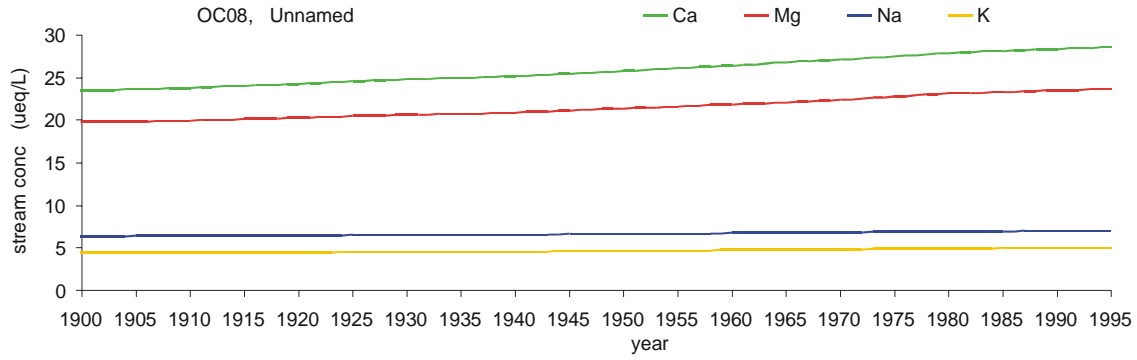


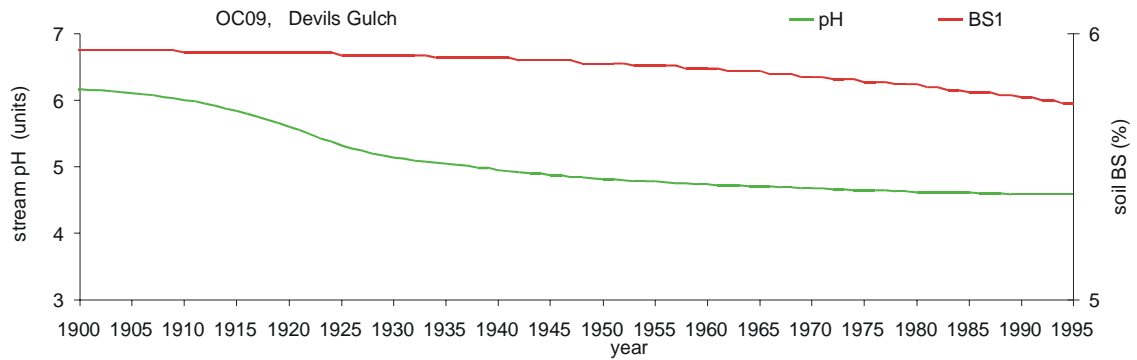
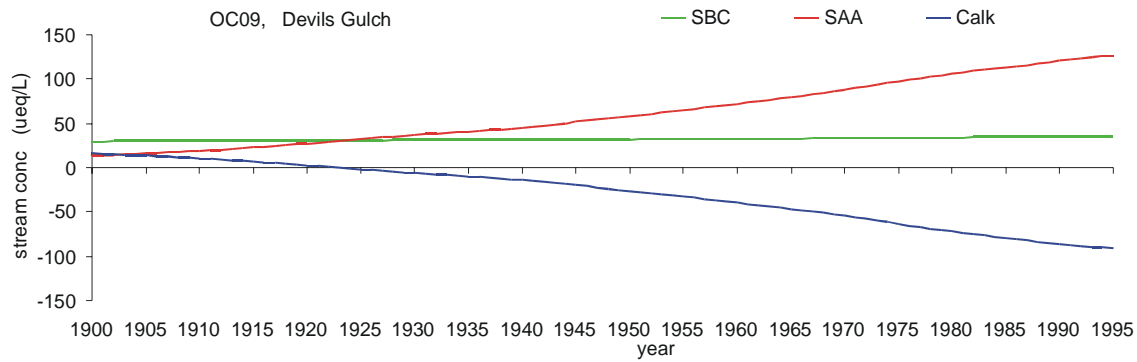
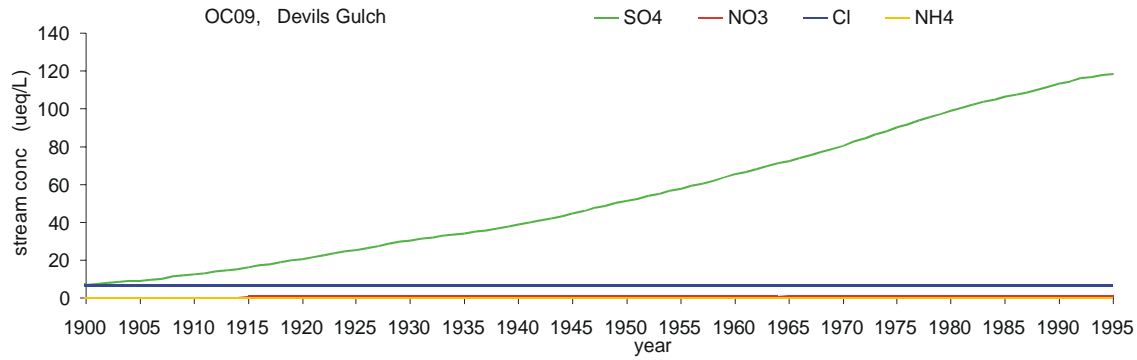
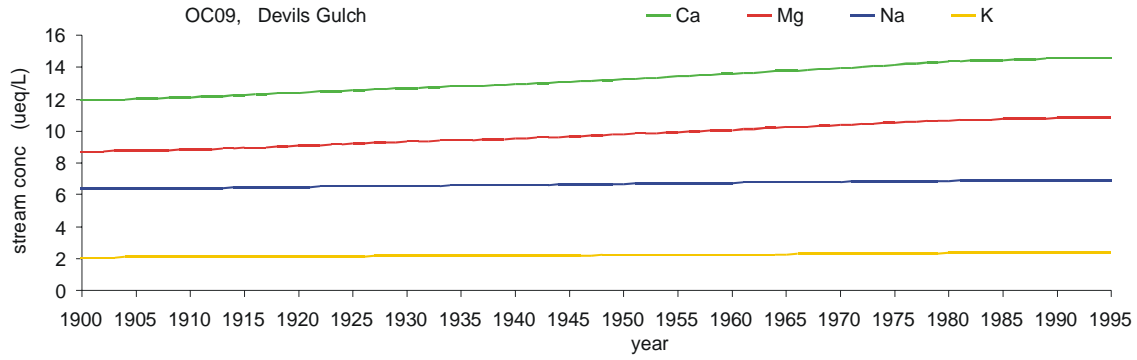


