Black Rock Forest:
an examination of chloride and sulfate

Barbara Kantzos
Barnard College, Columbia University

Black Rock Forest:
an examination of chloride and sulfate

Barbara Kantzos
Barnard College, Columbia University
May 11, 1995

Abstract: A dataset of chloride concentrations from analyses of water samples in the Black Rock Forest, New York watershed for the year 1994 in conjunction with other available data were used to calculate an estimate of the dry to wet deposition ratio of chloride aerosols. The drainage area consists of four brooks including Black Rock Brook, Canterbury Brook, Cascade Brook, and Mineral Springs Brook. Excluding extremes, all of the Brooks had very similar average annual values of chloride concentration of slightly above 2 ppm. Early in the 1994 year, anomalous high concentrations of chloride were found in the Black Rock Brook with values as high as 27 ppm. It is most likely a result of road salting from a nearby highway. Chloride concentrations rise in early October in Canterbury, Cascade and Mineral Springs brooks.

The maximum sulfate value is 13.95 ppm in February. The minimum is 7.15 ppm in August and the average sulfate value is 9.80 ppm for 1994. Sulfate is generally high values in the early wintertime months and drops in concentration in March. Sulfate rises again in October and ends the year at almost 10 ppm. Sulfate seems to follow the trend in chloride exhibited in Canterbury, Cascade, and Mineral Springs Brook.

These data which are the result of the author's own analysis, were manipulated in several ways to estimate the dry to wet deposition ratio. Only limited runoff data were available for the area in 1994. Thus, estimates of runoff were also made. When using the best estimate of runoff 12 year precipitation means from West Point, a dry:wet deposition ratio of 2.39 was calculated for chloride.

Quantifying dry deposition is an important step in understanding the factors affecting the biogeochemistry of an ecosystem. This better understanding of chloride deposition will provide insights about the impact of dry deposition on the forest canopy and also about the increases in dissolved ion concentrations in surface waters above that delivered in precipitation due to evaporation and transpiration losses of water vapor to the atmosphere.

Table of Contents

List of Figures

List of Tables

I. Introduction

Background

One of the reasons it is difficult to make assessments about the impact of human activities is the lack of information about the numerous inputs and outputs of an ecosystem. The dry deposition process in which gases and atmospheric particles are deposited in the absence of precipitation, potentially has a large impact on the biogeochemistry of an ecosystem because of the interaction between the forest canopy and the dry deposition which may include beneficial nutrients or harmful pollutants. However, dry deposition has been extremely difficult to measure or quantify (Hicks *et al.* 1986). Attempts have been made using various methods such as needle washing of native pines in the Emerald Lake Watershed in California (Blanchard, C.L. 1988), or using a micrometeorological approach where the fluxes of gases and particles are related to heat and momentum transfer (Droppo, 1985; Neumann and den Hartog, 1985); gradient methods where the concentration of a substance is measured at different heights (Davis and Wright, 1985), the use of surrogate surfaces (Davidson *et al.* 1985), and high frequency eddy correlation methods, models coupled to ambient air data (Hicks and Matt, 1988). However, it is possible to derive an estimate of the dry deposition of a nonreactive ion such as chloride using mass balance data, if the conditions are suitable. Within a small watershed underlain by impermeable bedrock there is negligible deep seepage and subsurface flow which are difficult or almost impossible to measure. Therefore, measuring inputs and outputs of water becomes simpler.

Most of the important chemical components of Black Rock Forest enter via wet or dry deposition. Most leave through the surface waters in solution or as suspended particles. Chloride is very soluble and very unreactive. It does not form important solute complexes and is not greatly adsorbed on mineral surfaces. It is not active in geochemical cycling and it has few vital biochemical functions (Hem 1970). Therefore, a basic assumption is that what chloride enters the forest in wet and dry deposition will exit

the forest in streamflow (Cleaves *et. al* 1974). Recent data however, indicates that the assumption that chloride is an inert tracer may be erroneous. Chloride may be involved in the biological cycle more so than previously thought (Peters 1991).

Dry deposition rates can be estimated using a 12 year mean chloride concentration from West Point precipitation as a representative of the average delivery of chloride to nearby Black Rock Forest. Subtracting this figure, representative of wet deposition only, from surface water data which includes wet and dry deposition, will yield an estimate of the dry deposition of chloride. By studying a healthy forested watershed, the effects of deforestation, water management or other types of human disturbances on an ecosystem can be better understood.

Possible Sources of Chloride and Sulfate

Sources of chloride in river water include several possibilities. Chloride can come from sea salt, hydrogen chloride (HCl) from precipitation produced by reactions with sea salt or possibly arising from magmatic gases or industrial sources. Dissolution during weathering of halite evaporites or halite in dispersed shales, thermal or mineral springs in volcanic areas and the redissolution of saline crusts in desert basins are possible sources as well. Pollution arising from domestic or industrial sewage, oil well brines, mining and road salt are also possible sources (Feth 1981). The probable inputs at Black Rock Forest of chloride are sea salt in precipitation, possibly chloride of pollutive origin in rain and road salt.

Sources of sulfate in river water also include several possibilities. Sulfate can come from rock weathering. It can also come from natural biogenically derived sulfate in rain, as well as sulfate of pollutive origin in rain. A very small fraction can come from cyclic salt and sometimes, a small fraction comes from volcanic activity (Berner and Berner 1987). At Black Rock Forest, the sources of sulfate include rain, and possibly rock weathering. Sulfate, however, is not unreactive like chloride. Therefore, deriving an

estimate of the dry deposition is much more complex for sulfate and cannot be done here. Note that the origin of chloride is unimportant in estimating the dry deposition (unless it came from a mineral source such as NaCl evaporites, which would alter assumptions about the chloride budget) and an exact determination of sulfate sources is not necessary to make comparisons of precipitation concentrations and streamflow concentrations, which is the objective here. However, especially in the case of sulfate, the origin is of particular significance when considering the impact of anthropogenic pollution; namely the burning of fossil fuels causing the production of sulfur dioxide gas which contributes considerably to acid rain.

Geographic Setting

Black Rock Forest

The Black Rock Forest is a 3700 acre natural area in the Hudson Highlands. Located in Cornwall, New York, Black Rock Forest was originally established as a facility for forest management research in 1928, and was acquired from Harvard University in 1989 by the Black Rock Forest Preserve. The area has been set aside as a natural area with a wide diversity of habitats, ranging from young to mature forests, both deciduous and coniferous, to numerous ponds, natural wetlands, and streams.

Black Rock Forest is situated on the western banks of the Hudson River at approximately 41.5 N and 74 W in Orange County New York. New York City is approximately 45 miles to the south. (see figures 1and 2)

Figure 1: Black Rock Forest Index Map

Black Rock Forest
Index Map

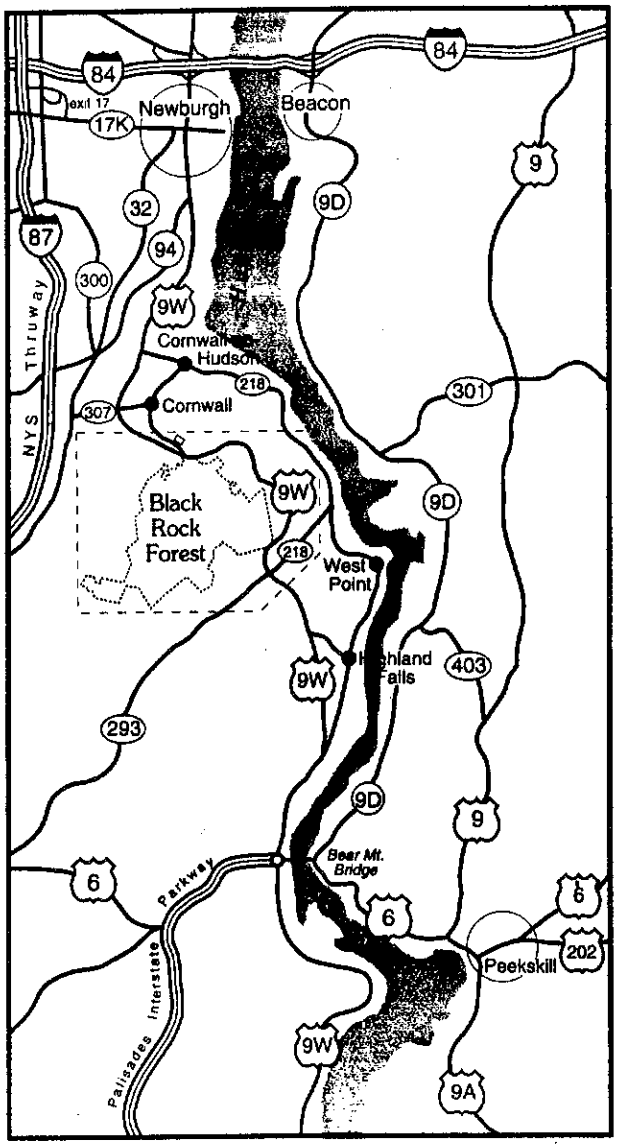
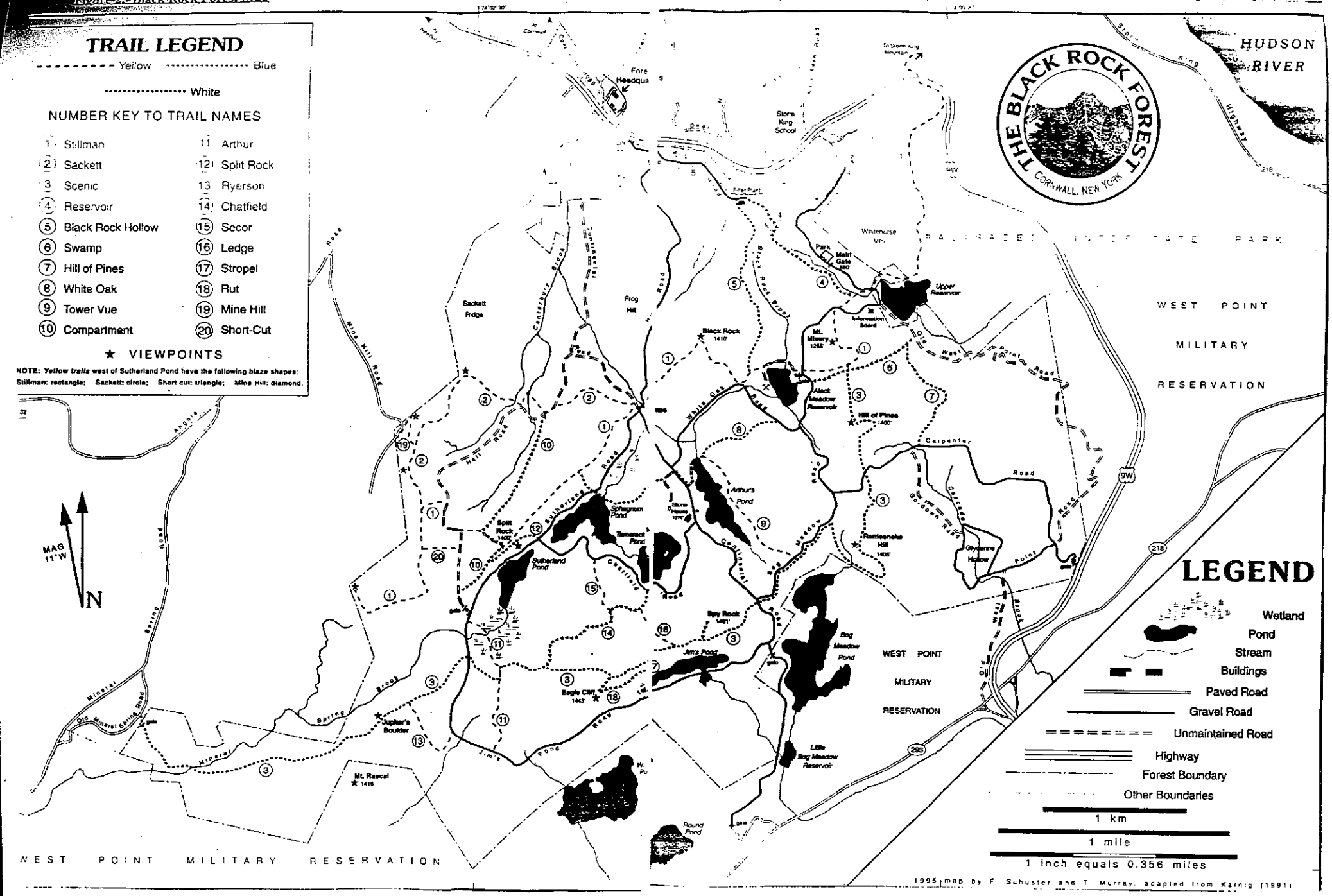


Figure 2: Black Rock Forest Map



Catchments

The Forest contains several watersheds, but this study focused on Black Rock Brook, Canterbury Brook, Cascade Brook, and the Mineral Springs Brook watersheds. Some of the water from Black Rock Forest provides the drinking water supply for Cornwall New York and is collected in reservoirs. The following areas are approximations due to map error, etc..

Black Rock Brook

Black Rock Brook flows out of Black Rock Forest to the north and is 299 hectares of contributory catchment area above the sampling point at Aleck Meadow Reservoir. However, about 5% of this is lost to Canterbury Brook through the Tamarack and Sphagnum Pond, making the total area contribution to the Black Rock Brook watershed approximately 294 hectares.

The headwaters of the watershed are comprised of several areas. The Upper Pond accounts for 108 hectares of the watershed. The Arthur's Pond outflow accounts for 65 hectares, while the Sanctuary outflow accounts for 18 hectares. Birch Spring constitutes 27 hectares, Swamp Trail which is not part of the Aleck Meadow Reservoir accounts for 20 hectares, and the Upper Reservoir Headwaters, for 93 hectares. The Deer Hill Brook constitutes 98 hectares of contributory area, and the Frog Rock watershed contributes its share from 32 hectares.

The Lower waters are made up of the Upper Collection, 23 hectares, the Lower Collection, 25 hectares, and an additional 13 hectares including the Aleck Meadow Reservoir itself, which is not included in the above watersheds. Not contributory to the Aleck Meadow Reservoir is Lower Aleck Meadow, 53 hectares, the Upper Reservoir, 62 hectares, and the Lower Upper Reservoir which accounts for 45 hectares. The area has a northern aspect and is managed heavily. There are several conifer plantations and early successional deciduous woods within the area, except for about 20 hectares of pure *Tsuga*

canadensis at the base of the watershed. There are four 8 hectare ponds and one 4 hectare open wetland. It is also important to note that a highway crosses Black Rock Brook allowing for potential inputs of contamination such as road salt. None of the other 3 brooks are affected by potential road inputs.

Canterbury Brook

Canterbury Brook flows out of Black Rock Forest to the north also, and is fed by 261 hectares above the sampling point. An additional 108 hectares drains partially into Canterbury Brook through a pipe in a diversion dam from Tamarack and Sphagnum Pond. The percentage of flow from this area is between 1% and 10% of the total volume and therefore, another 5 hectares contributes to the area feeding Canterbury Brook, resulting in a total of 266 hectares above the sampling point.

The headwaters of the Canterbury Brook are the broken down into a few separate areas. There is the West Branch, the West Fork, and Canterbury Brook which comprise 48 hectares. The East Branch, the West Fork, and Canterbury Brook comprise 65 hectares. Finally, the Upper Ponds are 108 hectares, but only an estimated 5% of flow contribution.

The Lower waters are comprised of several areas. The Lower West Fork and Canterbury Brook are 48 hectares, while the Lower East Fork, and Canterbury Brook are 45 hectares. The Lower section 2 and Canterbury Brook are 23 hectares and Lower section 1 and Canterbury Brook are 41 hectares.

The Canterbury Brook watershed has been largely undisturbed for the past 100 years and is composed of a diverse tree community. The area contains no ponds or wetlands and there is a significant component of *Tsuga canadensis*. However, it is not a pure stand. This area has deep glacial till in the lower reaches.

Cascade Brook

Cascade Brook has 135 hectares contributing to its waters above the sampling point. The headwaters are the Upper Cascade Brook, 65 hectares and the Lower waters are the Middle Cascade Brook with a contributing area of 70 hectares. Cascade Brook flows out of Black Rock Forest.

It has a southern aspect and has remained little affected for the past 70 years. The vegetation is 100% deciduous canopy made up of 80% *Quercus* species. There are no ponds and one 8 hectare wooded wetland in the bottom of the basin.

Mineral Springs Brook

The Mineral Springs Brook flows out of Black Rock Forest to the southwest. This watershed consists of 309 hectares above the sampling point. The headwaters consist of the Upper Sutherland Pond and the Northern Mineral Spring, each area accounting for 34 and 45 hectares, respectively. The Lower waters consist of Lower Sutherland Swamp, 60 hectares, and Mineral Springs and Lower (section 2), 87 hectares, and Mineral Springs and Lower (section 1), 83 hectares.

The area has a southern aspect, and the Upper Sutherland Swamp and the Lower Sutherland Swamp also have been relatively unaffected in the past 70 years. There is a 100% deciduous canopy, except for 12 hectares of pure *Tsuga Canadensis* at the base of the watershed. There is one 8 hectare pond and one 8 hectare open wetland. (see figure 3) The Black Rock Forest Preserve varies in elevation from feet to feet. Black Rock Forest is primarily crystalline bedrock overlain with glacial till of varying depths.

II. Methods

There are a variety of techniques used to determine the dry deposition of aerosols. A hydrologic mass-balance technique was used here. Data from several sources were used to to take this approach, including West Point precipitation data, Albany evaporation pan data, Black Rock Forest streamflow data, and Black Rock Forest stream chemistry (the latter from the author's own analysis). Also, precipitation data in Black Rock Forest was also used to compare the 12 year West Point precipitation mean with 1994 data.

A mass-balance approach requires several conditions:

1) a conservative ion within the watershed
2) negligible deep seepage and subsurface flow
3) groundwater storage in equilibrium
4) negligible input from weathering or other sources

i.e. only inputs are wet and dry deposition of aerosols

5) long term data

For chloride, conditions 1, 2, and 4 are met. It can be assumed that on a long term basis, groundwater storage is in equilibrium. However, for small catchment groundwater storage can vary on the short term. Condition 3 is a necessary assumption in this case. High quality precipitation chemistry and depth data are available from West Point, New York. The data represent 144 months or twelve years. The evaporation pan data is long term monthly means from Albany, New York. West Point is close to Black Rock Forest and is a good representative of chloride delivery to the watersheds under study. However, Albany data may not be an accurate representative of evapotranspiration in the Black Rock Forest due to catchment physiography (elevation, slope, aspect), distance, and possible differences in topography, vegetation, etc.. Also, transpiration is not included in

the evaporation data. Although several methods have been used to estimate evapotrapsiration from meteorological factors such as solar radiation, temperature, relative humidity, wind speed and surface wetness, there are errors associated with these types of computations and these computations are not possible with the data available. Typically, estimates derived in this manner are larger than those associated with the determination of evapotranspiration from water balance. However, neither are error-free (Lee 1970). In this case, however, precipitation and evaporation must be used here to estimate flow. Here it must be assumed that evaporation in Albany is representative of evapotranspiration in Black Rock Forest. Also, if long term streamflow data were available, then the streamflow derived from Precipitation- Evapotranspiration could be checked, and more accurate estimates could be made.

In order to calculate the dry deposition, streamflow estimates must be made. As mentioned, one method used involved Q=P-ET. All precipitation and evaporation data were converted to meters. The difference between the precipitation and evaporation were calculated. The resulting runoff was then multiplied by the total area of the 4 catchments. In the determination of the dry deposition a weighted chloride average was used.