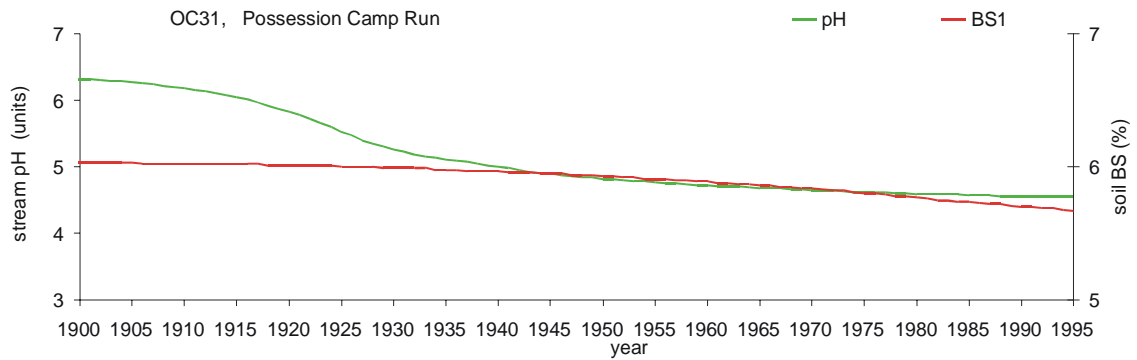
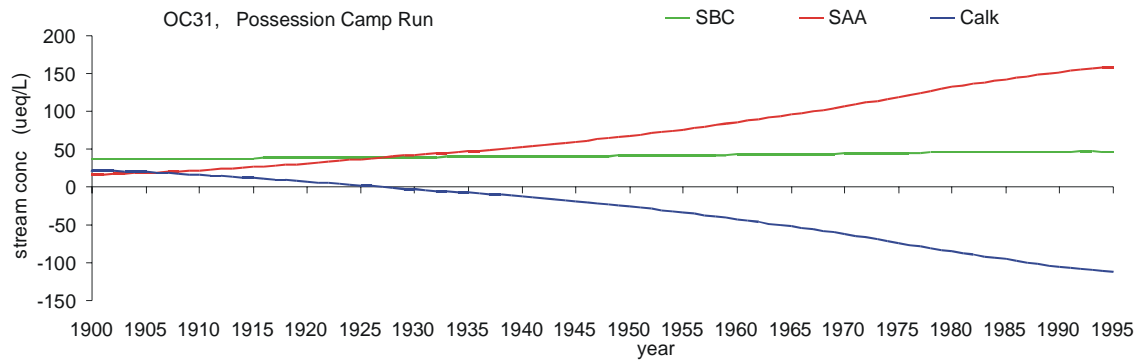
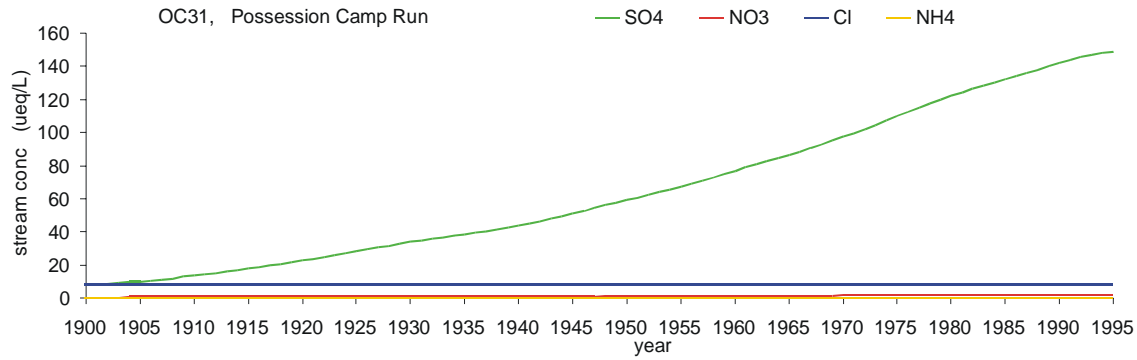
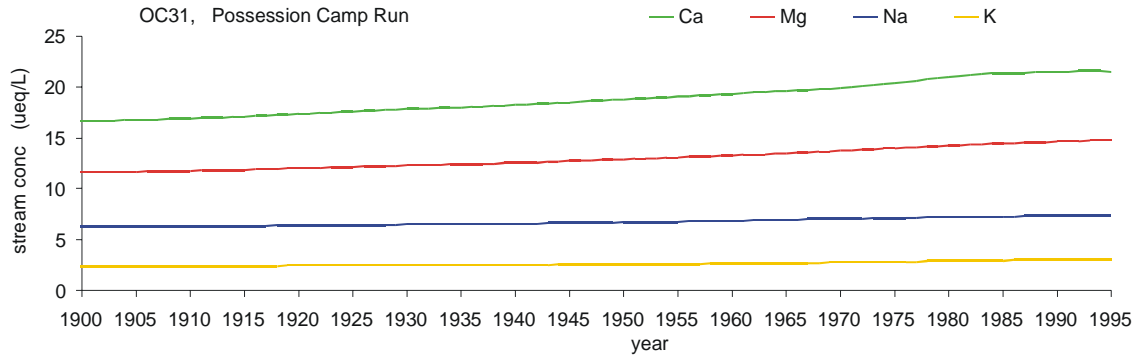




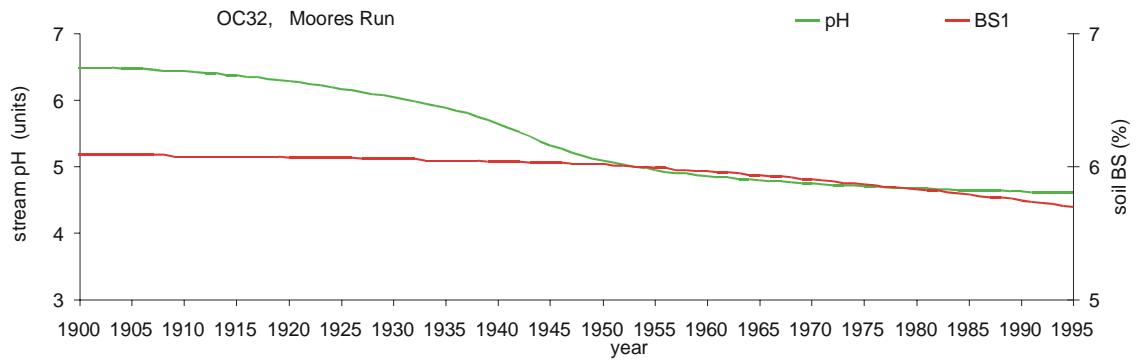
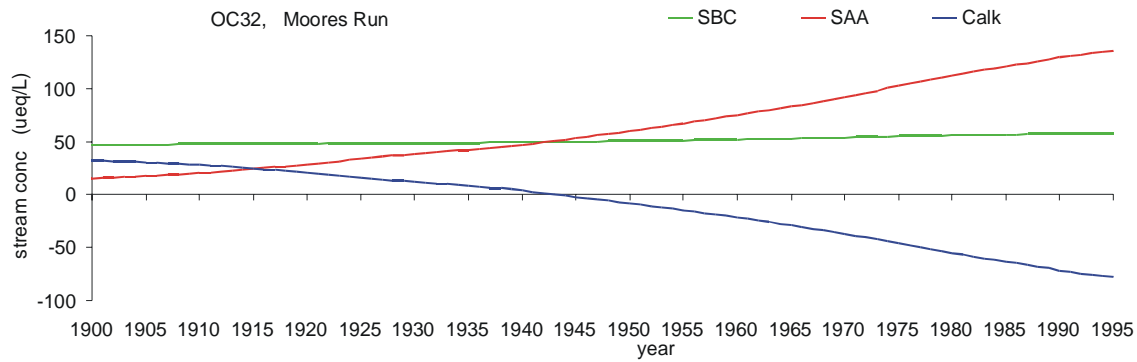
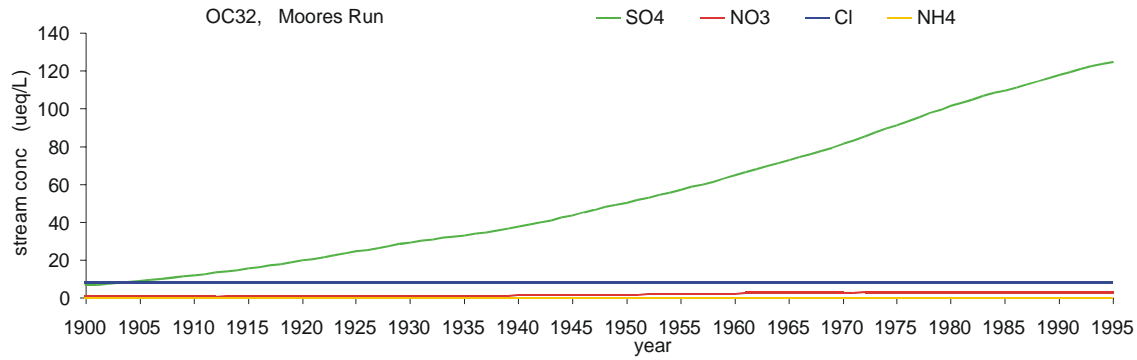
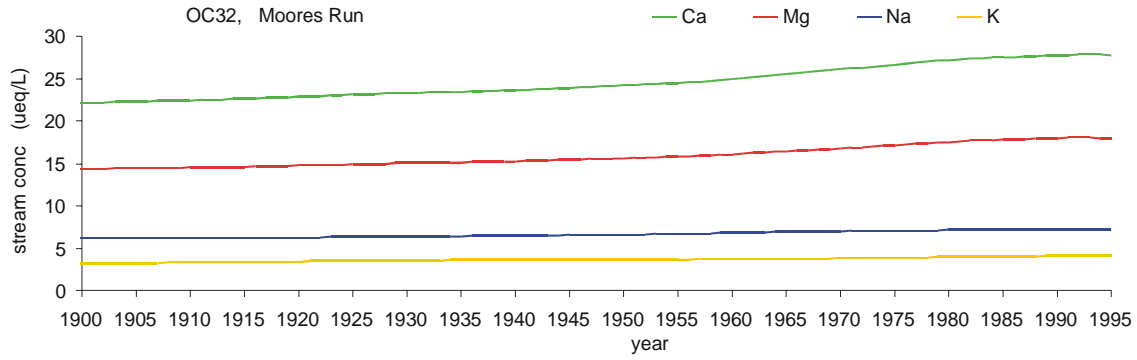