Another method used as a comparison is based on the known streamflow data from Black Rock Forest. Streamflow measurements for Canterbury and Cascade Brooks were available for March 1994- March 1995. However, the method used to measure streamflow is quite crude and in small catchments such as these, the response times of streamflow can be very rapid. The flows were measured at regular weekly intervals and may not be a accurate representative of the actual flow. The data available for streamflow in Black Rock Forest consists of weekly instantaneous flow obtained from a surface velocity reading then multiplied by the cross-sectional area of the stream at the gauging point. Then this figure must be multiplied by .85 because the velocity measurement is surface velocity, which is typically faster than the average velocity of the cross-sectional profile (personal communication with Bill Schuster). The flow each week was calculated

as the average of that week and the previous week. Then it was assumed that this average was representative of the entire week. Next, the obtained value was multiplied by the appropriate conversion factor (i.e. x 86400 for m3/day etc.). Finally, the flow for Black Rock Brook and Mineral Springs Brook were estimated using catchment area proportions. For weeks where flow was available for both brooks, the value of the flow in each of the other two brooks was calculated as the fraction of the sum of the Canterbury and Cascade Brooks flows. When only one stream had available data, the flow was calculated as a fraction of the area of the known flow. Also, another estimate of streamflow was made based on the flow ratio from Canterbury: Cascade Brook on a monthly basis. The flows were calculated as for above, but then the values were multiplied by the monthly flow ratio of Canterbury flow to Cascade flow. Following is a table of the area of the 4 catchments.

Table 1: Catchment Area in Black Rock Forest

Catchment	AREA cm2	m2	acres	hectares	%
Black Rock Brook	2.94E+10	2940000	727	294	29.3
Canterbury Brook	2.66E+10	2660000	657	266	26.5
Cascade Brook	1.35E+10	1350000	334	135	13.5
Mineral Springs Brook	3.09E+10	3090000	763	309	30.7
total area	1E+11	10040000	2481	1004	100

Chloride export can be calculated for the entire area under study by:

1) estimating Streamflow

a) Streamflow = Precipitation - Evapotranspiration (evaporation only here)

b) Streamflow = Black Rock Brook Streamflow + Canterbury Brook Streamflow + Cascade Brook Streamflow + Mineral Springs Brook Streamflow

2) Total Deposition = Streamflow x [Cl-] = Surface Outflow of Chloride

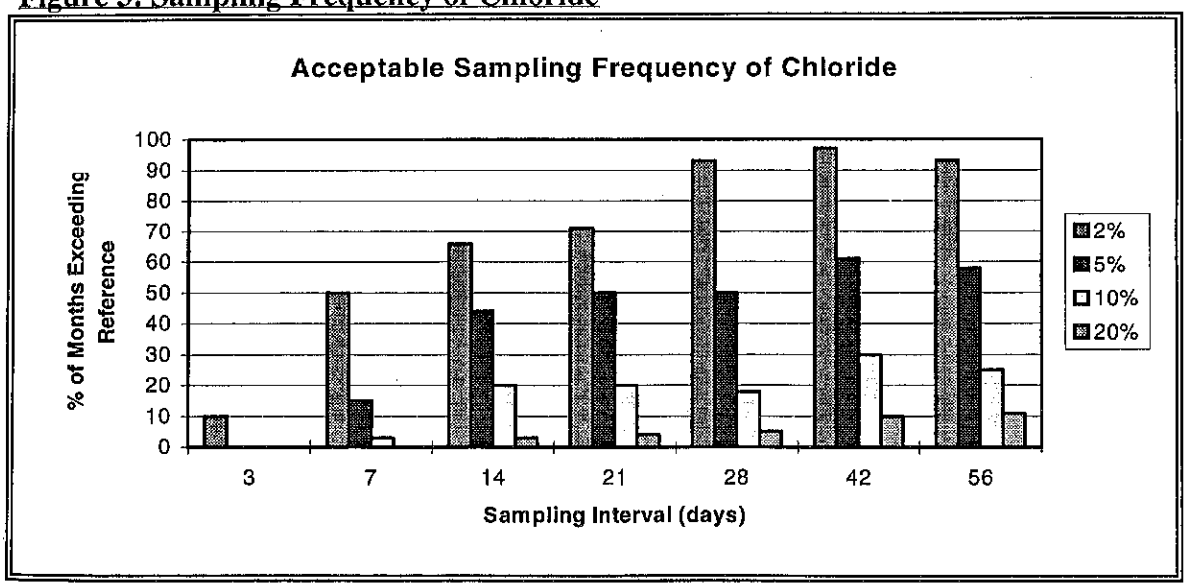
3) Wet Deposition = Precipitation x [Cl-] x Area = Precipitation Input of Chloride

4) Dry Deposition = Total Deposition - Wet Deposition

Sampling Frequency

Since chemical concentrations are of primary concern in this study, the accuracy of the mass fluxes that are calculated must be considered. Clair and Freedman (1986) and Freedman and Clair (1987) collected data for stream chemistry and hydrology on a daily basis in the Mersey River catchment in southern Nova Scotia from July 1980- June 1982. These data were used to illustrate an evaluation of sampling frequency for mass flux determinations. Using the optimal procedure of Schneider *et al.* (1979) artificial sampling frequencies of 1, 3, 7, 14, 21, 28, 42, and 56 days were used to calculate monthly and annual yields. The effectiveness of sampling frequencies was determined using a one day sampling frequency as a baseline.

Figure 3: Sampling Frequency of Chloride



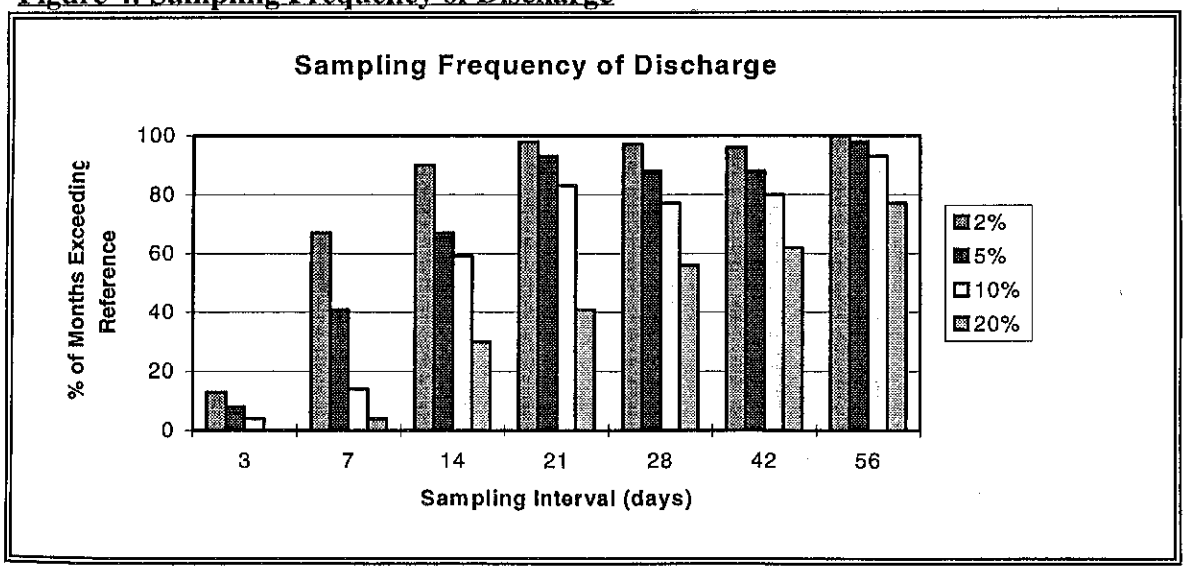
based on Clair and Freedman (1986) and Freedman and Clair (1987)

The categories are 2%, 5%, 10%, and 20%. If a researcher is willing to accept a 20% failure rate to reproduce monthly values within +/- 10% of the baseline levels, then a sampling frequency of 7-14 days is acceptable for chloride.

Pomeroy and Orlob (1976) related sampling frequency to catchment size. For catchments under 26 km2, collection twice weekly is required. Weekly sampling is justified for streams with max:min flow ratios less than 100.

Discharge is typically derived from continuous or frequent records of water level or stage and periodic determinations of discharge. The frequency of measurements generally used in catchments of 1-10 km2 in area is 15 minutes, but more frequent measurements may be needed for better accuracy since small catchments typically have a rapid response to flow changes (Rantz 1982). Accurate measurements of discharge are important because annual fluxes of elements from catchments relate directly to discharge (Johnson *et al.,* 1968). Clair and Freedman applied the same approach to sampling frequency to discharge. Notice that sampling must be done more frequently to achieve the same accuracy of results for chloride.

Figure 4: Sampling Frequency of Discharge



based on Clair and Freedman (1986) and Freedman and Clair (1987)

II. Results

Chloride

Black Rock Brook note that ppm=mg/L

Chloride concentrations were high in January averaging 16.12 ppm (figure 5). In February, the samples taken for the last two weeks were lost. The first two weeks data are the highest analyzed at 22.65 for February 2nd and 27.63 for February 9th. March is also missing a sample for the second week, but the average drops down to within a range more representative of the values found throughout the rest of the year and for the three other brooks for the entire year. The average for March is 2.70 ppm and in April the concentration drops down to 2 ppm. For the rest of the year chloride concentrations remain at approximately 2 ppm. The average annual concentration of chloride in Black Rock Brook is 4.03 ppm including the high values from the start of the year. Without those values the average is brought down to 1.93 ppm (figure 6). These high values are attributed to road salting and occur only in Black Rock Brook. No road salting affects the other 3 brooks.

Please note that the water year-October-September is typical for northern temperate forests. The beginning of the water year is generally defined as the time when the variation in storage between years is at a minimum. Since I do not have any knowledge of the water storage in Black Rock Forest and the available data run from January-December, results will not be presented as the water year.

Figure 5: Black Rock Brook Chloride in 1994

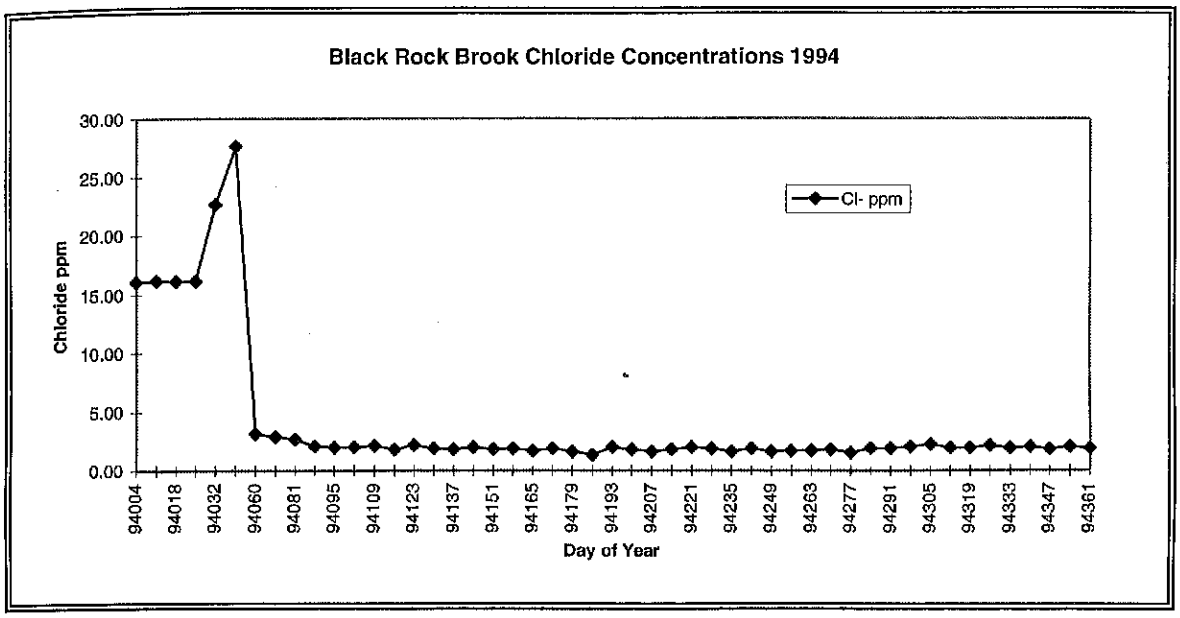
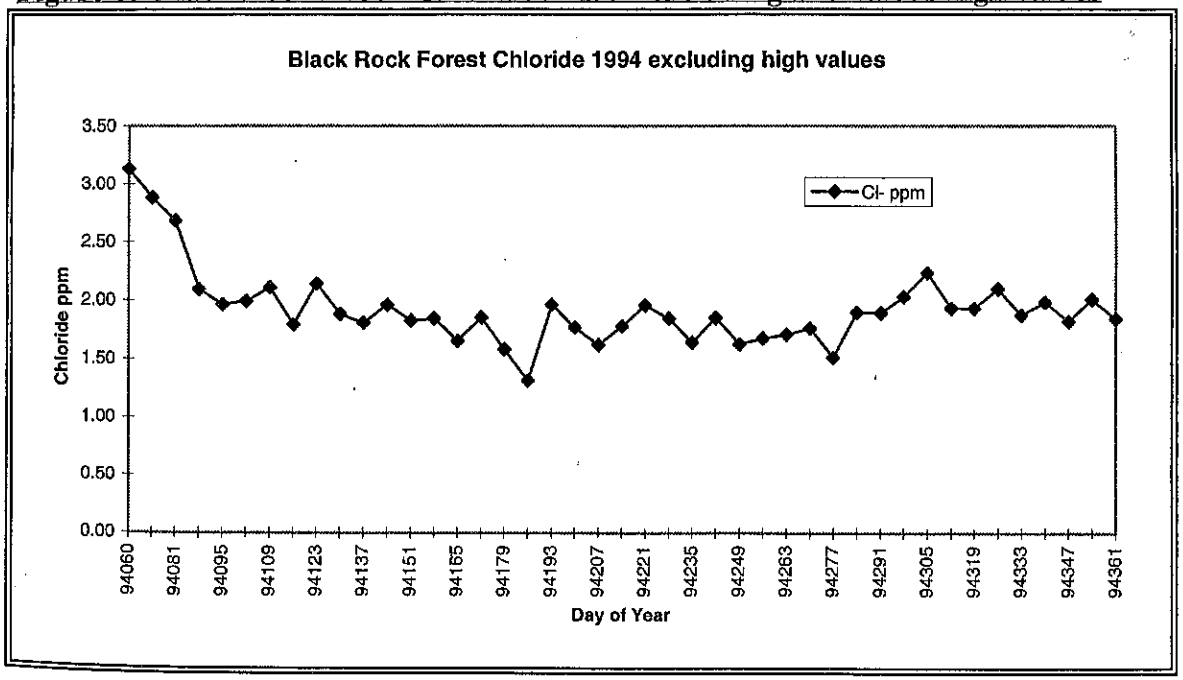


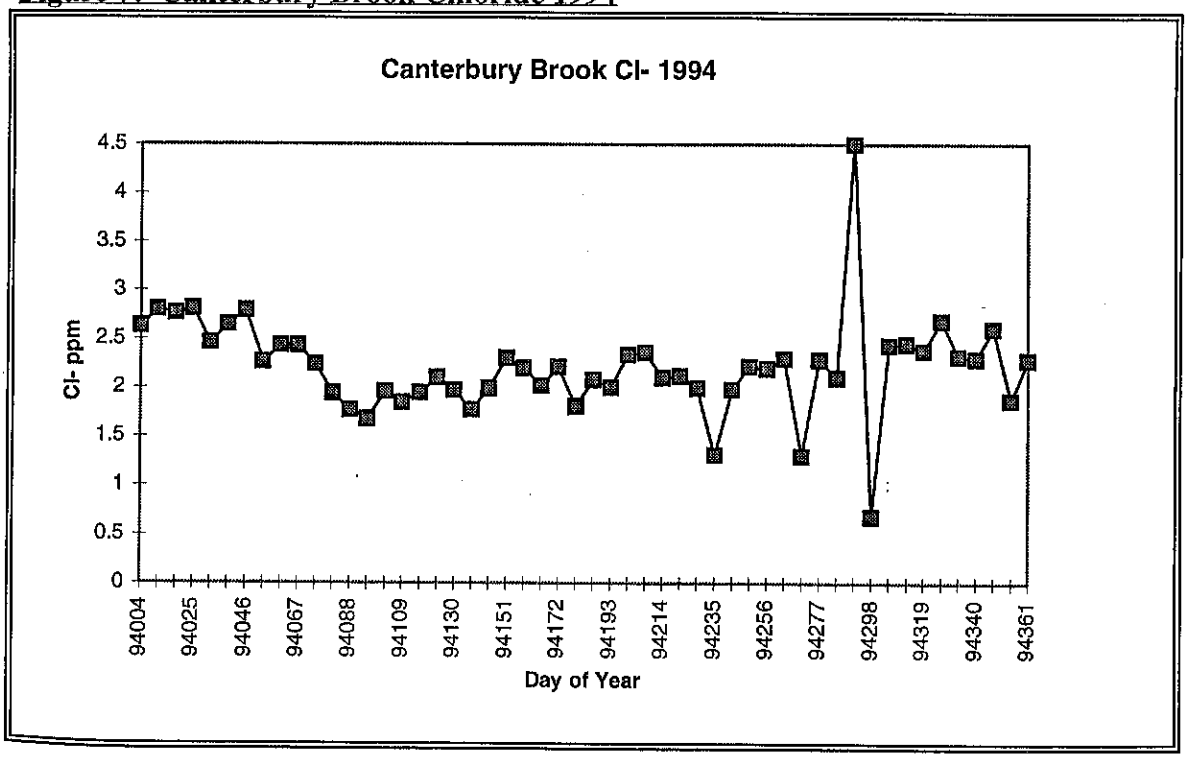
Figure 6: Black Rock Brook Chloride in 1994 excluding anomalous high values



Canterbury Brook

Canterbury Brook averages 2.75 ppm in January of 1994. February and March values are only slightly lower with an average of 2.54 ppm and 2.16 ppm respectively. the decline stops in April at 1.86 ppm and picks up again to 2 ppm and stays within .1 ppm until October when the average monthly value rises to 2.48 ppm Cl-. November concentrations at 2.45 are similar to October and the year ends in December with an average monthly concentration of 2.22 ppm. August 22nd, the last week in September and October 19 have concentrations of 1.31, 1.30 and .69 ppm respectively with standard deviation of replicate tests being under .15 for all three of these samples. The week of October 12 had an unuaually high chloride concentration of 4.5 ppm. This is the highest concentration seen in the samples excluding those to road salting in Black Rock Brook. The annual average concentration for Canterbury Brook is 2.22 ppm.

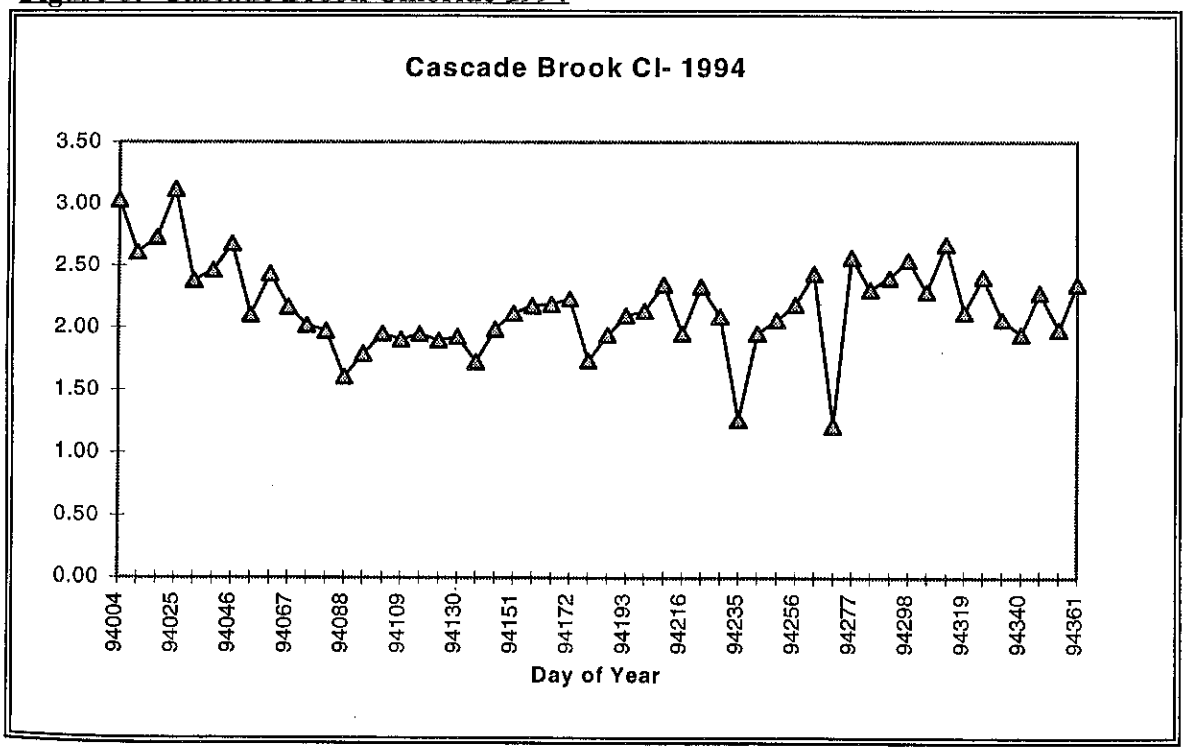
Figure 7: Canterbury Brook Chloride 1994



Cascade Brook

Cascade Brook begins 1994 with a monthly average chloride concentration of 2.87 ppm. February values drop to 2.40 ppm and values continue to drop slightly to about 2 ppm where they hover around until October, which sees an increase in average monthly chloride concentration to 2.45 ppm with November at 2.51 ppm and December ending 1994 with an average monthly concentration of 2.14 ppm. August 22nd had a low concentration of 1.26 ppm with a standard deviation of replicate tests of .09. In the last week of September, the stream chloride concentration was 1.21 ppm +/ .05. This is consistent with the low values in Canterbury Brook during those weeks. The annual average for Cascade Brook is 2.19 ppm.

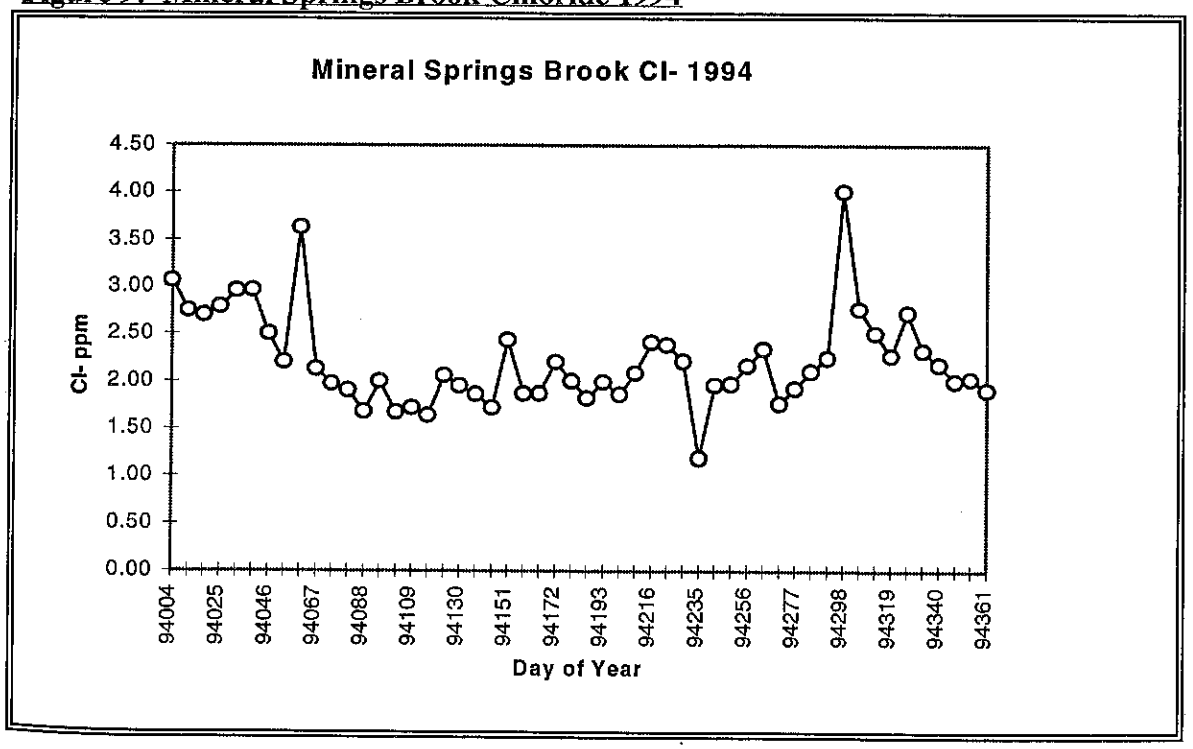
Figure 8: Cascade Brook Chloride 1994



Mineral Springs Brook

Mineral Springs Brook has a monthly average chloride concentration close to 3 ppm like Canterbury Brook. February has a monthly average of 2.66 and the monthly values decline to 1.76 ppm in April. Monthly averages from My until September remain very close to 2 ppm and in October, the average monthly chloride concentration rises to 2.61 ppm. The November value is 2.52 ppm and in December, the monthly average was 2.03 ppm. August 22nd and September 25th have concentrations of 1.19 +/- .15 and 1.77 +/- .03 ppm respectively. This occurs in Canterbury and Cascade Brooks for the same weeks. Although the September concentration of 1.77 ppm is not as low as those for the other 2 brooks, it does represent a decline from the concentrations in the previous weeks which had concentrations over 2 ppm. The average annual chloride concentration in Mineral Springs Brook was 2.23 ppm.

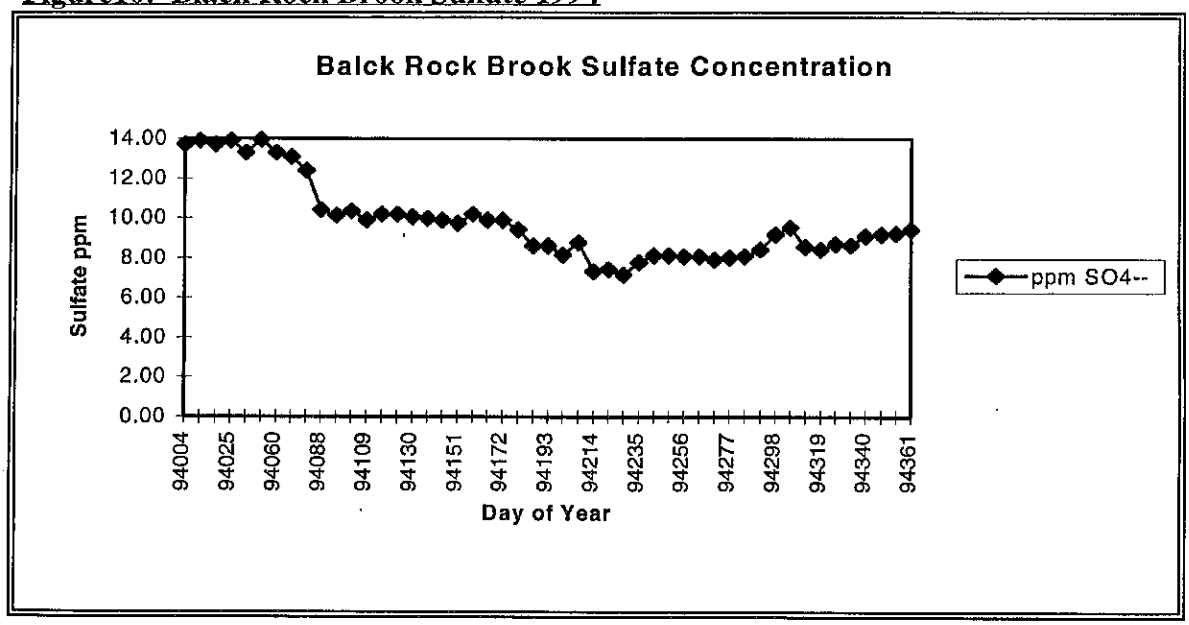
Figure 9: Mineral Springs Brook Chloride 1994



Sulfate

Sulfate values in Black Rock Brook also are highest at the beginning of 1994. In January, the average sulfate concentration is 13.8 ppm. In February the average drops negligibly to 13.63, but because the same samples were analyzed for both anions, there are two February data points missing for sulfate as well as for chloride. March begins the decreasing trend in sulfate concentrations from around 12 ppm to 8 ppm in July. The sulfate concentrations then hover around 8 ppm until October when they begin to rise slightly, ending the year with a concentration of 9.41 ppm in December.

Figure10: Black Rock Brook Sulfate 1994



Sulfate and Chloride

Chloride has a wider range of values in Black Rock Brook in 1994 than sulfate. However, excluding the high values attributed to road salt in January and February, sulfate has a wider range. The maximum value of chloride is 27.63 ppm if the highs are included. Without the highs, the maximum value is 3.13. The minimum chloride value is 1.31 ppm in July. Without the highs, the range is 1.31-3.13 ppm or 1.82 ppm. The maximum sulfate value is 13.95 ppm in February. The minimum is 7.15 ppm in August. The range of sulfate is 7.15-13.95 ppm or 6.8 ppm. The average chloride values are 4.03 ppm including the high values, but they drop down to 1.93 ppm if the highs are excluded as mentioned previously. The average sulfate value is 9.80 ppm for 1994. Both chloride and sulfate follow the general pattern of high values in the early wintertime months. These anions then drop in concentration in March. Whereas chloride tends to remain around 2 ppm from April throughout the rest of the year, sulfate rises again in October and ends the year at almost 10 ppm. Sulfate seems to follow the trend in chloride exhibited in the other 3 brooks, which have concentrations that also rise in October.

Figure 11: Black Rock Brook Chloride and Sulfate

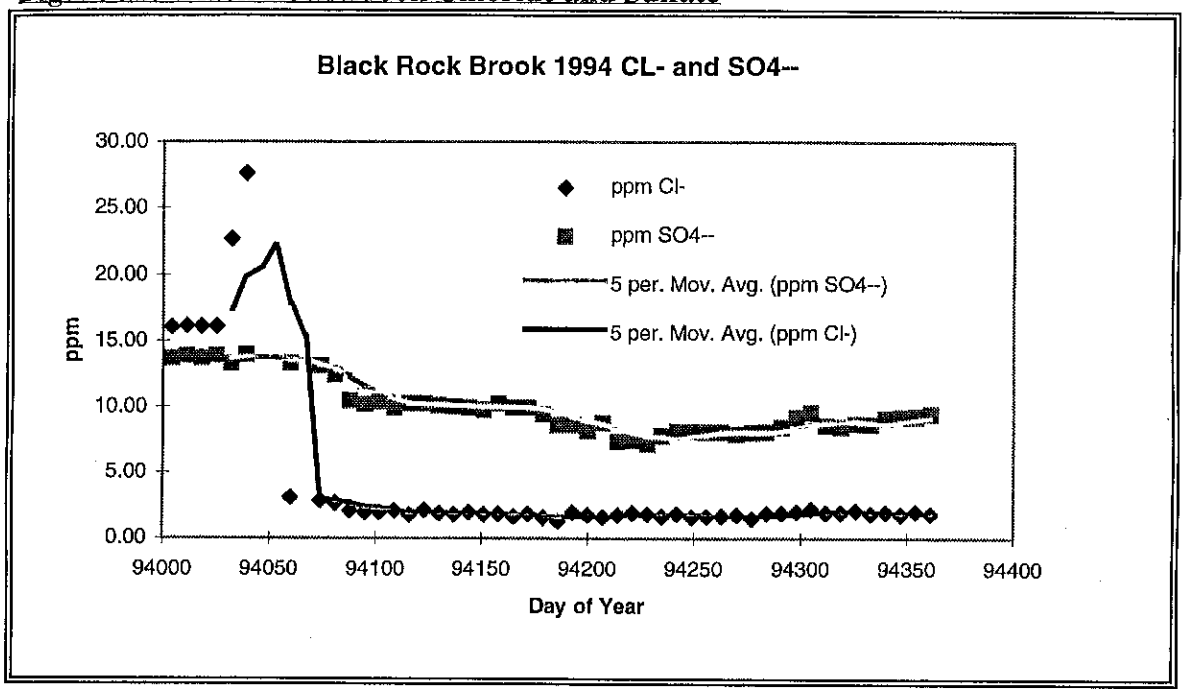
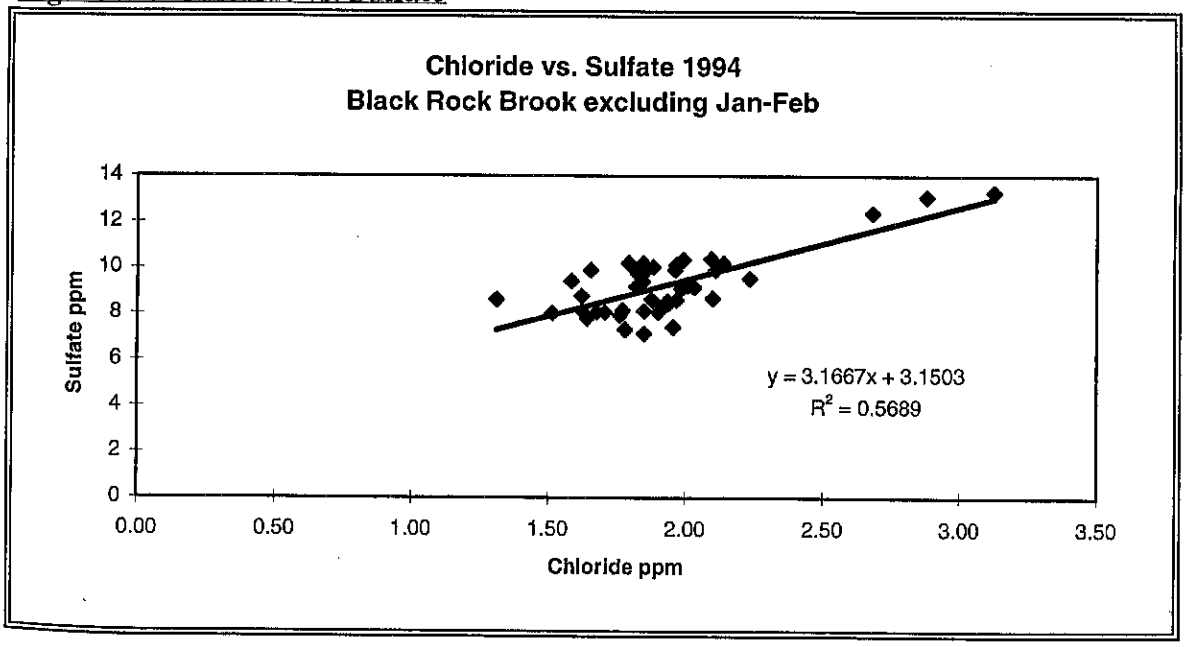


Figure 12: Chloride vs. Sulfate



Overall Trends

Canterbury Brook, Cascade Brook, and Mineral Springs Brook exhibit similar trends in chloride concentrations throughout the year with the year starting of slightly higher and making a slight and steady decline to about 2 ppm from early spring until autumn when the values increase slightly to end the year at about 2.5 ppm. All 3 of these brooks have concentrations of chloride lower than average during the weeks of August 22nd and September 25th. During October, Canterbuty and Mineral Springs brooks had high concentrations of chloride around 4 ppm followed by a subsequent decline in concentration in Canterbury brook only the following week to .69 ppm.

Black Rock Brook has unusually high values for January and February with monthly averages of 16.13 and 25.14 respectively. Then values for the rest of the remain close to 2 ppm without the slight increase in concentrations at the end of the year that the other three brooks experienced.

All of the Brooks had very similar average annual values except for Black Rock Brook. However, when the high concentrations measured early in the year were excluded, the average value for Black Rock Brook dropped to 1.93 ppm, much closer to the average annual chloride found in Canterbury Brook, 2.22 ppm, Cascade Brook, 2.19 ppm, and Mineral Springs Brook at 2.23 ppm.

Figure 13: Monthly Chloride Averages for 4 Black Rock Forest Brooks

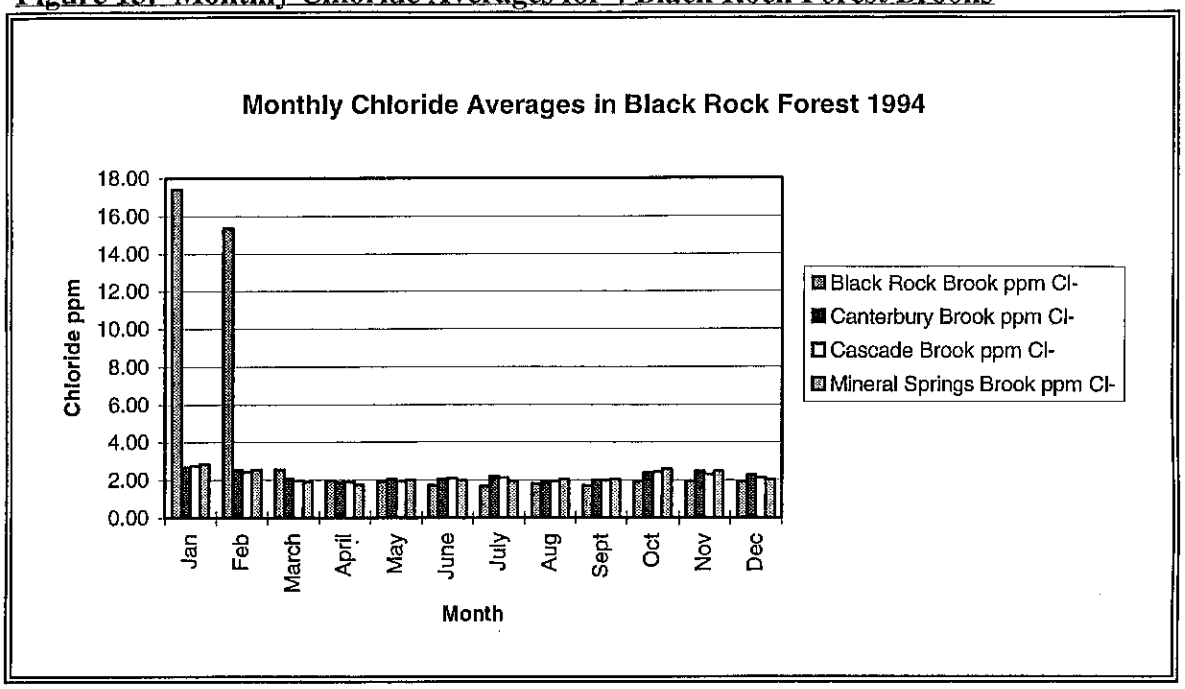


Table 2: Summary of Monthly chloride concentrations in Black Rock Forest- 1994

Month	Black Rock Brook ppm Cl-	stdev *	Canterbury Brook ppm Cl-	stdev *	Cascade Brook ppm Cl-	stdev *	Mineral Springs Brook ppm Cl-	stdev *
Jan	17.42	2.92	2.69	0.15	2.77	0.30	2.85	0.15
Feb	15.38	17.33	2.53	0.23	2.42	0.24	2.56	0.32
March	2.55	0.41	2.09	0.30	1.94	0.24	1.92	0.19
April	1.97	0.13	1.86	0.13	1.90	0.08	1.76	0.16
May	1.92	0.13	2.03	0.19	1.93	0.14	2.01	0.27
June	1.74	0.14	2.06	0.19	2.08	0.23	1.99	0.16
July	1.67	0.28	2.20	0.18	2.13	0.17	1.94	0.12
Aug	1.81	0.12	1.90	0.34	1.92	0.40	2.03	0.50
Sept	1.69	0.06	2.00	0.47	1.97	0.53	2.06	0.25
Oct	1.91	0.26	2.40	1.36	2.42	0.13	2.61	0.84
Nov	1.96	0.10	2.46	0.16	2.32	0.28	2.46	0.21
Dec	1.91	0.10	2.26	0.30	2.14	0.21	2.03	0.11
annual average	4.03	2.21		2.17		2.22		
stdev	5.92		0.51		0.36		0.50	
w/o highs	1.93							
	0.33							