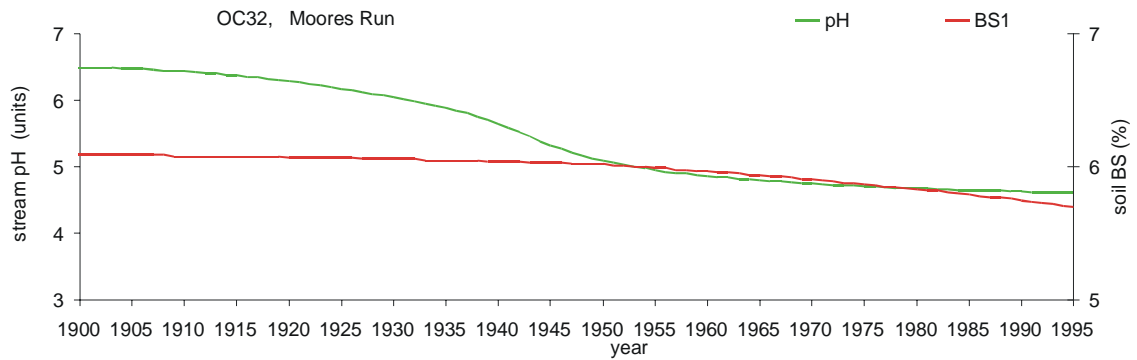
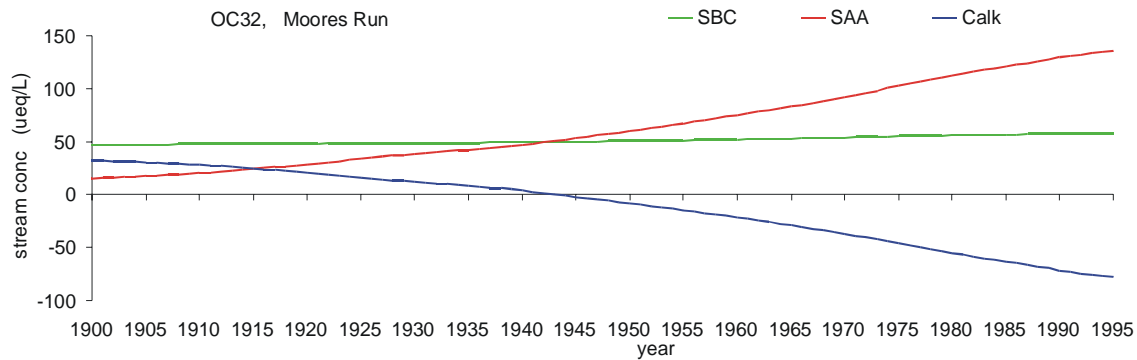
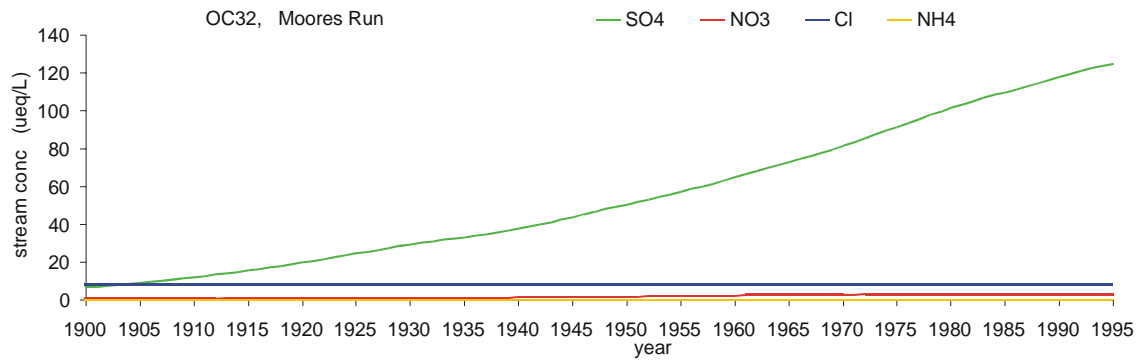
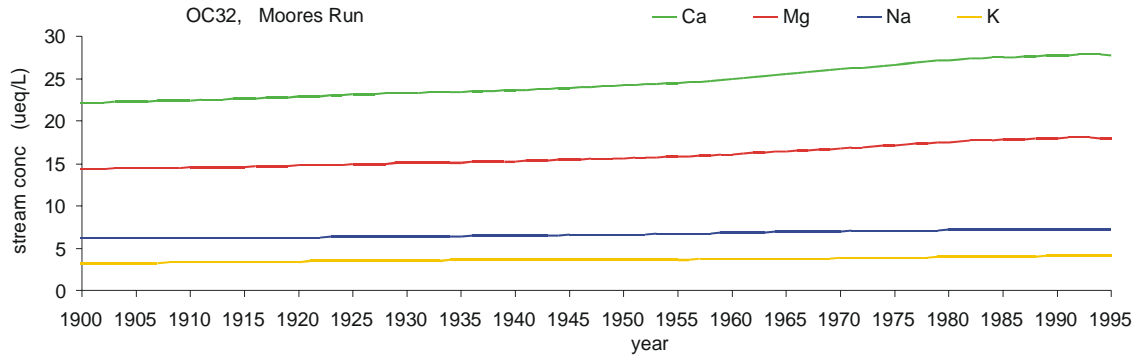