* stdev's of replicate sample tests

Figure 14: Weekly Chloride Concentrations in Black Rock Forest 1994

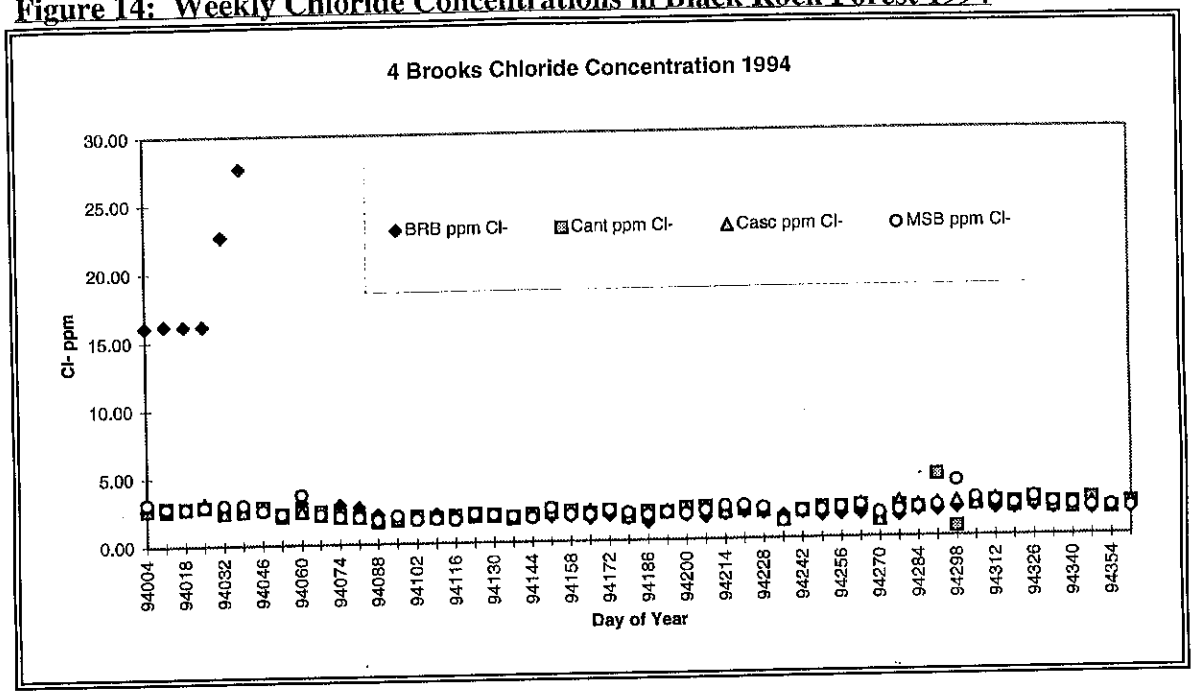
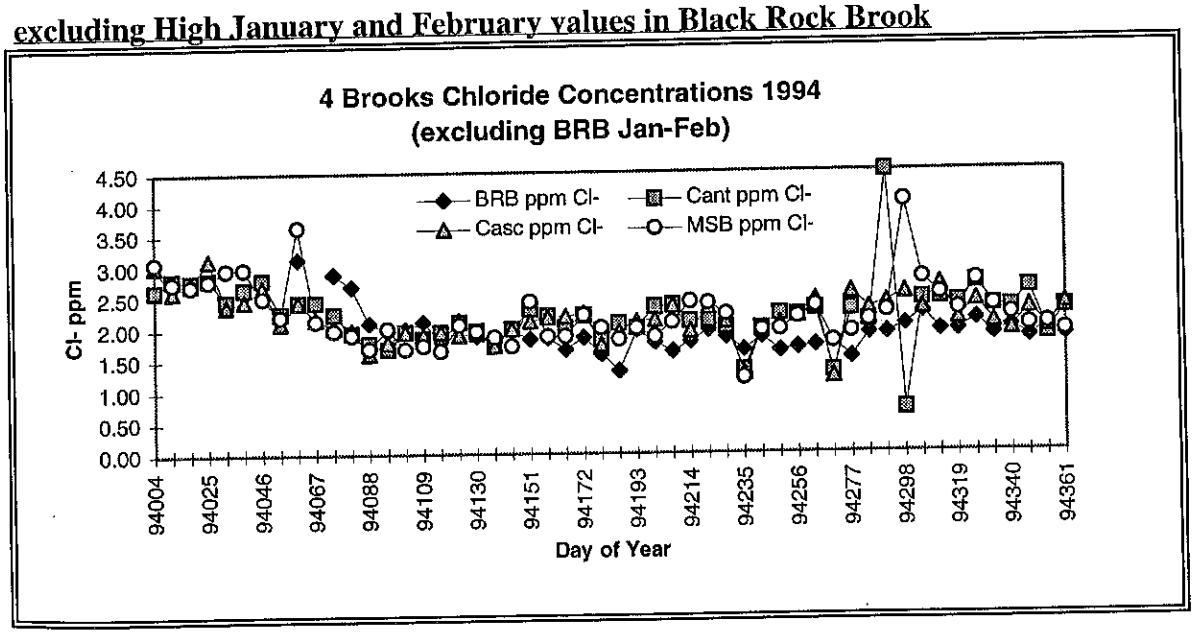


Figure 15: Weekly Chloride Concentrations in Black Rock Forest 1994 excluding High January and February values in Black Rock Brook



Analytical Quality of Chemistry Data

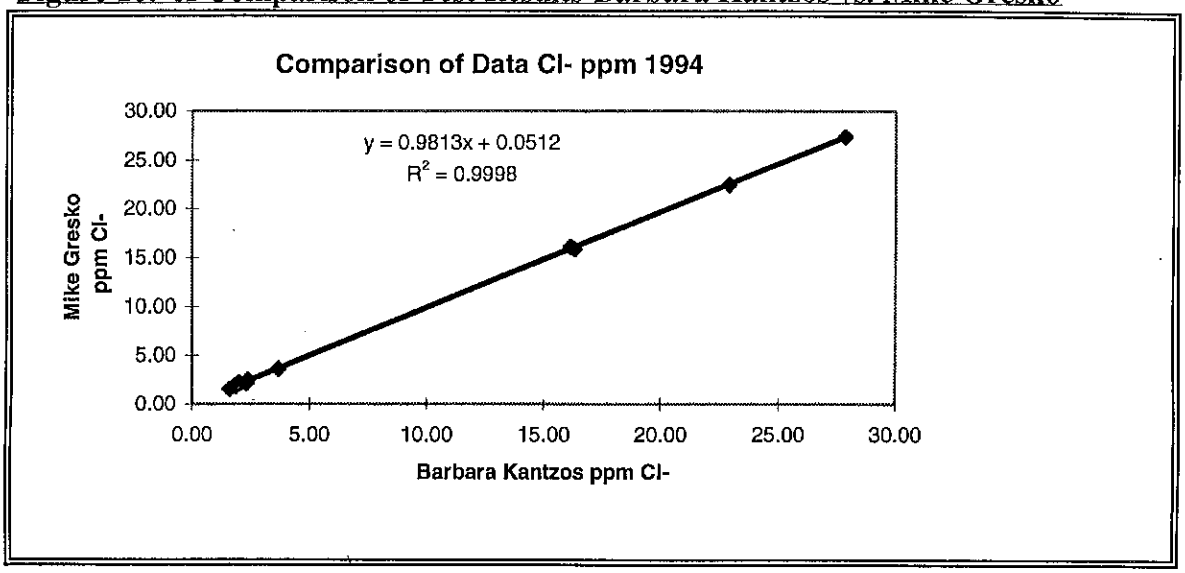
Samples from January until July were tested by my predecessor on this project, Michael Gresko. Several of the sample values were questionable not because of any suspect in measurement, but because the values seemed unusually high. These were retested by myself along with other values that did not fall within the 1-3 ppm range. Those values that were tested by two different technicians agree quite nicely.

Table 3: A Comparison of Test Results

Comparison of test results for chloride concentration in 4 Black Rock Forest Brooks					
	1994	Barbara Kantzos		Mike Gresko	
Sample	date	ppm Cl-	stdev *	ppm Cl-	stdev *
cant 09	94060	2.38	0.04	2.45	0.04
cant 18	94123	2.02	0.08	2.16	0.04
cant 27	94186	2.05	0.18	2.10	0.06
casc 18	94123	1.85	0.04	1.93	0.02
casc 27	94186	1.93	0.12	1.95	0.04
msb 09	94060	3.70	0.04	3.59	0.21
msb 18	94123	1.97	0.09	2.12	0.04
msb 27	94186	1.86	0.09	1.79	0.08
brb 01	94004	16.33	0.05	15.79	0.08
brb 02	94011	16.15	0.32	16.02	0.22
brb o3	94018	16.15	0.05	16.10	0.25
brb 04	94025	16.18	0.14	16.09	0.12
brb 05	94032	22.91	0.42	22.39	0.04
brb 06	94039	27.87	0.16	27.40	0.17
brb 18	94123	2.32	0.10	2.14	0.12
brb 27	94186	1.61	0.01	1.51	0.12

* of replicate sample tests

Figure 16: A Comparison of Test Results-Barbara Kantzos vs. Mike Gresko



Precipitation at West Point

The average annual monthly chloride concentrations in West Point precipitation have remained relatively stable over the past 12 years. There was a peak in 1981 of .75 mg/L, but otherwise the annual monthly mean concentrations hover around .5 mg/L. Values for chloride concentration in West Point precipitation exceed 1 mg/L in September of 1979 with a value of 1.27 mg/L, January, February, and March of 1982 with values of 1.82, 2.47, and 1.1 mg/L respectively. In 1983 and 1984 have values exceeding 1 in February and December and February and November respectively, but they do not exceed 1.6 mg/L. Values of chloride in precipitation do not exceed 1 again until November of 1990 when they reach 1.32 mg/L.

Sulfate in Black Rock Forest has a small range of annual monthly averages as well. From 1979-1980 the sulfate monthly average was 2.98 ppm. From 1981-1982 the annual monthly averages are 3.36 and 3.12 respectively. In 1983-1984 the annual monthly average drops to 2.10 and 2.03 respectively. In 1985 the monthly average is 2.44 ppm and jumps to above 3 in 1986 at 3.12 ppm. In 1988 the annual monthly average remains near 3 at 2.89 ppm and falls to 2.58 in 1989. In 1990 the sulfate monthly concentrations average 2.08 ppm and in 1991 and 1992 the annual monthly sulfate averages are 2.28 and 2.43 ppm respectively. The range of annual monthly sulfate averages from 1979-1992 is 2.03-3.36 ppm or 1.33 ppm.

The average monthly annual depth of precipitation in Black Rock Forest varies by several centimeters from 1980-1992. The monthly average for 1979-1980 is 11.19 centimeters. It declines in 1981-1982 to 9.26 and 8.58 cm respectively. The average jumps to 14.02 in 1983 and drops again in 1984 to 12.64 cm. The average declines to 8.8 cm in 1985 and rises in 1986 and 1987 to 9.72 and 11.04 cm respectively. The average drops to 9.51 cm in 1988 and rises to 10.49, 11.61, and 11.81 cm in 1989, 1990, and 1991 respectively before dropping to 10.23 cm in 1992.

There doesn't seem to be any direct correlation between the level of precipitation and chloride or sulfate concentrations. Neither is there an anticorrelation. Concentrations of chloride and sulfate are influenced by factors other than just the level of precipitation. If chloride concentrations and sulfate concentrations remained constant in the atmosphere, an anticorrelation would be expected. Higher levels of rainfall will dilute the chloride and sulfate. However, these ions are not present at constant concentrations. There are variable sources as explained in the introduction and the inputs from these sources fluctuate.

Note that the sulfate to chloride ratio averages 7.05 for the 12 years of data and the low is 4.32 while the high is 10.76.

Table 4: West Point Annual Precipitation Totals: 1979-1992

year	1980	1981	1982	1983	1984	1985	1986	1987	1988	1989	1990	1991	1992
Ppt-cm	134.3	111.1	103	168.2	151.7	105.6	116.6	132.4	114.1	125.8	139.3	141.8	122.8

max- 168.2 min- 103 average- 128.2 stdev- 19

Figure 17: West Point Precipitation annual totals 1979-1992

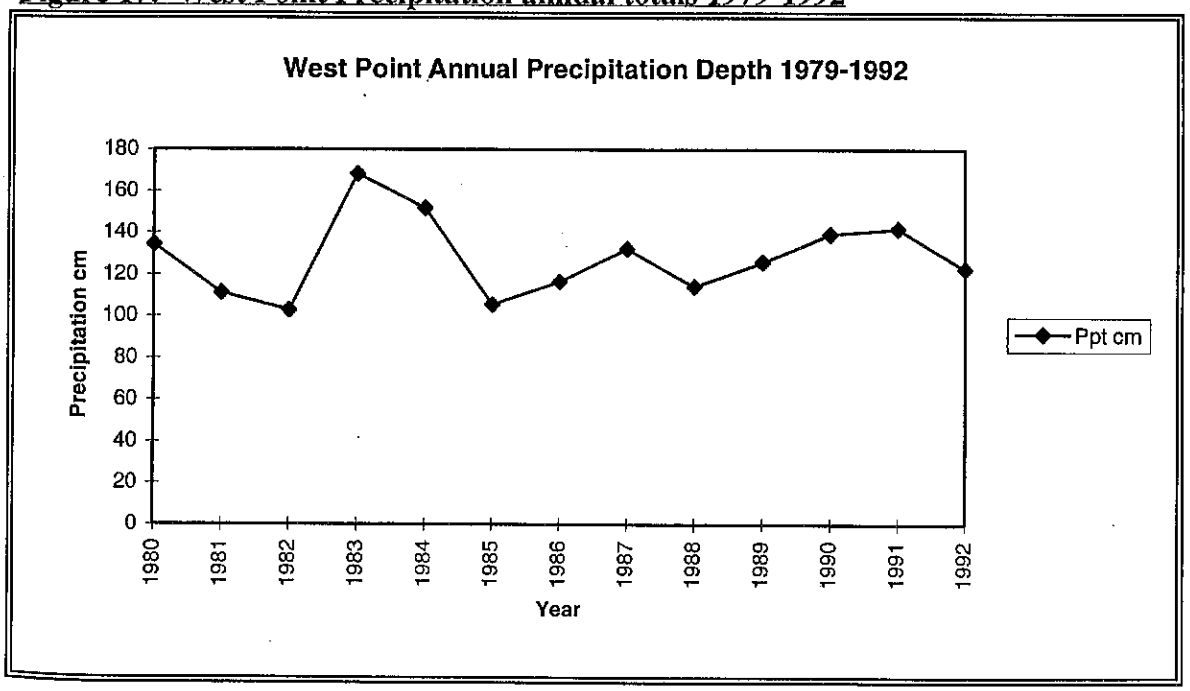


Table 5: Annual Monthly Precipitation Averages at West Point 1979-1992

June-May	year	Cl mg/l	SO4-- mg/l	Ppt cm	SO4--/Cl- ratio
	1980	0.48	2.98	11.19	6.21
	1981	0.70	3.36	9.26	4.8
	1982	0.29	3.12	8.58	10.76
	1983	0.39	2.10	14.02	5.38
	1984	0.47	2.03	12.64	4.32
	1985	0.36	2.44	8.80	6.78
	1986	0.37	3.12	9.72	8.43
	1987	0.37	2.80	11.04	7.57
	1988	0.33	2.89	9.51	8.76
	1989	0.44	2.58	10.49	5.86
	1990	0.41	2.08	11.61	5.07
	1991	0.47	2.28	11.81	4.85
	1992	0.42	2.43	10.23	5.79
	max	0.70	3.36	14.02	10.76
	min	0.29	2.03	8.58	4.32
	ave	0.39	2.53	10.77	7.05
	stdev	0.05	0.37	1.58	

Figure 18: West Point Annual Monthly Average Precipitation 1979-1992

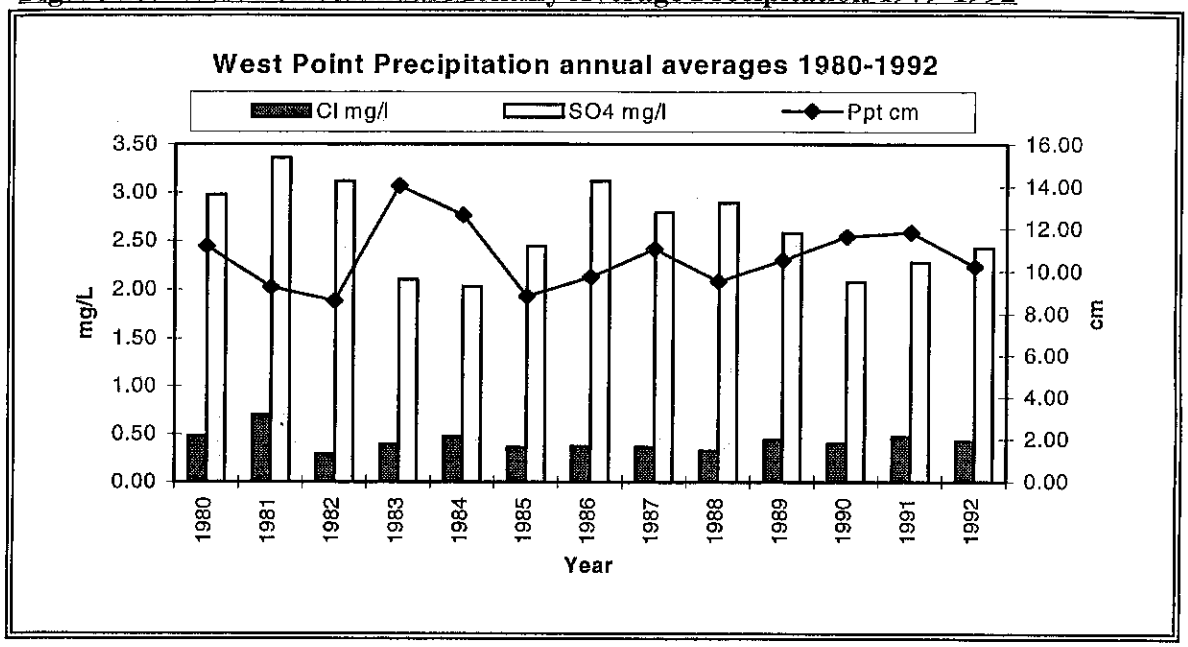
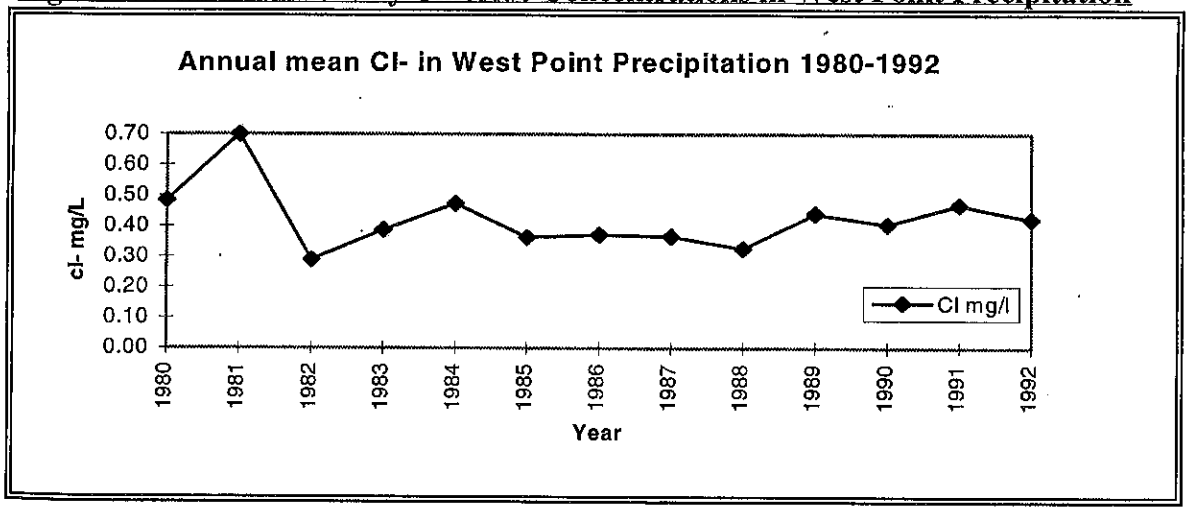


Figure 19: Annual Monthly Chloride Concentrations in West Point Precipitation



Monthly Precipitation averages at West Point 1979-1992

Chloride in West Point precipitation averages .61 mg/L in January and peaks at .79 mg/L in February (table 6, figure 20). Chloride concentrations then decline from .45 mg/L in March to .21 mg/L in August. In September chloride concentrations rise to .34 mg/L and rise to .65 mg/L in October. November and December values are .54 and .63 mg/L respectively. Chloride values are higher in the wintertime months and are lowest in the summertime.