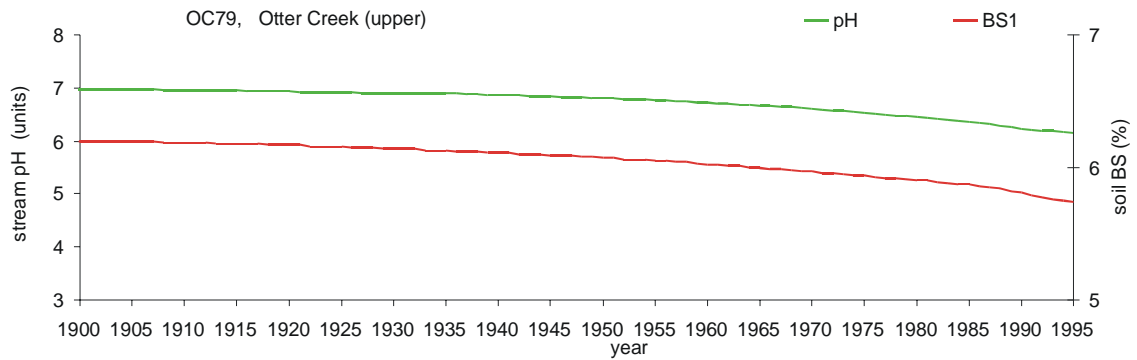
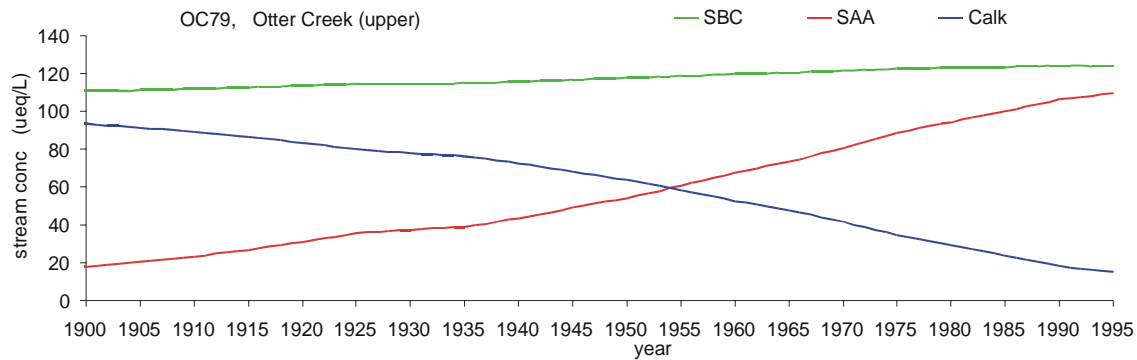
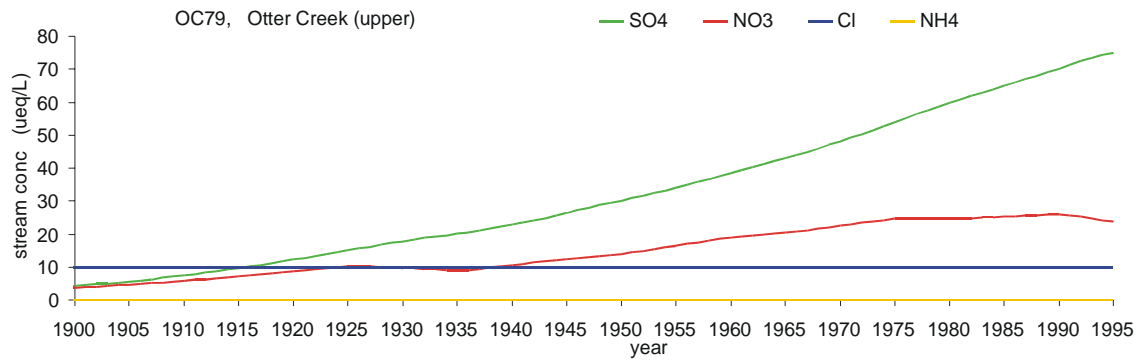
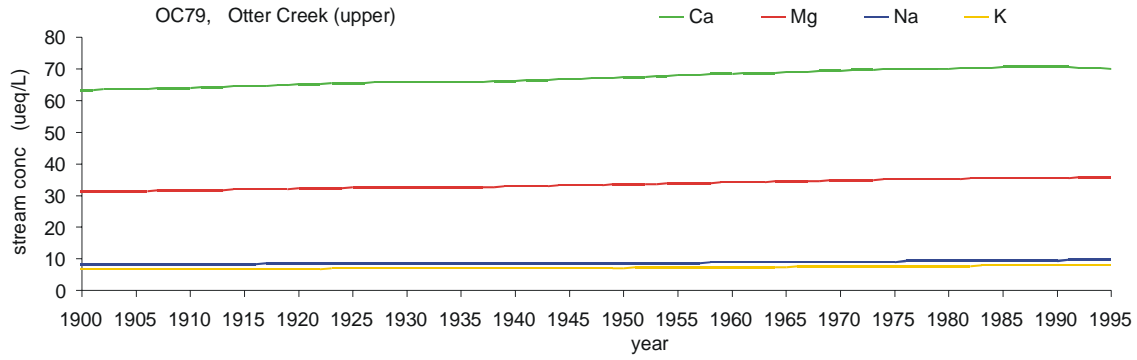


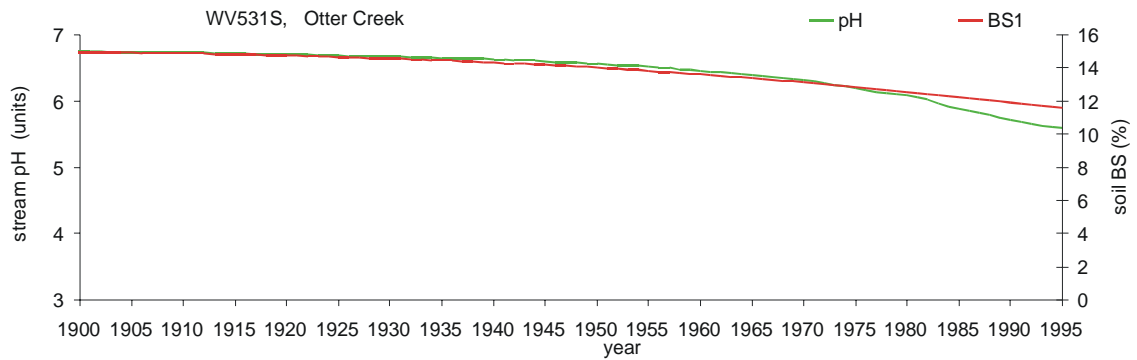
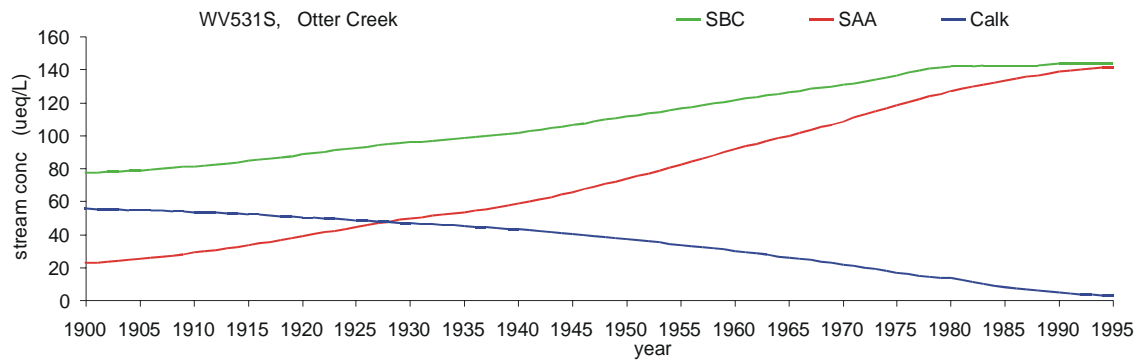
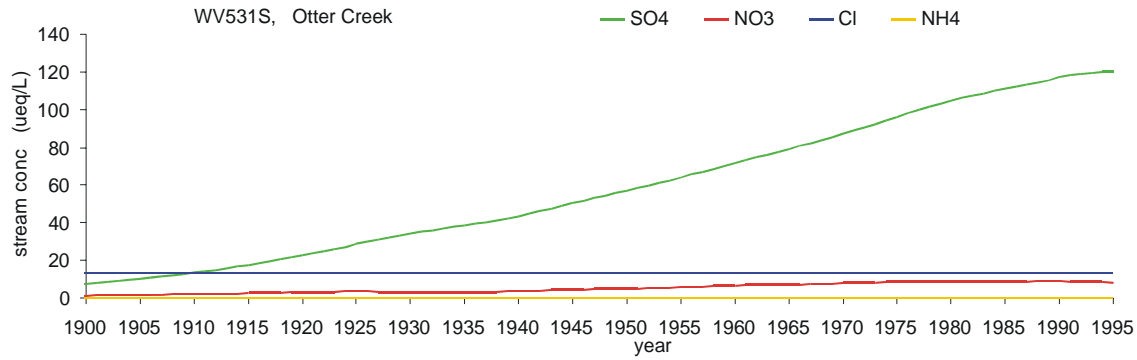
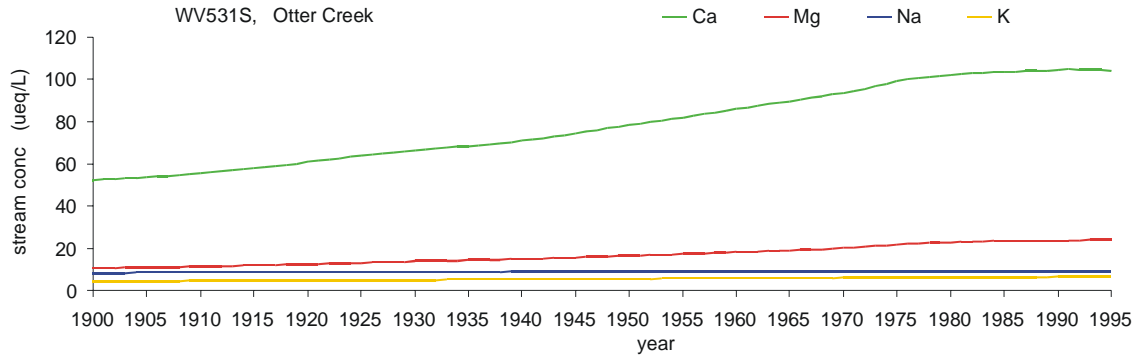


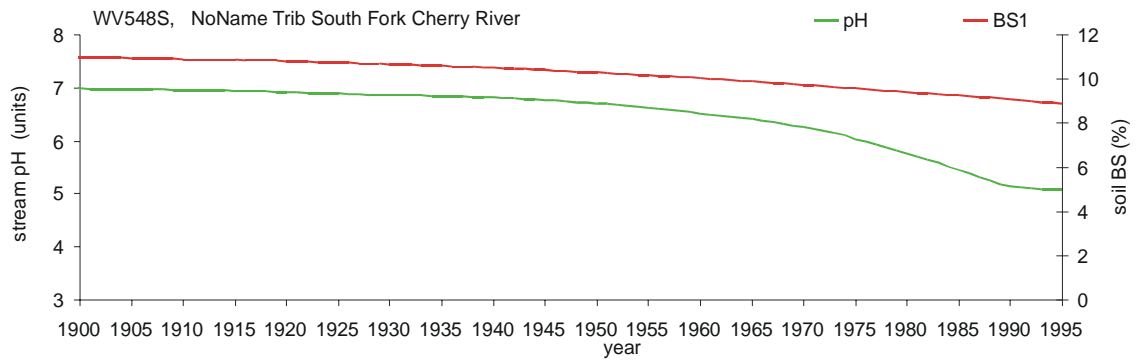
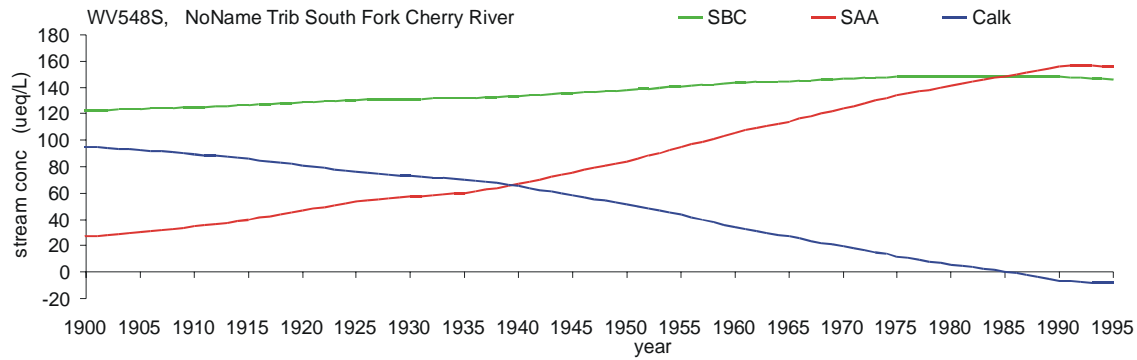
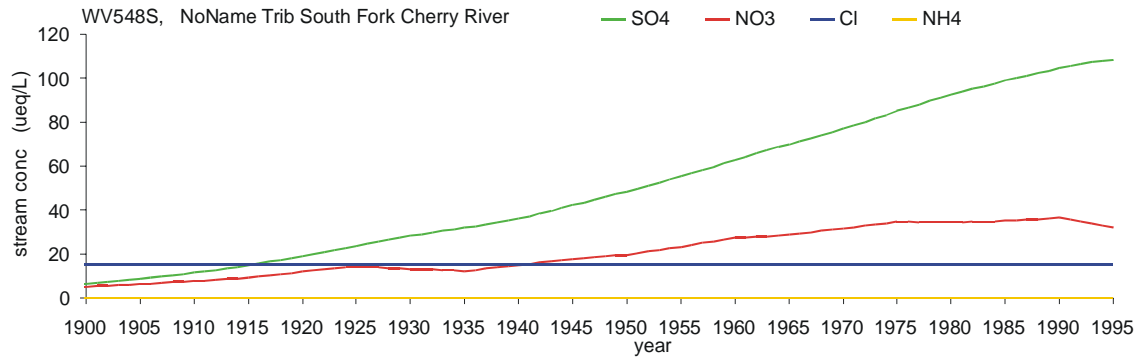
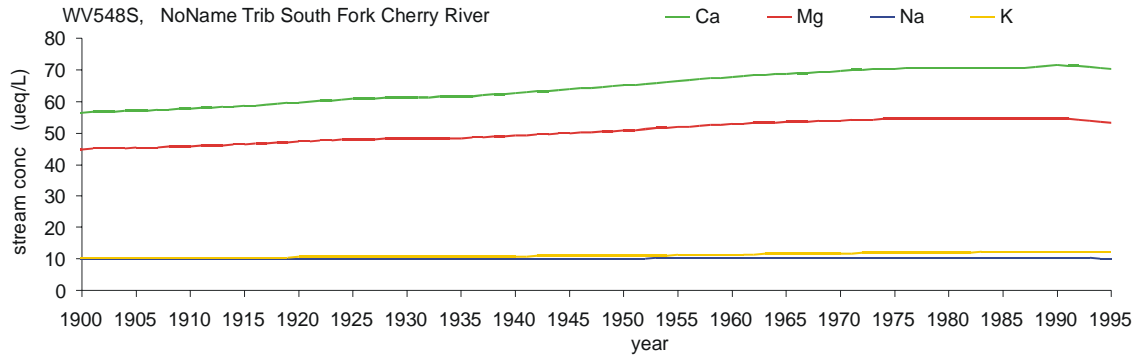