The monthly sulfate concentrations in West Point precipitation follow the opposite trend that chloride concentrations follow. That is sulfate values are higher in the summer months and lower in the winter months. January concentrations are on average 1.63 mg/L. Concentrations rise to 2, 2.21, 2.67, 3.23, 3.52, and 3.8 mg/L in February, March, April, May, June, and July respectively. After the July peak, concentrations decline in August to 3.46 mg/L. In September, sulfate concentrations average 2.5 mg/L, but rise slightly in October to 2.79 mg/L and fall to 1.68 mg/L in November. December values rise again to 1.9 mg/L and values drop in January to 1.63 mg/L.

Precipitation depth ranges from 7.56 cm in January to 13.54 cm in November spanning 5.98 cms. From a low 7.56 cm in January, precipitation levels rise to 8.4 in February. Springtime values are higher with 12.16, 13.42, and 12.88 centimeters in March, April, and May respectively. Precipitation remains high in June and July at 11.96 and 12.11 centimeters respectively. In August, precipitation depth is 10.74 cm and is 9.55 cm in September. In October and November precipitation is 10.67 and 13.54 cm respectively. In December precipitation falls to 8.89 cm and a low of 7.56 cm in January.

Note the ratios of sulfate to chloride (table 6). On a monthly basis there is a wider range than the annual basis. A low ratio of 2.53 occurs in February and a high of 17.27 occurs in July. The average is 7.94. This is .89 higher than the average ratio obtained using the average of the annual monthly averages of sulfate and chloride.

Table 6: Monthly 12 year means in West Point Precipitation

month	Cl mg/l	SO4 mg/l	Ppt cm	SO4--/Cl- ratio
January	0.61	1.63	7.56	2.67
February	0.79	2.00	8.40	2.53
March	0.45	2.21	12.16	4.91
April	0.38	2.67	13.42	7.03
May	0.27	3.23	12.88	11.96
June	0.24	3.52	11.96	14.67
July	0.22	3.80	12.11	17.27
August	0.21	3.46	10.74	16.48
September	0.34	2.50	9.55	7.35
October	0.65	2.79	10.67	4.29
November	0.54	1.68	13.54	3.11
December	0.63	1.90	8.89	3.02
sum			131.87	
average0.44	2.62	10.99	7.94	
stdev-ann	0.20	0.75	2.01	
max	0.79	3.80	13.54	17.27
min	0.21	1.63	7.56	2.53

Figure 20: 12 Year Monthly Means of West Point Precipitation

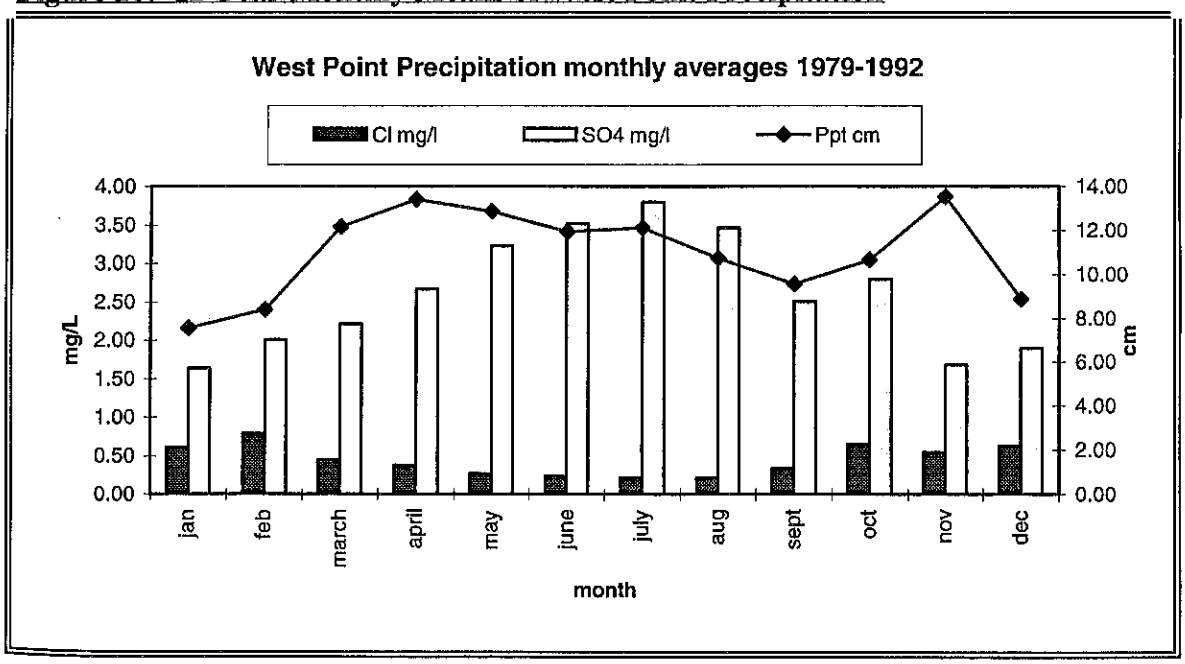
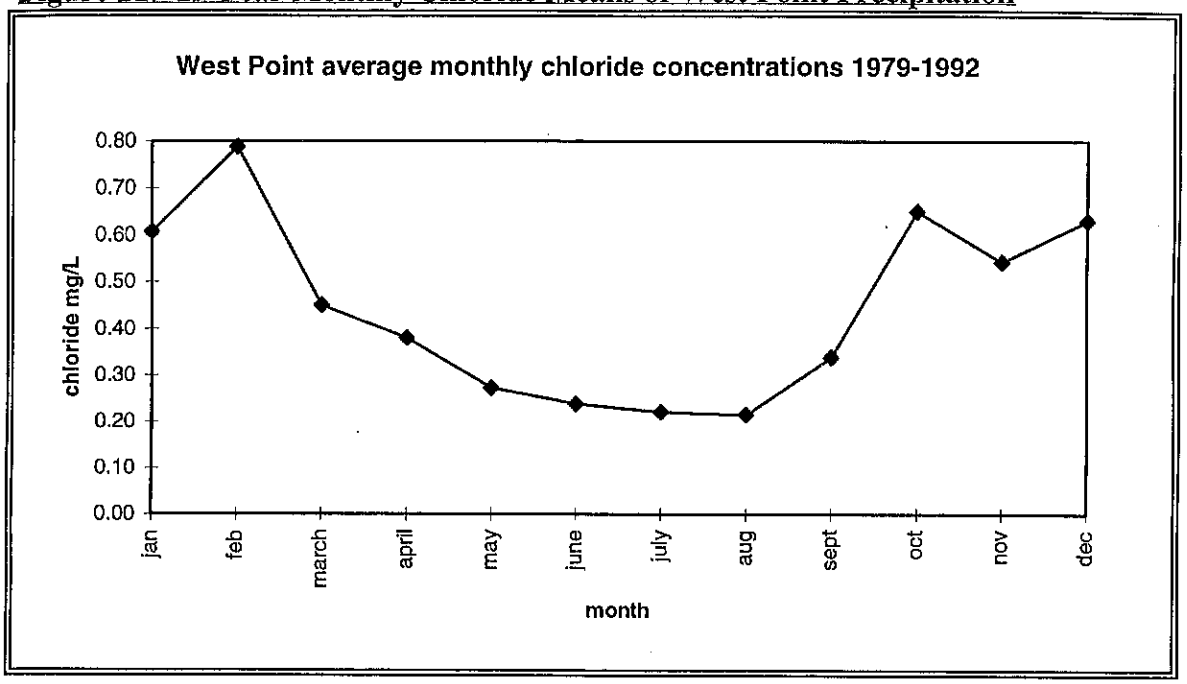


Figure 21: 12 Year Monthly Chloride Means of West Point Precipitation



Precipitation Comparison

The precipitation data from both sources seem fairly consistent. There are however, a few exceptions. January 1994 had 5.31 centimeters of rain above the 12 year West Point mean at 12.87 centimeters. February is about 2 centimeters lower than the mean and March is very close to the mean. April 1994 had 4.25 centimeters less rain than the 12 year monthly mean at 9.17 centimeters. May of 1994 is slightly below the 12 year mean of 12.88 centimeters at 11.06 centimeters. June is somewhat above the West Point monthly mean at 14.76 resulting in a difference of 2.8 centimeters. July sees an increase in the deviation from the monthly mean. July values are 12.11 centimeters for West Point and 17.29 centimeters for Black Rock Forest. August experiences the largest deviation from the West Point data. It rained 23.14 centimeters in August of 1994 compared to a 10.74 centimeter 12 year mean for that month. September is above the 12 year monthly mean by 3.09 centimeters. October-December have monthly means within 2 centimeters of the West Point data.

Overall, 1994 experiences about 24 centimeters above the annual mean of 128.2 centimeters, resulting in 152.35 centimeters of precipitation. This amount of precipitation is at the high end of the range experienced at West Point from 1979-1992. 1983 and 1984 is the only year of that 12 year record with a similar amount of precipitation with 168.2 cm and 151.2 cm respectively. The annual range of precipitation was 103 cm- 168.2 cm.

Figure 22: A Comparison of Precipitation

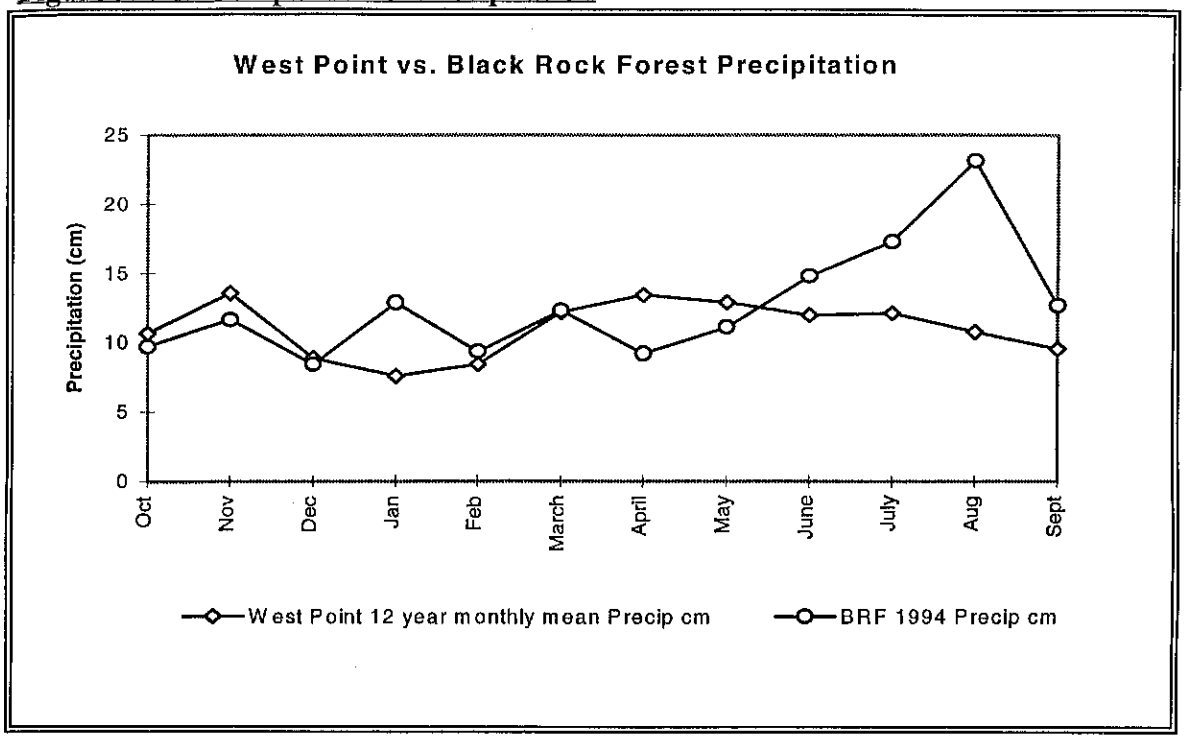


Table 7: A Comparison of West Point and Black Rock Forest Precipitation

Month	West Point	BRF 1994	
	Precip cm	Precip cm	difference
Oct	10.67	9.73	0.94
Nov	13.54	11.66	1.88
Dec	8.89	8.42	0.47
Jan	7.56	12.87	5.31
Feb	8.40	9.32	0.92
March	12.16	12.29	0.13
April	13.42	9.17	4.25
May	12.88	11.06	1.82
June	11.96	14.76	2.80
July	12.11	17.29	5.18
Aug	10.74	23.14	12.40
Sept	9.55	12.64	3.09
annual	131.87	152.35	20.48
average	10.99	12.70	1.71
stdev	2.01	2.84	0.83
max	13.54	23.14	9.60
min	7.56	0.00	7.56

Estimating Streamflow

Estimations of Runoff based on Evaporation Pan Data

Using the basic water budgeting equation outlined earlier

Runoff = Precipitation - Evapotranspiration.

In the Table 8, all negative runoff and streamflow values are assumed to be zero. These values result from the above equation. Therefore, evapotranspiration doesn't exceed precipitation and runoff or streamflow cannot exceed zero.

As expected, evaporation is lower in the winter and steadily increases throughout the spring to peak in the summertime. The evaporation then declines steadily to low wintertime values.

Precipitation ranges from 758,952 m3/month to 1,359,361 m3/month delivered to Black Rock Forest. Precipitation is low in January and rises to 1,220,434 m3 in March and 1,347,368 m3 in April. Precipitation then declines to 1,200,354 m3 in June and rises slightly in July to 1,292,650 m3 and in August precipitation falls to 1,078,296 m3. Precipitation is lower in September at 958,820m3 and rises to 1,071,268 m3 in October. In November precipitation peaks with an average delivery of 1,359,631 m3 and precipitation decreases in December and January with 892,607 m3 and 758,952 m3.

The following is a graph of evaporation from Albany, New York, representative of evapotranspiration in Black Rock Forest, monthly averages from West Point 1979-1992 and the resultant estimated streamflow in Black Rock Forest. Streamflow and evapotranspiration are fairly well anticorrelated in this estimation. Streamflow values are highest when evaporation is lowest. Snowmelt lag-time is not taken into account in this estimation. Probably, total annual streamflow would not be different, but streamflow in the coldest months when precipitation falls as snow would be lower while the spring months would have higher streamflow as the snow melts and increases total streamflow.

Figure 23: An Estimate of Streamflow in Black Rock Forest

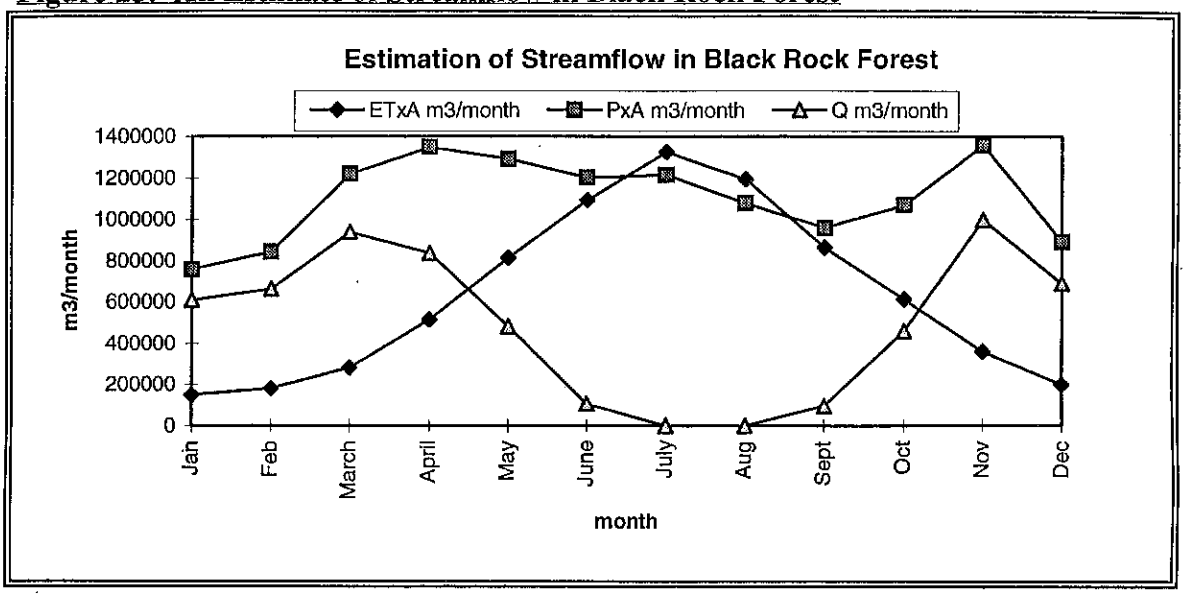


Table 8: Estimate of Streamflow in Black Rock Forest

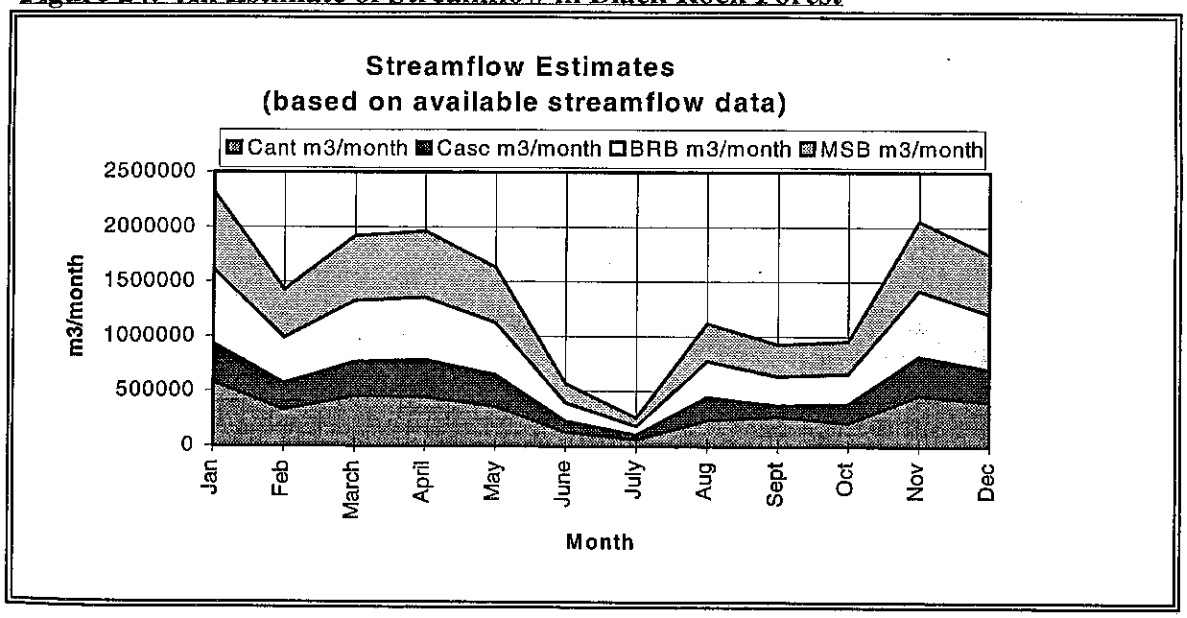
	ET m	x A m3	Ppt m	x A m3	Runoff m	Q m3/month
Jan	0.0150	150600	0.0756	758952	0.0606	608352
Feb	0.0180	180720	0.0840	843288	0.0660	662568
March	0.0280	281120	0.1216	1220434	0.0936	939314
April	0.0510	512040	0.1342	1347368	0.0832	835328
May	0.0810	813240	0.1288	1292650	0.0478	479410
June	0.1090	1094360	0.1196	1200354	0.0106	105994
July	0.1320	1325280	0.1211	1215629	-0.0109	-109651
Aug	0.1190	1194760	0.1074	1078296	-0.0116	-116464
Sept	0.0860	863440	0.0955	958820	0.0095	95380
Oct	0.0610	612440	0.1067	1071268	0.0457	458828
Nov	0.0360	361440	0.1354	1359631	0.0994	998191
Dec	0.0200	200800	0.0889	892607	0.0689	691807
sum	0.7560	7590240	1.3187	1323930	0.5852	5875172
ave	0.0630	632520	0.1099	110327	0.0585	522193
stdev	0.0417	418867	0.0201	202260.03102	398642	
max	0.1320	1325280	0.0201	202260.0994	1305054	
min	0.0150	150600	0.0756	758950.0000	74705	

Estimates based on Flow at Canterbury and Cascade Brooks

There is one full year of flow data available for Canterbury and Cascade Brooks starting in March 1994 and ending March 1995. Preferably, flow data would have been available for all four of the brooks and on a time scale corresponding to the stream chemistry data (January 1994 - December 1994). However, since this is not the case, the first months of 1995 were used to represent early 1994.