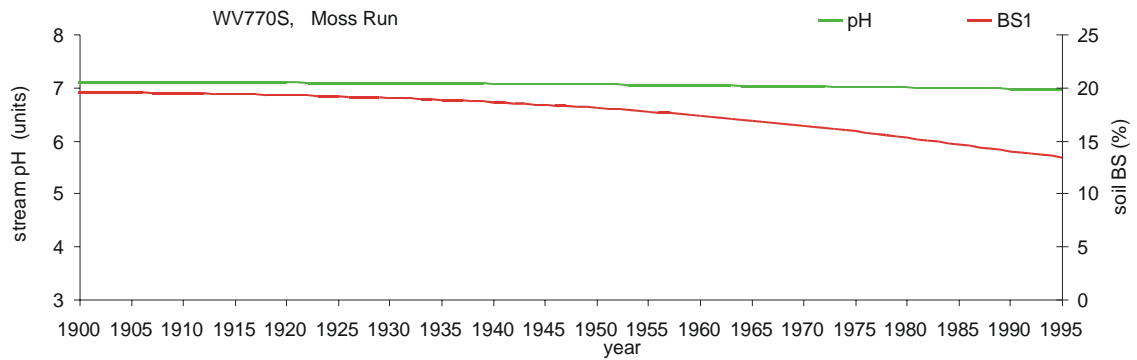
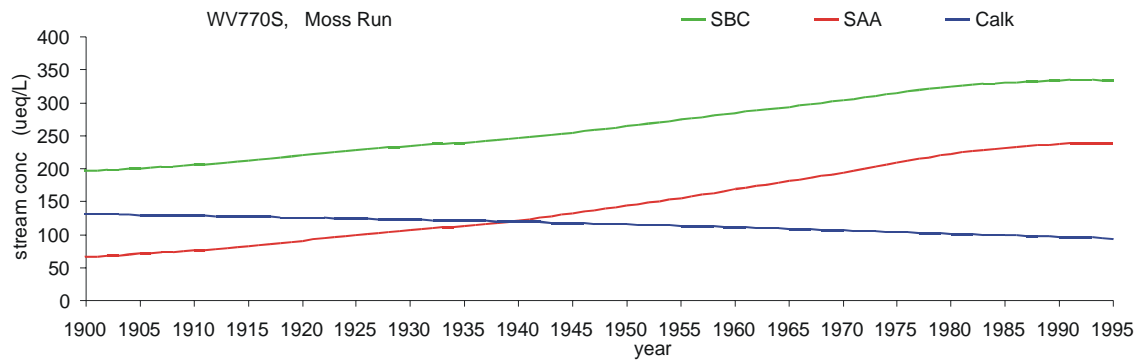
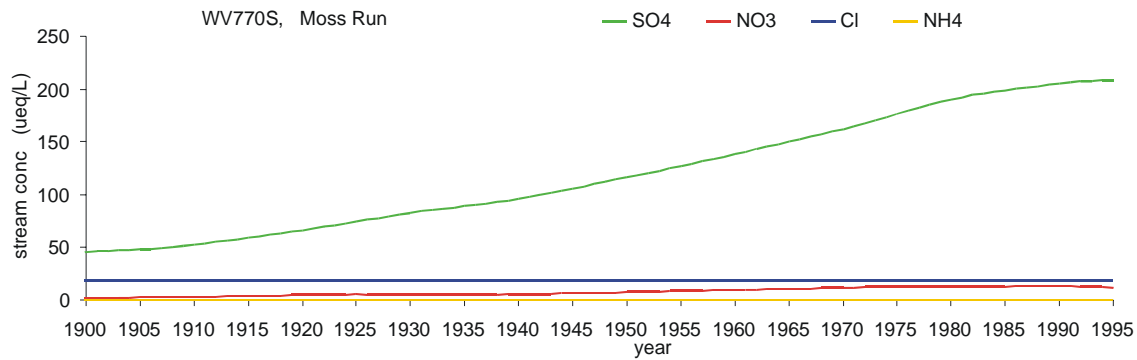
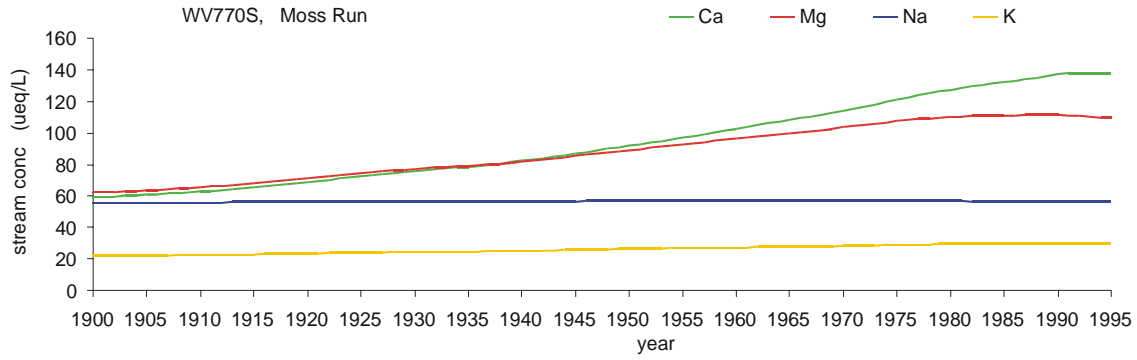


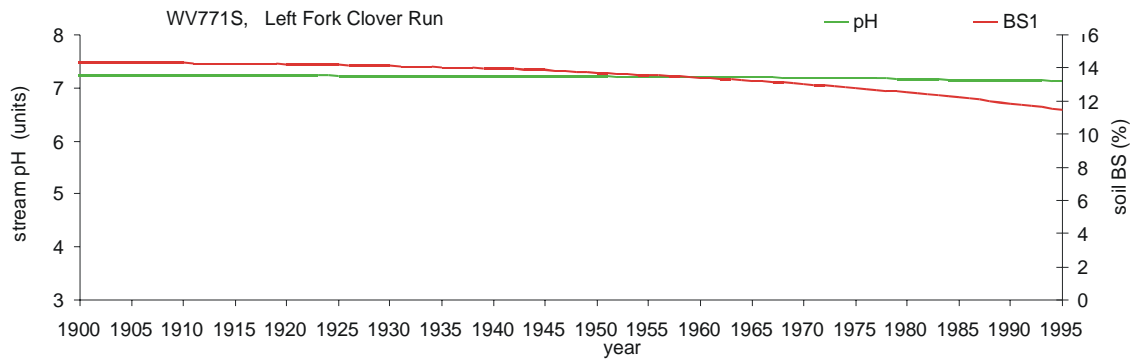
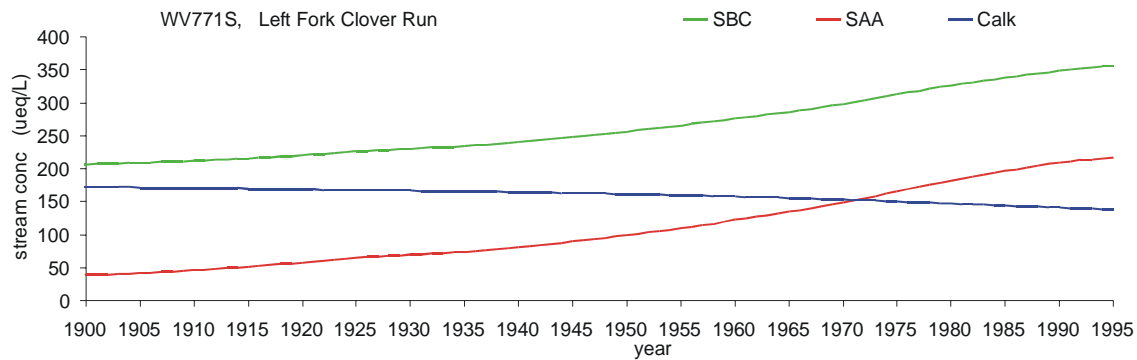
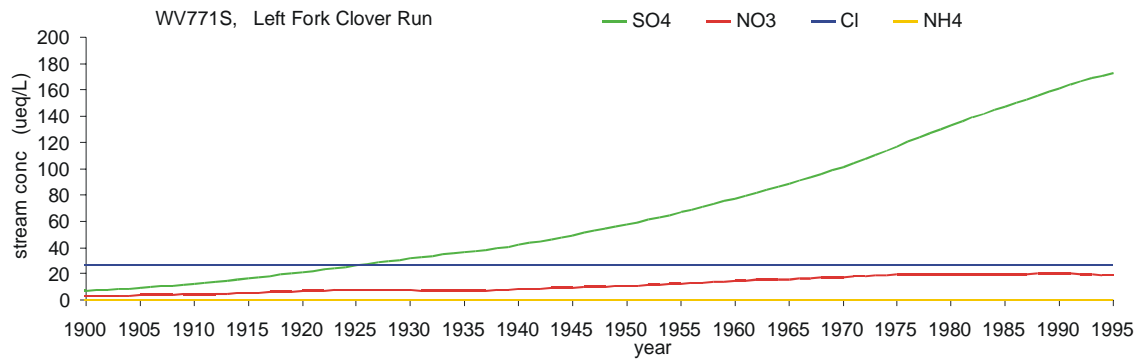
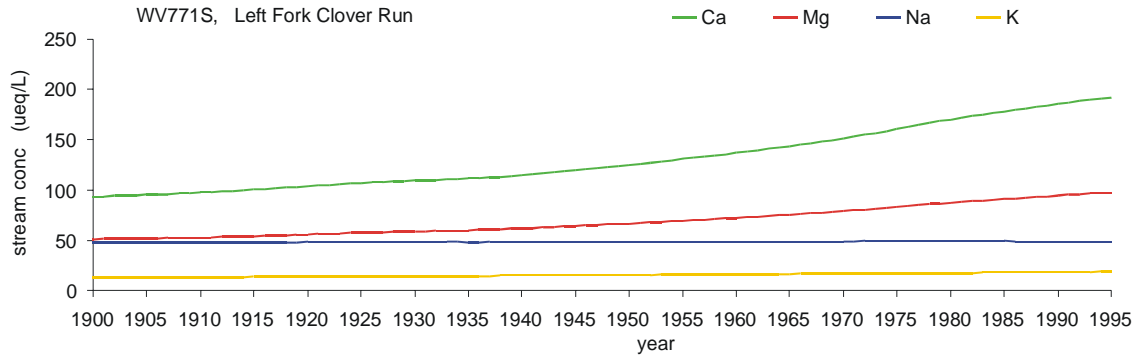