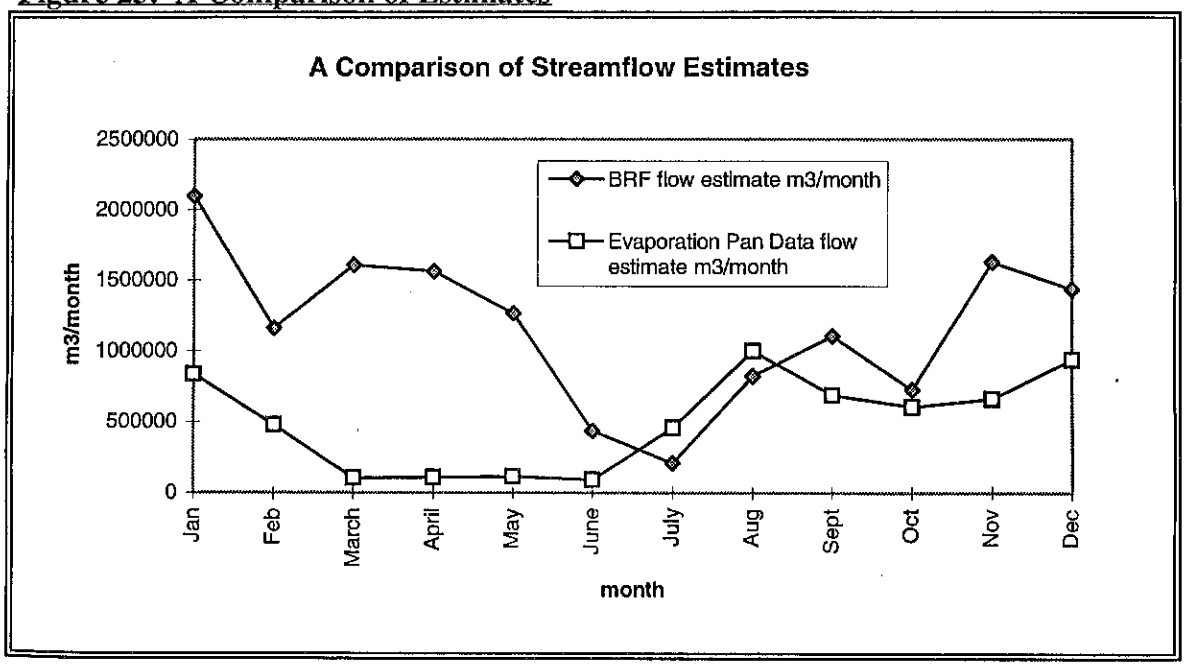
Using an area based proportion, streamflow was estimated for Black Rock and for Mineral Springs Brook. A second estimate was made based on the ratio of actual flow measured at Canterbury and Cascade Brooks.

Figure 24: An Estimate of Streamflow in Black Rock Forest



Obviously the major problem with the Albany evaporation pan data estimates are that they do not account for snowmelt lag-time. The largest difference in the estimates are in spring streamflow. The actual measurements in Black Rock Forest at that time indicate that streamflow is quite high with volumes of about 1,500,000 m3 leaving the forest in March, April and May. Otherwise, there is a peak in streamflow in January of more than 2,000,000 m3 exiting the forest while the evaporation estimates have only about 800,000 m3 being discharged in January. Also, streamflow in the fall is actually higher in November and December than what is predicted by the evaporation estimates.

Figure 25: A Comparison of Estimates



Clearly the difference in using the 12 monthly means as compared to just one year of precipitation data can be seen in the estimates made for June, July, August and September. In Black Rock Forest August 1994 had an unusually high input of rain: 23.14 cm compared to the 12 year monthly mean for August of 10.74 cm making a difference of 12.4 cm of rain. This evidently results in high streamflow for August. From the comparison made earlier with the streamflow volume based on actual streamflow readings and the streamflow volume based on evaporation pan data, it is seen that there is quite a disparity in the numbers. As explained earlier there are many assumptions made to estimate the flow. 1994 does have a higher than usual amount of precipitation especially in August. June, July and September also have higher than normal inputs of precipitation with 3-5 cm of rain above the 12 year means for those months. These 4 months alone account for 99% of the precipitation input in 1994 above the annual mean. Therefore, using 1994 data makes the estimates using evaporation pan data more similar to the estimates based on actual streamflow, but this is probably not representative of the average output of the area.

Figure 26:

A Comparison of Estimates using Evaporation Data and 2 Precipitation Data Sets

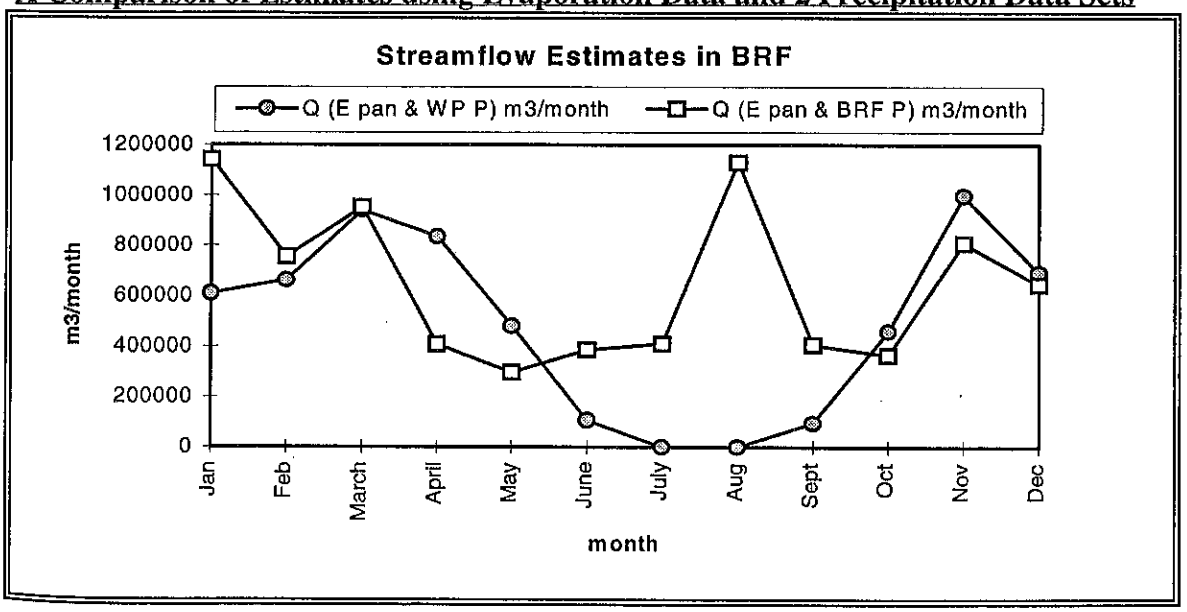
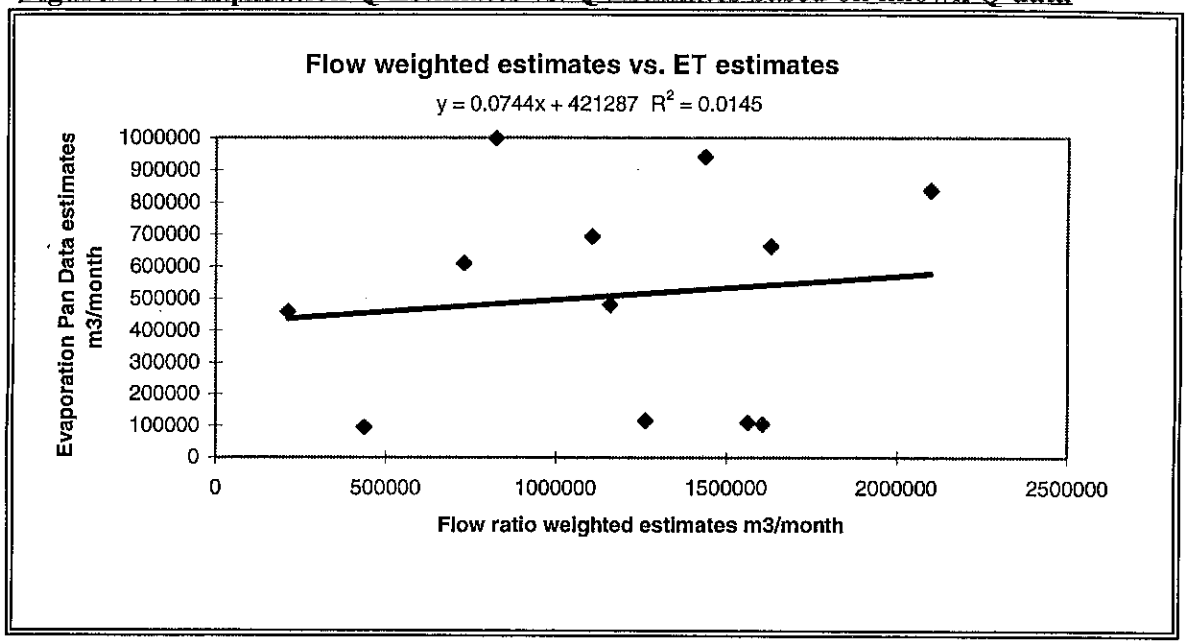
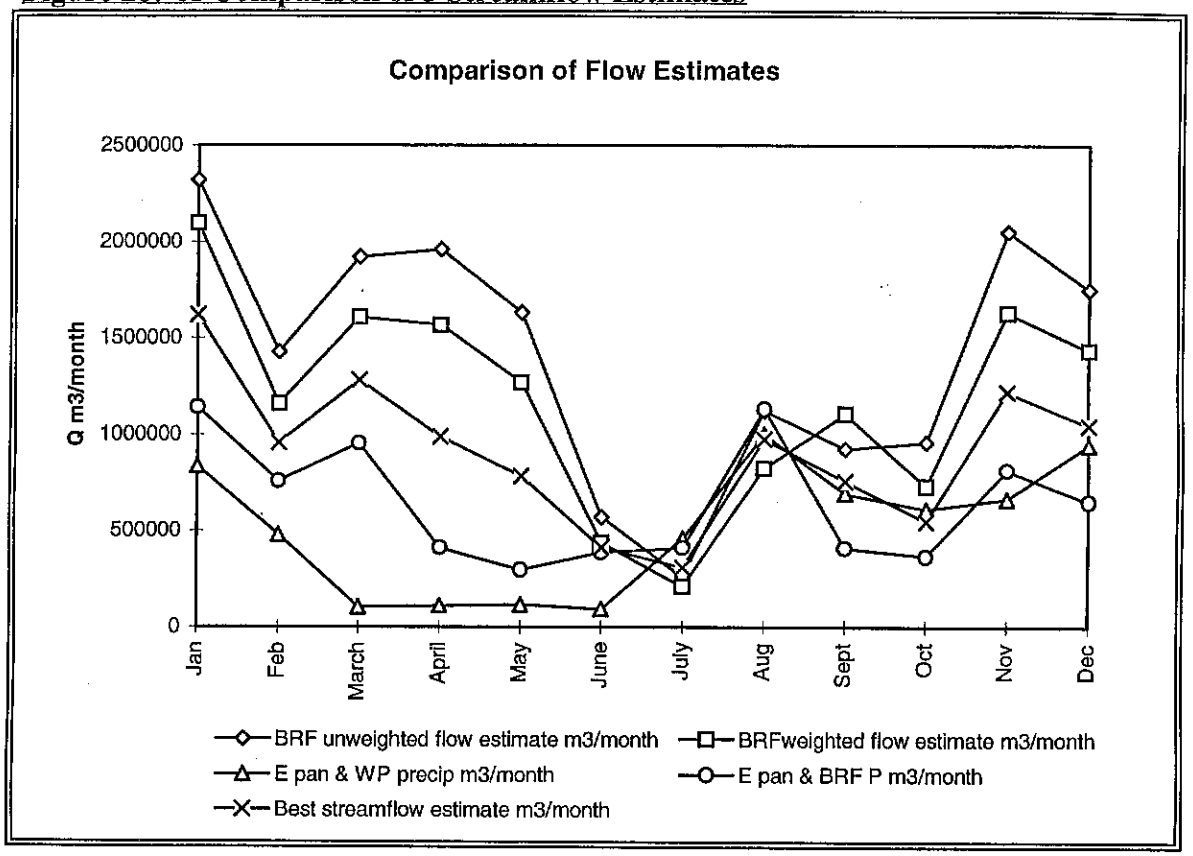


Figure 27: Evaporation Q Estimates vs. Q Estimates based on known Q data



As stated previously, the largest disparity in the estimates is in the spring months when snowmelt would contribute to streamflow. However, there is also a large difference in the volume of streamflow estimated in the winter months. The estimates using the known flow data are substantially higher than those using the evaporation estimates. Because so many assumptions were made using both methods, an average of the weighted Black Rock Forest streamflow estimate and the estimate made using the evaporation pan data and Black Rock Forest precipitation data were used as the best estimate of streamflow. Therefore, the best estimate values fall between the weighted estimates and the evaporation pan and Black Rock Forest precipitation estimates.

Figure 28: A Comparison of 5 Streamflow Estimates



Chloride Budgeting

Chloride export can be calculated for the entire area under study now that streamflow estimates have been made. The following table is in units of kg/ha per month. As stated previously:

Total Deposition= [Cl-] x Q = Surface Outflow of Chloride

Wet Deposition Flux = rainwater [Cl-] x P x A

Dry Deposition Flux = Total Deposition - Wet Deposition

The dry deposition of chloride is high in January at 3.59 kg/ha. The delivery of chloride declines in February to 1.39 kg/ha. The decrease continues throughout March, April, May and June with values of .91, .71, .69 and .11 kg/ha each month respectively. In July the delivery of chloride via dry deposition increases to.24 kg/ha and increases further in August to 1.08 kg/ha. In September the dry deposition of chloride remains close to 1 kg/ha at .97 kg/ha. In October, there is a drop in the chloride delivery via dry deposition with .45 kg/ha. Values in November and December are above average at 1.23 and 1.34 kg/ha respectively. The range of monthly delivery of chloride is .11 kg/ha- 3.59 kg/ha and the average is 1.06 kg/ha.

Table 9: Estimate of Dry Deposition

Month	Chloride Export kg/ha month	Chloride Import kg/ha month	Dry Deposition kg/ha month	Dry:Wet Ratio
January	4.05	0.46	3.59	7.82
February	2.05	0.66	1.39	2.10
March	1.46	0.54	0.91	1.67
April	1.22	0.51	0.71	1.40
May	1.04	0.35	0.69	1.99
June	0.39	0.28	0.11	0.39
July	0.50	0.27	0.24	0.88
August	1.31	0.23	1.08	4.73
September	1.30	0.32	0.97	3.03
October	1.15	0.70	0.45	0.65
November	1.97	0.74	1.23	1.68
December	1.90	0.56	1.34	2.39
sum	18.3	5.61	12.72	
average	1.52	0.47	1.06	2.39
stdev	0.95	0.18	0.90	2.07
max	4.05	0.74	3.59	7.82
min	0.39	0.23	0.11	0.39

Figure 29: An Estimate of Chloride Flux in Black Rock Forest

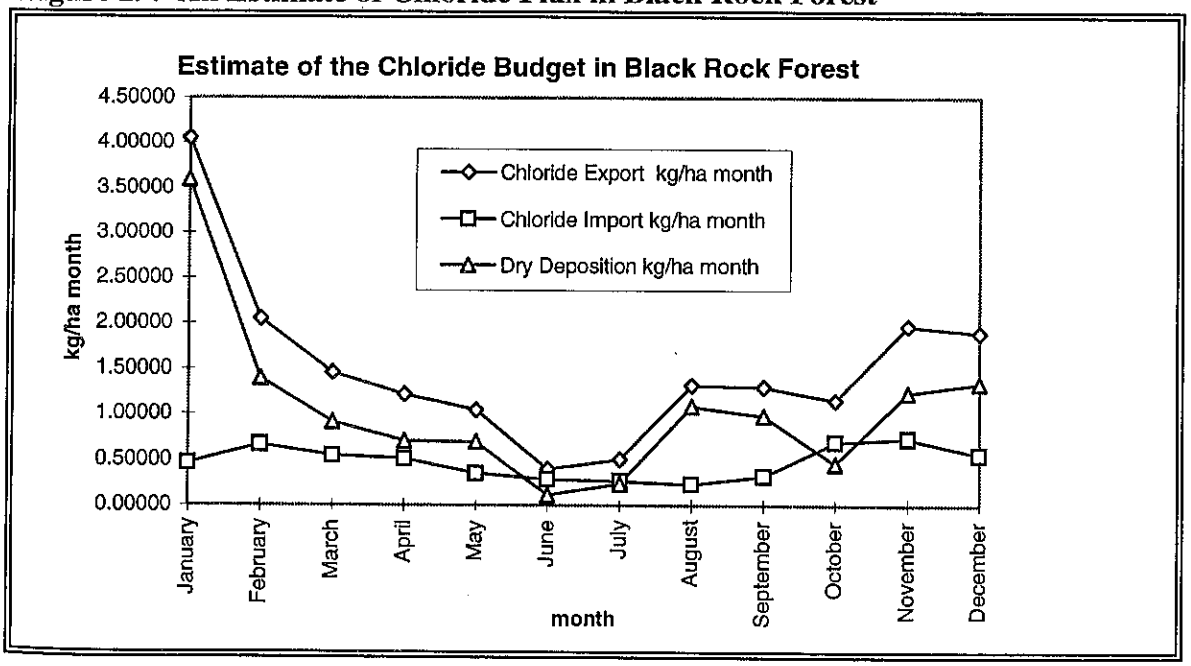
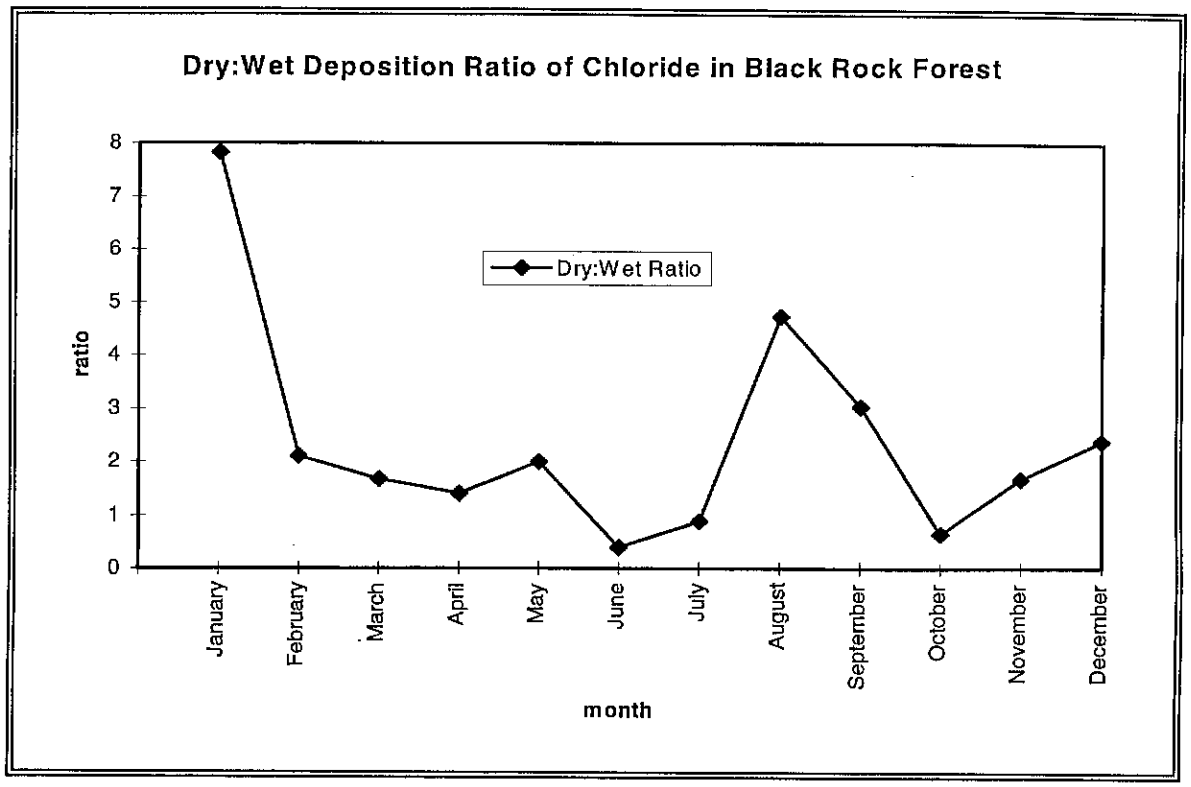


Figure 30: Monthly Dry:Wet Deposition Ratio of Chloride in Black Rock Forest


Dry:Wet Deposition Ratio of Chloride in Black Rock Forest
Dry:Wet Ratio
ratio
0
1
2
3
4
5
6
7
8
January
February
March
April
May
June
July
August
September
October
November
December
month

VI. Discussion and Conclusions

Canterbury Brook, Cascade Brook, and Mineral Springs Brook exhibit similar trends in chloride concentrations throughout the year with the year starting off slightly higher and making a slight and steady decline to about 2 ppm from early spring until autumn when the values increase slightly to end the year at about 2.5 ppm.