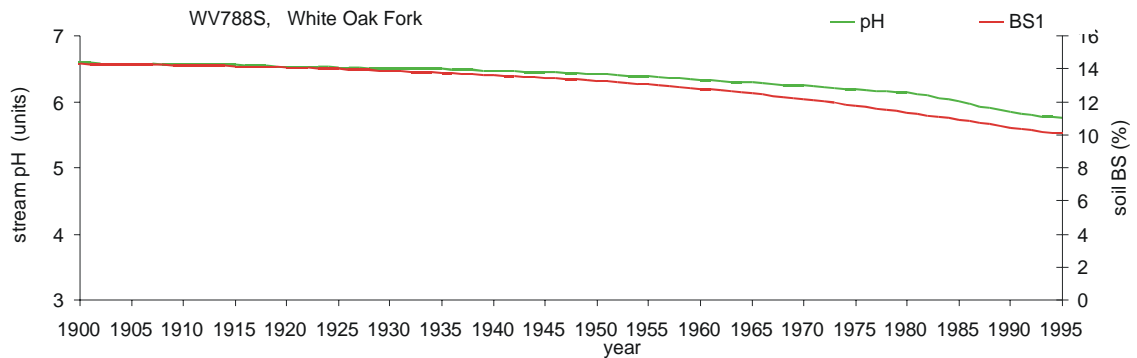
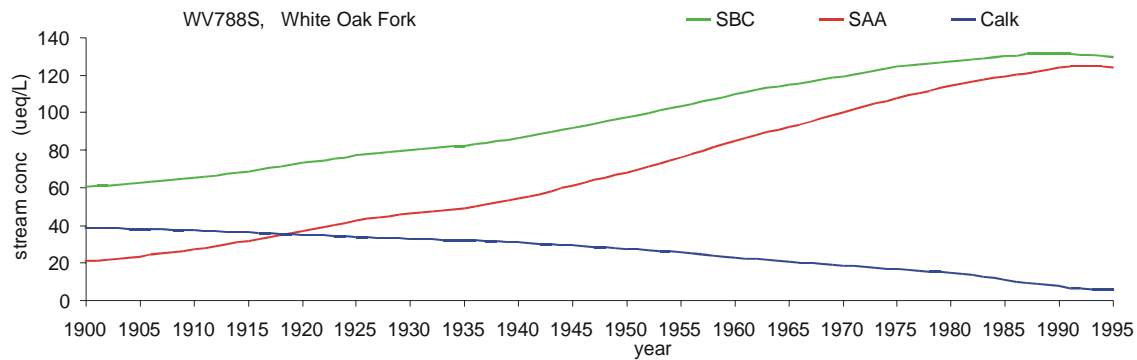
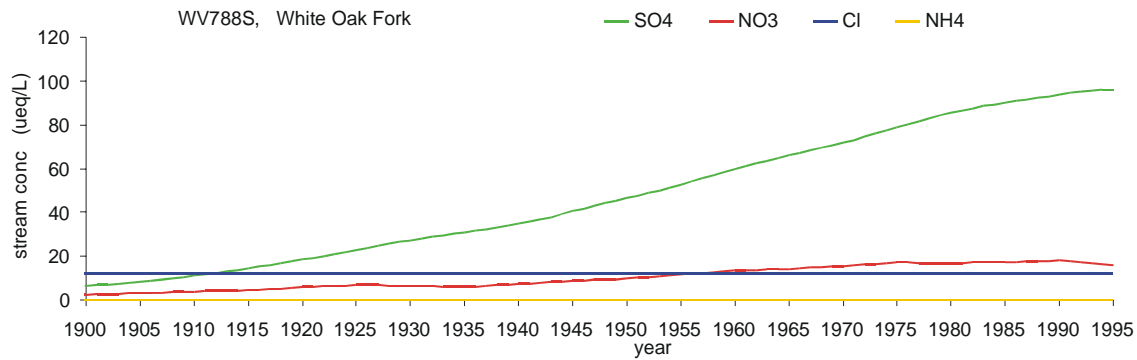
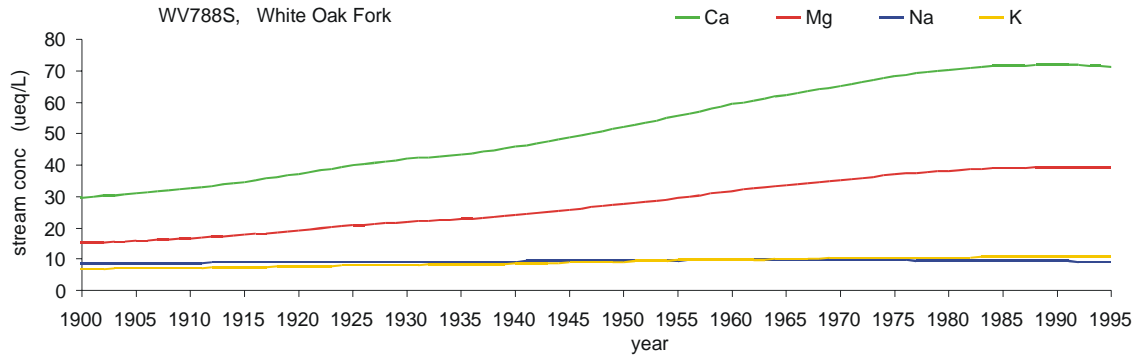




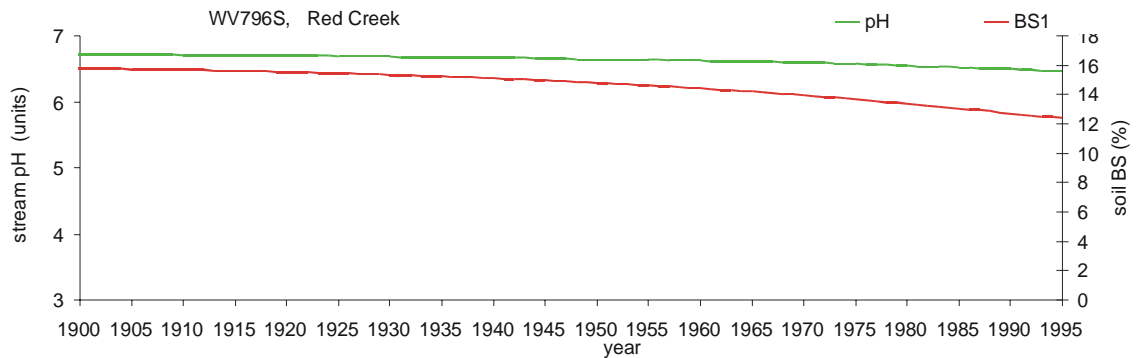
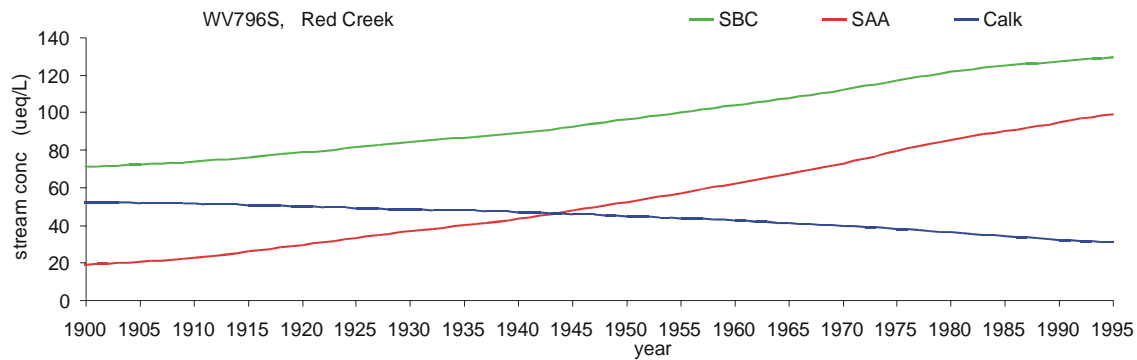
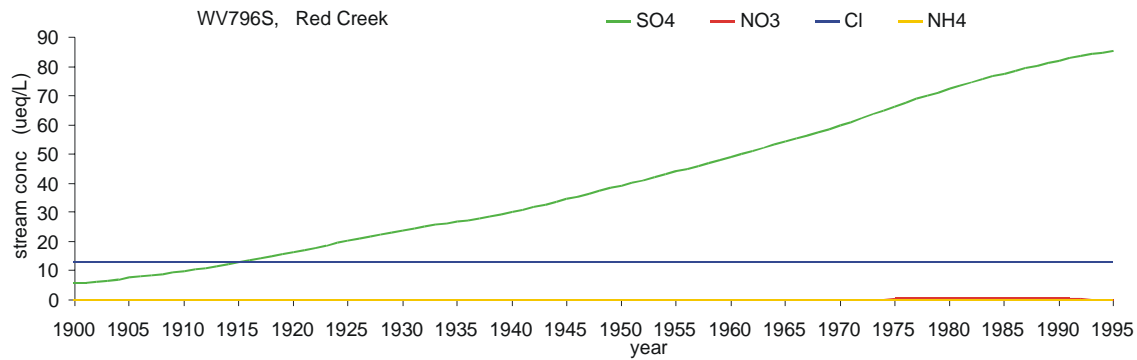
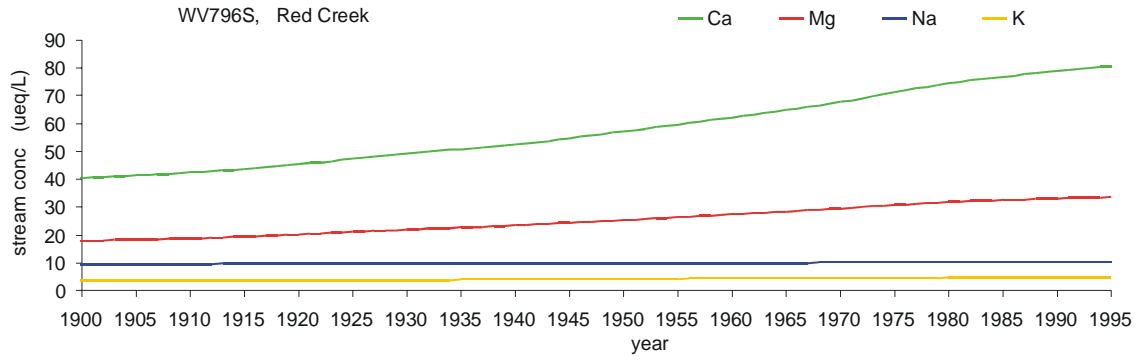












## APPENDIX C

### UNCERTAINTY

The MAGIC model, like any process-based model of acid-base chemistry, is a simplification of an array of physical, chemical, and biological processes. Such simplification invariably results in uncertainty with respect to model structure and performance. Unfortunately, models of ecosystem behavior can never truly be validated because environmental systems are not closed and because some processes might assume importance only under particular circumstances. Furthermore, with any model, it is possible to get the right answer for the wrong reason (c.f., Oreskes et al. 1994 for a discussion of model validation). Nevertheless, the MAGIC model has been extensively tested against independent measurements of chemical acidification and recovery. These tests have included many comparisons between model projections of ANC or pH and the results of whole-watershed manipulation experiments and comparisons between model hindcasts of pH and diatom-inferred pH. In general, the MAGIC model has shown good agreement with these independent measurements or estimates of chemical change. See the review of Sullivan (2000) for additional information.

For the SAMI study, data were available from the VTSSS with which to evaluate the agreement between MAGIC simulated and observed values over a ten-year period of record. MAGIC was calibrated to 33 VTSSS sites. The root mean squared error (RMSE) was selected as the statistic for comparing the goodness of fit between simulated and observed values. It is equal to the square root of the average squared difference between the 10 pairs of simulated and observed values (one for each of the 10 years of record) at each site. The RMSE for the 33 sites ranged from 3 to 13  $\mu\text{eq/L}$ , with a mean of 7.1  $\mu\text{eq/L}$ .

The aggregated nature of the MAGIC model requires that it be calibrated to observed data from a system before it can be used to examine potential system response. Calibration is achieved by setting the values of certain parameters within the model that can be directly measured or observed in the system of interest (called “fixed” parameters). The model is then run (using observed and/or assumed atmospheric and hydrologic inputs) and the outputs (stream water and soil chemical variables, called “criterion” variables) are compared to observed values of these variables. If the observed and simulated values differ, the values of another set of parameters in the model (called “optimized” parameters) are adjusted to improve the fit. After a number of iterations, the simulated-minus-observed values of the criterion variables usually

converge to zero (within some specified tolerance). The model is then considered calibrated. If new assumptions (or values) for any of the fixed variables or inputs to the model are subsequently adopted, the model must be re-calibrated by re-adjusting the optimized parameters until the simulated-minus-observed values of the criterion variables again fall within the specified tolerance.

The estimates of the fixed parameters and deposition inputs used for calibration are subject to uncertainties so a multiple optimization procedure was implemented for calibrating the model at each site. The multiple optimization procedure consisted of repeated calibrations of each site using random values of the fixed parameters drawn from the observed possible range of values for each site, and random values of deposition from a range including uncertainty about the interpolated values for each site. Each of the calibrations began with (1) a random selection of values of fixed parameters and deposition, and (2) a random selection of the starting values of the optimized parameters. The optimized parameters were then adjusted using a steepest-descent algorithm to achieve a minimum error fit to the “criterion” or target variables. This procedure was undertaken ten times for each SAMI site. The final calibrated model for a site is represented by the ensemble of parameter values and variable values of all of the successful calibrations.

The effects of the uncertainty in the assumptions made in calibrating the model (and the inherent uncertainties in the available data) can be assessed by using all successful calibrations for a site when simulating the response to different future deposition. The model then produces an ensemble of simulated values for each site. The median of all simulated values is considered the most likely response of the site. The projections from MAGIC reported here and throughout the SAMI report are the median values from the ensemble of calibrations for each of the SAMI sites. The simulated values in the ensemble can also be used to estimate the magnitude of the uncertainty in the projection. Specifically, the difference in any year between the maximum and minimum simulated values from the ensemble of calibrated parameter sets can be used to define an “uncertainty” (or “confidence”) width for the simulation at any point in time. All ten of the successful model calibrations will lie within this range of values.

The uncertainty widths for simulated ANC for the SAMI reference year are of the same order as the uncertainties in the observed values (as discussed above). The average ANC uncertainty width reported by Sullivan et al. (2002a) for the 164 calibrated SAMI sites was 15  $\mu\text{eq/L}$  in the year 2010.

There were errors introduced into the modeling effort as a consequence of not having soils data available for all of the MAGIC modeling sites. For Tier II sites, soils data were borrowed from a nearby Tier I site located on the same geology. For Tier III sites, soils data were borrowed from the Tier I site judged to be most comparable with respect to streamwater ANC (an integrator of watershed soils conditions), geologic sensitivity class, location, elevation and streamwater sulfate concentration (an integrator of sulfur adsorption on soils). The error associated with needing to borrow soils data for Tier II and Tier III sites was quantified by calibrating selected Tier I watersheds twice, once using the appropriate site-specific soils data, and a second time using borrowed soils data from an alternate site, using either Tier II or Tier III protocols. Multiple Emissions Controls Strategies were then simulated for each of the two calibrations at each site. The results showed generally good agreement between model projections of streamwater ANC using measured versus borrowed soils data. Errors were generally less than about 10  $\mu\text{eq/L}$ . The RMSE of the observed differences between model projections based on site-specific versus borrowed soils data was 3.9  $\mu\text{eq/L}$  for Tier II protocol applications, based on four sites and seven simulated ANC values at each site. Similarly, the RMSE was 2.9 for Tier III protocol applications, based on seven sites and seven simulated ANC values at each site.