Black Rock Brook has unusually high values for January and February with monthly averages of 16.13 and 25.14 respectively. Then values for the rest of the year remain close to 2 ppm without the slight increase in concentrations at the end of the year that the other three brooks experienced.

All of the Brooks had very similar average annual values except for Black Rock Brook. However, when the high concentrations measured early in the year were excluded, the average value for Black Rock Brook dropped to 1.93 ppm, much closer to the average annual chloride found in Canterbury Brook, 2.22 ppm, Cascade Brook, 2.19 ppm, and Mineral Springs Brook at 2.23 ppm. The overall average of stream water exiting Black Rock Forest using a weighted average is 1.45 ppm without the highs and 1.78 ppm with the Black Rock Brook highs. The unweighted average for all 4 brooks is 2.72 ppm including the highs and 2.16 without the highs.

Seasonal variability in chloride concentrations are due to changes in input unless chloride is more involved in biological cycling than assumed (Peters 1991). In 3 of the 4 brooks, concentrations increased on the fall months. Christopherson *et. al* 1990 measured stream [Cl-] which demonstrates an autumnal increase in October at Birkne, southern Norway as well. The increase in stream water chloride concentrations was attributed to seasonally elevated Cl- concentrations in precipitation due to storm sources and partly to evaporative concentrations of soil solutions during the preceding months.

In the Hubbard Brook Experimental Forest, chloride concentrations in bulk precipitation ranges from .25 mg/L to 1.07 mg/L. In the stream water chemistry, the chloride concentrations range from .37 mg/L to .70 mg/L. Bulk precipitation as explained

contains dry and wet deposition because the collector doesn't close during precipitation events. Bulk precipitation collectors do not efficiently collect dry deposition (Eriksson 1954). Therefore, it makes sense that there is more chloride in the streamwater than in the precipitation for 75% of the year at Hubbard Brook. One would expect the input to equal the output in this situation. The average input at Hubbard Brook has a concentration of .47 mg/L in 1967-1974. The output for the same period had a very similar concentration of .55 mg/L. Even though bulk precipitation collectors do not efficiently capture dry deposition of aerosols, the similarity of the input and output concentrations in Hubbard Brook suggest that dry deposition of chloride is probably a small fraction of bulk precipitation. Notice that the average value for precipitation chloride concentrations are similar in Black Rock Forest and Hubbard Brook with values of .44 mg/L and .47 mg/L respectively. There is also a seasonality to chloride input at Hubbard Brook attributed to a larger influence from marine aerosols during this time of the year in the eastern United States (Likens *et. al* 1977). The fact that dry deposition is higher in Black Rock Brook could be due to the fact that Hubbard Brook measurements were made 20-27 years ago. Perhaps the chloride aerosols are a result of recent increases in pollution. Also, it could be due to spatial differences, distance from the coast, climatic influences etc.. Hubbard Brook is in New Hampshire.

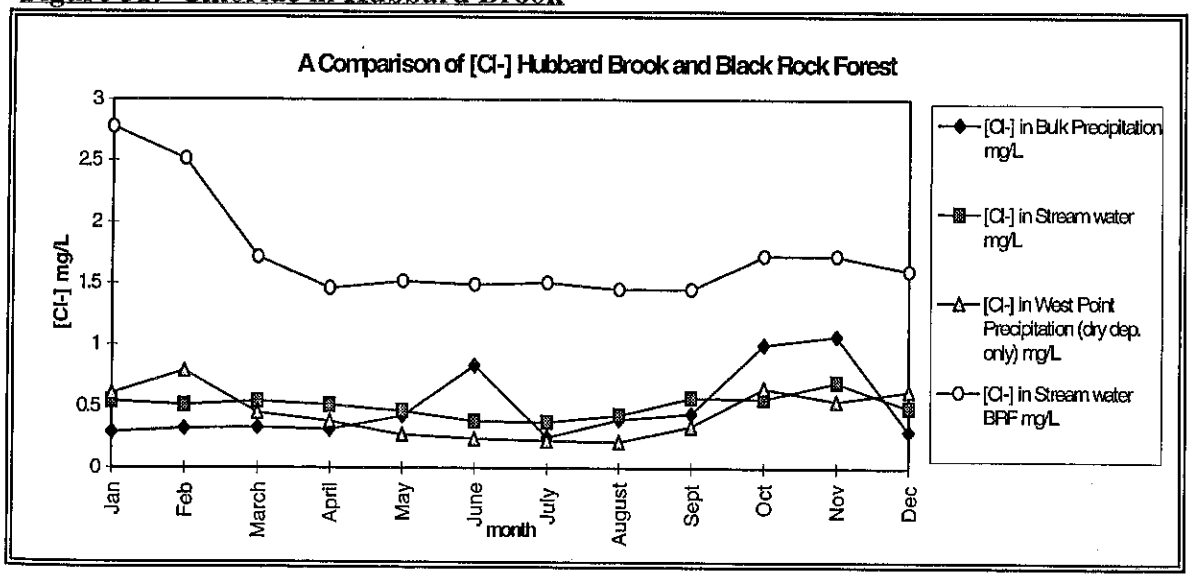
Table 10: A Comparison of Chloride Concentrations-

Hubbard Brooks and Black Rock Forest Brooks

[Cl-] Month	Hubbard Brook Bulk Precipitation mg/L	Hubbard Brook Stream water mg/L	Black Rock Forest West Point Precipitation (dry dep. only) mg/L	Black Rock Forest Stream water BRF mg/L
Jan	0.29	0.54	0.61	2.78
Feb	0.32	0.51	0.79	2.52
March	0.33	0.54	0.45	1.71
April	0.31	0.51	0.38	1.46
May	0.42	0.46	0.27	1.51
June	0.83	0.38	0.24	1.49
July	0.25	0.37	0.22	1.51
August	0.39	0.43	0.21	1.45
Sept	0.44	0.57	0.34	1.45
Oct	1	0.56	0.65	1.72
Nov	1.07	0.7	0.54	1.73
Dec	0.3	0.49	0.63	1.60
ave	0.51*	0.55*	0.44	1.74
stdev	0.29	0.09	0.20	0.44
max	1.07	0.70	0.79	2.78
min	0.25	0.37	0.21	1.45

* these averages must have been computed from a larger data set; the obtained averages from the above compilation of monthly data do not agree with the average values presented in Likens *et. al* 1977.

Figure 31: Chloride in Hubbard Brook



In comparison to other rivers throughout the world, actual chloride concentrations are on the low end of the range. Chloride in precipitation at West Point averages .44 mg/L and is also at the low end of the range of observed chloride concentrations. The following table displays selected precipitation chloride concentrations. Values near coastal stations are higher than the values presented in the table. For example, Brownsville, Texas had an average chloride concentration in precipitation of 22 mg/L in 1955-1956 and the U.S. coastal average is 4.83 mg/L. In West Ireland, an unpolluted 1967 average of chloride concentrations in precipitation was 36.42 mg/L. Following is a summary of chloride concentrations in world rivers and precipitation taken from Berner and Berner 1987.

Table 11: [Cl-] in Runoff and Precipitation-comparison

Runoff		Precipitation	
Location	[Cl-] mg/L	Location	[Cl-] mg/L
Black Rock Brooks	2.16	West Point	.44
Hubbard Brooks	.55	Hubbard Brooks	.51
Africa	4.1	Kampala, Uganda	.9
Asia	10	USSR-Asian	1.5
S. America	4.1	Amazon River basin	.49
N. America	9.2	N.E.U.S	
Europe	20	ave.1978-1979	.40
Oceania	6.8	N. Europe	
World		ave. 1955-1956	3.37
average	8.3	World ave. coastal	6

Sulfate values in Black Rock Brook also are highest at the beginning of 1994. In January, the average sulfate concentration is 13.8 ppm. In February the average drops negligibly to 13.63. March begins the decreasing trend in sulfate concentrations from around 12 ppm to 8 ppm in July. The sulfate concentrations then hover around 8 ppm until October when they begin to rise slightly, ending the year with a concentration of 9.41 ppm in December.

Table 12:]SO4--] in Hubbard Brooks and Black Rock Forest

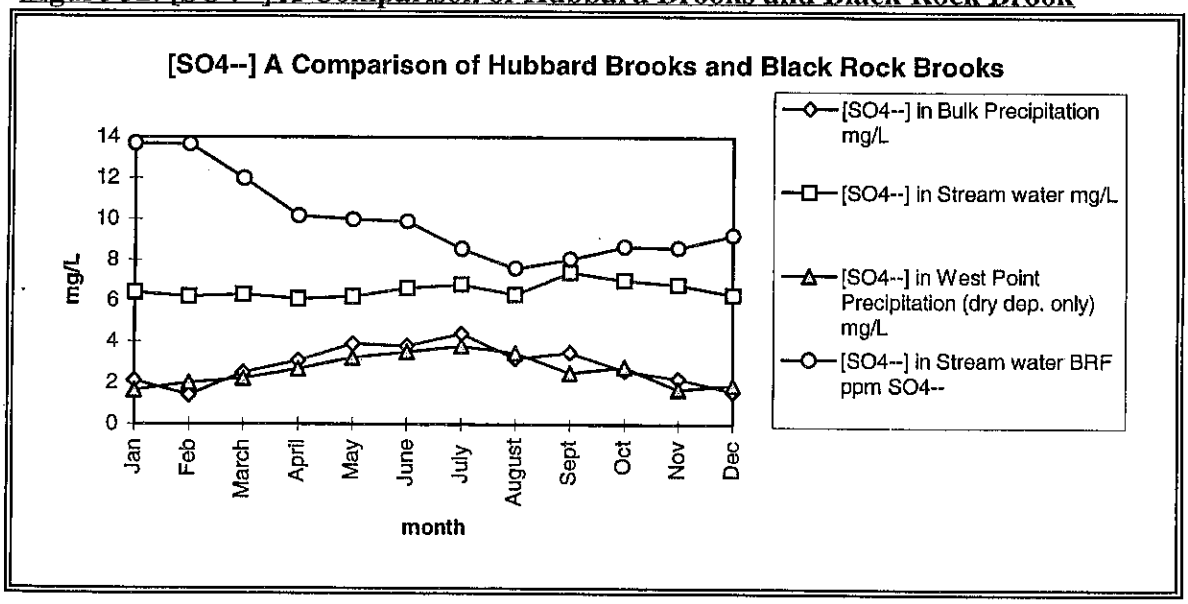
	Hubbard Brook		**Black Rock Forest**	
[SO4--]	Bulk Precipitation	Stream water	West Point P (dry dep. only)	Stream water BRF
	mg/L	mg/L	mg/L	mg/L
Jan	2.1	6.4	1.63	13.70
Feb	1.4	6.2	2.00	13.63
March	2.5	6.3	2.21	11.97
April	3.1	6.1	2.67	10.15
May	3.9	6.2	3.23	9.98
June	3.8	6.6	3.52	9.86
July	4.4	6.8	3.80	8.54
August	3.2	6.3	3.46	7.56
Sept	3.5	7.4	2.50	8.05
Oct	2.6	7	2.79	8.64
Nov	2.2	6.8	1.68	8.58
Dec	1.6	6.3	1.90	9.22
average	2.86	6.3*	2.62	9.80
stdev	0.95	0.39	0.75	2.07
max	4.40	7.40	3.80	13.70
min	1.40	6.10	1.63	7.56

* This value must have been obtained from an expanded data set since the average obtained from the above table does not agree with the average given in Likens *et. al* 1977.

Notice that the delivery of sulfate in precipitation is very similar at Hubbard Brook and West Point. However, caution in comparing the data sets must be taken because the Hubbard Watershed precipitation is bulk, while the West Point precipitation is not. Still, both show a trend of values around 2 mg/L in January increasing steadily to a peak in July of around 4 mg/L and then a steady decline to less than 2 mg/L in the autumn and early winter.

The stream concentrations of sulfate are much higher in the Black Rock Brooks in the early part of the year. Sulfate concentrations in Black Rock Brook average almost 14 mg/L in January and February while in Hubbard Brook, sulfate is approximately 6 mg/L from January thru May. Sulfate concentrations in Black Rock Brook decline in March to about 12 mg/L and April thru June exhibit sulfate concentrations of about 10 mg/L. From July throughout the rest of the year values for sulfate are closer in the 2 systems than in the first half of the year. Sulfate in Black Rock Brook is at a minimum of 7.56 mg/L in August and increase steadily to 9.22 mg/L in December. In Hubbard Brook there is much less variability in the sulfate concentrations and values from July-December range from 6.3 mg/L to 7.4 mg/L. Differences in the stream concentration of sulfate could be due to differences in input i.e. dry deposition in Black Rock Forest, differences in geology causing weathering inputs of sulfate, climactic differences, changes in pollution etc..

Figure 32: [SO4--] A Comparison of Hubbard Brooks and Black Rock Brook



Average continental sulfate concentrations in rivers throughout the world exhibit a range from 3.8 mg/L for African rivers to 35.5 mg/L for European rivers. Following is a summary of sulfate concentrations in rivers by continent and precipitation concentrations

adapted from Berner and Berner 1987. The average in Black Rock Brook is slightly below the actual world average of 11.5 mg/L, but far below the North American average of 18 mg/L. Precipitation sulfate is 1.63 mg/L at West Point and falls within the range presented in Berner and Berner 1987. However, values can be as high as sulfate in Brownsville, Texas in 1955-1956, 10.68 mg/L and 6.29 mg/L on the West coast of Ireland in 1967.

Table 13: [SO4--] in Runoff and Precipitation-a Comparison

Location	[SO4--] mg/L	Location	[SO4--] mg/L
Black Rock Brook	9.80	West Point	1.63
Hubbard Brook	6.3	Hubbard Brook	2.87
Africa	4.2	Kampala, Uganda	1.8
Asia	13.3	USSR-Asia	4.35
S. America	3.8	Amazon River basin	.49
N. America	18.0	N.E. U.S	
Europe	35.5	ave. 1978-1979	2.81
Oceania	7.7	Northern Europe	
World		ave. 1955-1956	2.19
Average	11.5	World ave.coastal	1.45

The sulfate to chloride ratio are very high in the West Point precipitation data with an average of 7.05 (derived from average of annual monthly averages over 12 years) or 7.94 (derived from 12 year monthly averages for each month) depending on the calculations. In seawater, the sulfate/chloride ratio is .14. If the only source of chloride is sea salt aerosols as is usually assumed, excess sulfate above sea salt concentrations is very high. This sulfate may be a result of acid rain which is a problem in the northeast U.S. because of transport of sulfur dioxide from the mid-west. The ratio of sulfate/chloride in streamwater is somewhat lower at 5.91, possibly due to reduced delivery of sulfate in 1994 below the 12 year means, biochemical reactions etc.

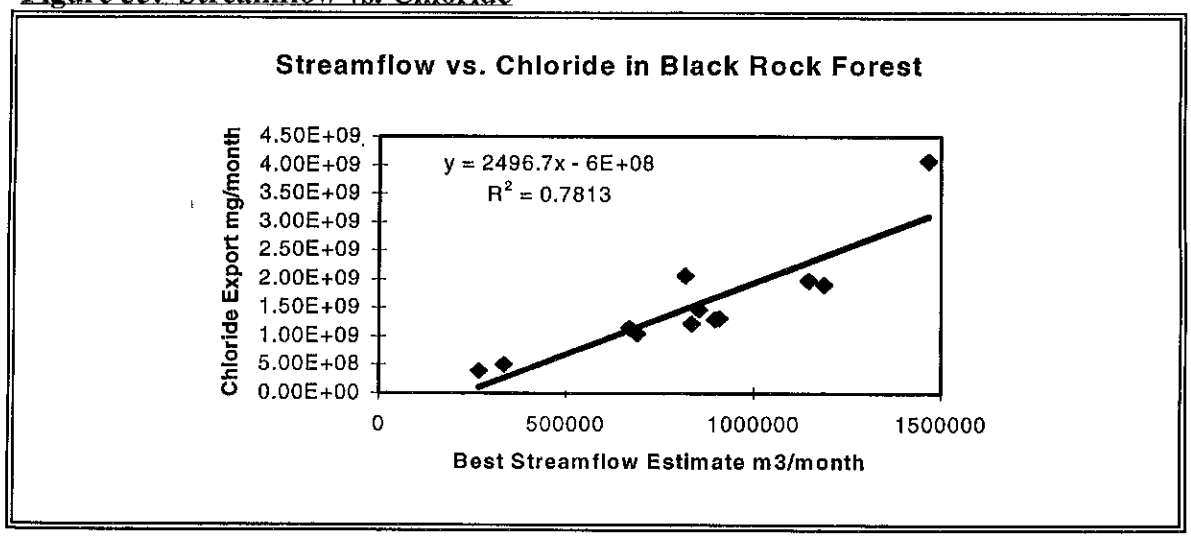
Various estimates of runoff were made. The best estimate of streamflow exhibits fairly high flow in January with flow dropping somewhat in February, then increasing in March. From March, streamflow declines to a low in July and then streamflow increases

in August and generally increases in the fall with a high in November close to the January peak. There was a fairly high range in the estimates of streamflow due to the many assumptions that were necessary in the different approachs. The range of estimates was from zero in some months due to the fact that evaporation exceeded precipitation to a highs of 2 million plus m3 exported in one month.

The calculated runoff ratio averages .55. This is a bit higher than the world average of .46. The runoff ratio is the ratio of runoff per unit area to rainfall per unit area. A value of .55 indicates that roughly half of the water input to the forest is lost as evapotranspiration (Berner and Berner 1987).

When runoff is plotted against chloride concentration, there is a correlation of .78. There is not an inverse relationship between the two. Therefore, this is not a simple dilution of a limited number of highly concentrated sources such as mineral deposits of halite or other point sources (Holland 1978).

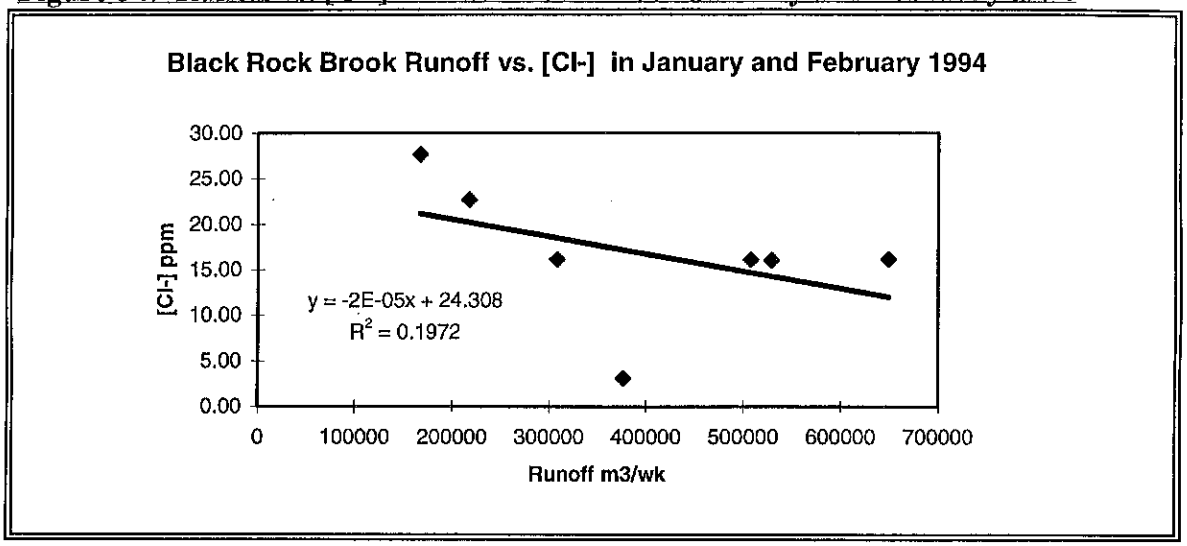
Figure 33: Streamflow vs. Chloride



Notice in January and February that there is an inverse relationship between runoff and chloride concentration in Black Rock Brook providing further evidence to support the road salt contribution of chloride. Remember, a highway in close proximity

to Black Rock Brook in all likelihood is the cause of elevated chloride concentrations in January and February to Black Rock Brook.

Figure 34: Runoff vs. [Cl-] in Black Rock Brook January and Febraury 1994



The dry deposition of chloride calculated using a weighted average of chloride concentrations averages 1.06 kg/ha month. The dry deposition is high in January at 3.59 kg/ha. The delivery of chloride declines in February to 1.39 kg/ha. The decrease continues throughout March, April, May and June with values of .91, .71, .69 and .11 kg/ha each month respectively. In July the delivery of chloride via dry deposition increases to.24 kg/ha and increases further in August to 1.08 kg/ha. In September the dry deposition of chloride remains close to 1 kg/ha at .97 kg/ha. In October, there is a drop in the chloride delivery via dry deposition with .45 kg/ha. Values in November and December are above average at 1.23 and 1.34 kg/ha respectively. The range of monthly delivery of chloride is .11 kg/ha- 3.59 kg/ha.

This results in an average dry to wet deposition ratio of 2.39 meaning that 2.39 times as much chloride falls to the forest as dry deposition as falls to the forest as wet deposition in precipitation. The range of monthly deposition ratios ranges from .39 to 7.82. Unfortunately, no recent estimates of the dry deposition of chloride could be located. The only estimate of this sort was found in Eriksson (1960). Eriksson, using the same mass balance approach derives a dry:wet deposition ratio of approximately 3. However, this estimate is made using bulk precipitation data and the tacit assumption that the precipitation collection funnels do not collect dry deposition. This value seems to agree fairly well with the estimate of 2.39 as a dry:wet deposition ratio of chloride derived in this study especially since it is likely that the collection funnels catch some aerosols of dry deposition. This implies that if the dry deposition is not accounted for in element fluxes, large errors could be made. The potential impact of dry deposition can be quite important if it is generally 3 times as much as is deposited in precipitation.

VII. Recommendations for Further Research

Dry deposition estimates depend on a number of assumptions in this study. It is assumed that groundwater storage is in equilibrium. It is much more likely that groundwater recharge = groundwater discharge over a long period of time. If streams were gauged for a period of a decade, and flow measurements were taken on at least a weekly basis, the estimate arrived at in this paper would be better. Precipitation data from within the forest itself would also be helpful for future determinations of dry deposition, but the quality of the West Point data is excellent. Of course, long term means would prove the most useful.

Research within small catchments such as Black Rock Forest provide methods of assessing forest management practices on water resources. Catchment research provides principles and guidelines for improved management strategies. There is a need to conduct research from an integrated multidisciplinary approach to better utilize results and there implications for ecosystems. Studies should be planned with careful theoretical considerations so that models which can be scaled up from extrapolated results to apply to larger areas can be formulated.

There are many opportunities to use small catchment research to address major environmental problems. The long term records for baseline forest ecosystems at hydrologic stations provide a solid, unique basis for examining changes in forest health and water quality from the perspective of primary pollutants and climate change.

Acknowledgments

I wish to thank Dr. James Simpson for providing me with the opportunity to work on such an interesting and thought-provoking project. I would like to thank Dr. Stephanie Pfirman for recommending me for an internship at Lamont-Doherty Earth Observatory. I would like to thank Jordan Clark for his patience and guidance throughout the semester and Steve Chilrud who also was extremely patient and provided helpful insights onto my estimation dilemmas and allowed me access to his laboratory and texts. The sediment laboratory workers allowed me access to the lab and equipment. I would like to also acknowledge my fellow students of The Environmental Senior Seminar who gave me valuable feedback on this work in progress which allowed me to present the information in this paper better. Drs. Peter Bower and Joseph Liddicoat supported me through my years of study at Barnard and Lila Hicks and Molly Rivera always provided sound advice. My thanks also to the Black Rock Forest Consortium whose grant made it possible to undertake this project.

References

Bormann, F.H., Likens, G.E. (1979) Pattern and Process in a Forested Ecosystem. New York, New York: Springer- Verlag, 43, 47-48, 55-59, 181-182, 186.

Canter, Larry (1986) Acid Rain and Dry Deposition. Chelsea, Michigan: Lewis Publishers, Inc., 137-140, 321.

Christopherson, N., Robson, A., Neal, C., Whiteheaad, P.G., Vigerust, B. and Heinriksen, A (1990) Evidence for a long-term deterioration of streamwater chemistry and soil acidification at the Birknes catchment, southern Norway. *J. Hydrol.* **116:** 63-76.

Clair, T.A. and Freedman, B. (1986) Patterns and importance of DOC in four acidic groundwater streams in Nova Scotia, Canada. *Water Air Soil Poll.* **31**: 139-147.

Cleaves, E.T., Godfrey, A.E. and Brickner, O.P. (1970) Geochemical balance of a small watershed and its geomorphic implications. *Geol. Soc. Am. Bull.* **85:** 3015-3032.

Davis, C.S. and Wright, R.G. (19850 Sulphur dioxide velocity by a concentration gradient measurement system. *J. Geophys. Res.* **90**:2091-2095.

Drever, J.I. (1988) The Geochemistry of Natural Waters. Englewood Cliffs, New Jersey: Prentice Hall, pp. 6,15,30.

Droppo, J.G. (1985) Concurrent measurements of ozone dry deposition using eddy correlation and profile methods. *J. Geophys. Res.* **90**: 2111-2118.

Eriksson, Erik (1960) The Yearly Circulation of Chloride and Sulfate in Nature; Meterological, Geochemical and Pedological Implications. Part II. *Tellus* **12:** 63-109.

Feth, J. H. (1980) Chloride in natural Continental Waters- A review, U.S.G.S. Water Supply Paper No. 2176. 30 pp.

Fowler, D., Cape, J.N. and Leith, I.D. (1990) Field Methods for determining the atmospheric inputs of major plant nutrients. In: Nutrient Cycling in Terrestrial Ecosystems, edited by A.F Harrison, P. Ineson, and O.W. Heal, 36-45, London: Elsevier Applied Science.

Freedman, B. and Clair, T.A. (1987) Ion mass balances and seasonal fluxes from four acidic brownwater streams in Nova Scotia. *Can. J. Fish. Aquat. Sci.* **44**: 538-548.

Harrison, A.F., Ineson, P., and Heal, O.W. (1990) Nutrient Cycling in a Terrestrial Ecosystem. London: Elsevier Applied Science, pp.69-73.

Hem, J.D. (1970) Study and interpretation of the chemical characteristics of natural water (2nd ed): U.S Geological Survey Water Supply Paper 1473, 363.

Hicks, B.B., Wesley, M.L., Lindberg, S.E. and Bromberg, S.M. (Eds) (1986) Proceedings of the Dry Deposition Workshop of the National Acid Precipitation Assessment Program. March 1986. NOAA/ATDD, PO Box 2456, Oak Ridge, TN 37831.

Hicks, B.B. and Matt, D.R. (1988) Combining biology, chemistry, and meteorology in modelling dry deposition. *J Atmosph. Chem.* **6**: 177-133.

Holland, H.D. 1978. The chemistry of the atmosphere and oceans. New York: John Wiley. 351 pp.

Johnson, Likens, G.E, Bormann, F.H. and Pierce, R.S. (1968) Rate of chemical weathering of silicate minerals in New Hampshire. *Geochem. Cosmochim. Acta* **32**: 531-545.

Lee, Richard (1970) Theoretical estimates versus forest water yield. *Water Resources Res.* **6**: 1327-1334.

_____(1980) Forest Hydrology. New York, New York: Columbia University Press, 34-71,154-180.

Likens, Gene E., Bormann, H.F., Pierce, R.S, Eaton, J.S. and Noye, J.M. (1977) Biogeochemistry of a Forested Ecosystem. New York, New York: Springer- Verlag,

Lindsey, Ray, Kohler, Max, and Paulhus, Joseph (1958) Hydrology for Engineers. New York, New York: McGraw Hill Book Company, Inc.,

McRae, G.J. and Russel, A.G. (1984) Dry Deposition of Nitrogen-Containing Species. In: Deposition Both Wet and Dry. Boston, Mass.:Butterworth Publications, 153-193.

Neumann, H.H.and den Hartog, G. (1985) Eddy correlation measurements of atmospheric ozone, sulphur, and particulates during the Champaign intercomparison study. *J. Geophys. Res.* **90**: 2097-2110.

Newson, Malcolm (1994) Hydrology and the River Environment. Oxford: Clarendon Press, 155.

Peters, N.E. (1991) Chloride cycling in 2 forested lake watersheds in the west-central Adirondack Mountains, New York, USA. *Wat. Air Soil Poll.* **59:** 201-215.

Pomeroy, R.D. and Orlob, G.T. (1976) Problems of setting standards and of surveillance for water quality control. California State Water Control Commision, Publ. No. 36, Sacramento, CA.

Rantz, S.E. (1982) Measurement and computation of streamflow: volume 2. Computation of discharge. U.S. Geological Water-Supply Paper 2175.

Schneider, W.A., Moss, J.J. and Dillon, P.J. (1979) Measurement and uses of hydraulic and nutrient budgets. US EPA 440/5-79-001, Washington D.C..

Appendix A

Black Rock Brook chloride concentrations sampled weekly- 1994				
Month	Sample	Date	ppm Cl-	stdev *
Jan	brb 1	94004	16.06	0.3
	brb 2	94011	16.15	0.28
	brb 3	94018	16.12	0.16
	brb 4	94025	16.13	0.13
	brb 5	94032	22.65	0.39
average		17.42		
stdev			2.92	
max			22.65	
min			16.06	
Feb	brb 6	94039	27.63	0.29
	brb 9	94060	3.13	0.1
average		15.38		
stdev			17.33	
max			27.63	
min			3.13	
March	brb 11	94074	2.88	0.12
	brb 12	94081	2.68	0.04
	brb 13	94088	2.09	0.05
average		2.55		
stdev			0.41	
max			2.88	
min			2.09	
April	brb 14	94095	1.97	0.11
	brb 15	94102	1.99	0.23
	brb 16	94109	2.11	0.07
	brb 17	94116	1.79	0.1
average		1.97		
stdev			0.13	
max			2.11	
min			1.79	
May	brb 18	94123	2.14	0.1
	brb 19	94130	1.88	0.14
	brb 20	94137	1.81	0.04
	brb 21	94144	1.96	0.08
	brb 22	94151	1.83	0.09
average		1.92		
stdev			0.13	
max			2.14	
min			1.81	

June	brb 23	94158		1.85	0.04
	brb 24	94165		1.65	0.07
	brb 25	94172		1.86	0.07
	brb 26	94179		1.58	0.07
average			1.74		
stdev				0.14	
max				1.86	
min				1.58	
July	brb 27	94186		1.31	0.6
	brb 28	94193		1.97	0.04
	brb 29	94200		1.77	0.21
	brb 30	94207		1.62	0.16
average			1.67		
stdev				0.28	
max				1.97	
min				1.31	
August	brb 31	94214		1.78	0.02
	brb 32	94221		1.96	0.03
	brb 33	94228		1.85	0.02
	brb 34	94235		1.64	0.06
	brb 35	94242		1.85	0.08
average			1.81		
stdev				0.12	
max				1.96	
min				1.64	
Sept	brb 36	94249		1.62	0
	brb 37	94256		1.68	0.04
	brb 38	94263		1.71	0.04
	brb 39	94270		1.76	0.02
average			1.69		
stdev				0.06	
max				1.76	
min				1.62	
Oct	brb 40	94277		1.51	0.37
	brb 41	94284		1.90	0.04
	brb 42	94291		1.90	0.12
	brb 43	94298		2.03	0.12
	brb 44	94305		2.24	0.14
average			1.91		
stdev				0.26	
max				2.24	
min				1.51	
Nov	brb 45	94312		1.94	0.09
	brb 46	94319		1.94	0.09
	brb 47	94326		2.10	0.11
	brb 48	94333		1.88	0.08
average			1.96		
stdev				0.10	

max				2.10	
min				1.88	
Dec	brb 49	94340		1.99	0.05
	brb 50	94347		1.82	0.03
	brb 51	94354		2.01	0.15
	brb 52	94361		1.85	0.06
average			1.91		
stdev				0.10	
max				2.01	
min				1.82	
annual	averagew/highs		4.03		
	stdev			5.92	
	averagew/o highs		1.93		
	stdev			0.33	
	max	w/highs		27.63	
	min			1.31	
	max	w/o highs		3.13	

Appendix B

Table 2a: Canterbury Brook chloride concentrations sampled weekly- 1994					
	Sample	date		ppm Cl-	
Jan	cant 1	94004		2.63	0.06
	cant 2	94011		2.8	0.14
	cant 3	94018		2.76	0.08
	cant 4	94025		2.81	0.08
	cant 5	94032		2.46	0.13
average			2.69		
stdev				0.15	
max				2.81	
min				2.46	
Feb	cant 6	94039		2.65	0.09
	cant 7	94046		2.79	0.08
	cant 8	94053		2.26	0.09
	cant 9	94060		2.43	0.05
average			2.53		
stdev				0.23	
max				2.79	
min				2.26	
March	cant 10	94067		2.43	0.08
	cant 11	94074		2.24	0.03
	cant 12	94081		1.94	0.07
	cant 13	94088		1.77	0.03
average			2.09		
stdev				0.30	
max				2.43	
min				1.77	
April	cant 14	94095		1.68	0.05
	cant 15	94102		1.96	0.08
	cant 16	94109		1.85	0.08
	cant 17	94116		1.95	0.09
average			1.86		
stdev				0.13	
max				1.96	
min				1.68	
May	cant 18	94123		2.10	0.09
	cant 19	94130		1.97	0.12
	cant 20	94137		1.77	0.1
	cant 21	94144		1.99	0.06
	cant 22	94151		2.3	0.15
average			2.03		
stdev				0.19	

max				2.30	
min				1.77	
June	cant 23	94158		2.20	0.03
	cant 24	94165		2.02	0.06
	cant 25	94172		2.21	0.05
	cant 26	94179		1.81	0.02
average			2.06		
stdev				0.19	
max				2.21	
min				1.81	
July	cant 27	94186		2.08	0.1
	cant 28	94193		2.00	0.08
	cant 29	94200		2.34	0.04
	cant 30	94207		2.36	0.18
average			2.20		
stdev				0.18	
max				2.36	
min				2.00	
August	cant 31	94214		2.10	0
	cant 32	94221		2.12	0.36
	cant 33	94228		2.00	0.09
	cant 34	94235		1.31	0.12
	cant 35	94242		1.98	0.04
average			1.90		
stdev				0.34	
max				2.12	
min				1.31	
Sept	cant 36	94249		2.22	0.1
	cant 37	94256		2.19	0.04
	cant 38	94263		2.30	0.08
	cant 39	94270		1.30	0.05
average			2.00		
stdev				0.47	
max				2.30	
min				1.30	
Oct	cant 40	94277		2.28	0.03
	cant 41	94284		2.10	0.01
	cant 42	94291		4.50	0.43
	cant 43	94298		0.69	0.15
	cant 44	94305		2.44	0.01
average			2.40		
stdev				1.36	
max				4.50	
min				0.69	
Nov	cant 45	94312		2.45	0.03
	cant 46	94319		2.38	0.04
	cant 47	94326		2.69	0.02

	cant 48	94333		2.32	0.13
average			2.46		
stdev				0.16	
max				2.69	
min				2.32	
Dec	cant 49	94340		2.30	0.01
	cant 50	94347		2.60	0.10
	cant 51	94354		1.87	0.18
	cant 52	94361		2.28	0.10
average			2.26		
stdev				0.30	
max				2.60	
min				1.87	
annual					
average			2.21		
stdev				0.51	
max				4.50	
min				0.69	

* of replicate sample tests

Appendix C

Cascade Brook chloride concentrations sampled weekly- 1994					
	Sample	Date	ppm Cl-	stdev *	
Jan	casc 01	94004	3.03		0.10
	casc 02	94011	2.61		0.02
	casc 03	94018	2.73		0.05
	casc 04	94025	3.12		0.05
	casc 05	94032	2.38		0.12
average				2.77	
stdev			0.30		
max			3.12		
min			2.38		
Feb	casc 06	94039	2.46		0.08
	casc 07	94046	2.67		0.11
	casc 08	94053	2.10		0.16
	casc 09	94060	2.43		0.06
average				2.42	
stdev			0.24		
max			2.67		
min			2.10		
March	casc 10	94067	2.17		0.03
	casc 11	94074	2.02		0.03
	casc 12	94081	1.98		0.06
	casc 13	94088	1.61		0.09
average				1.94	
stdev			0.24		
max			2.17		
min			1.61		
April	casc 14	94095	1.79		0.03
	casc 15	94102	1.95		0.06
	casc 16	94109	1.91		0.08
	casc 17	94116	1.95		0.00
average				1.90	
stdev			0.08		
max			1.95		
min			1.79		
May	casc 18	94123	1.90		0.05
	casc 19	94130	1.93		0.15
	casc 20	94137	1.73		0.03
	casc 21	94144	1.99		0.19
	casc 22	94151	2.12		0.2
average				1.93	
stdev			0.14		
max			2.12		

min			1.73		
June	casc 23	94158	2.18		0.02
	casc 24	94165	2.19		0.19
	casc 25	94172	2.23		0.12
	casc 26	94179	1.73		0.07
average				2.08	
stdev			0.23		
max			2.23		
min			1.73		
July	casc 27	94186	1.94		0.07
	casc 28	94193	2.10		0.06
	casc 29	94200	2.13		0.17
	casc 30	94207	2.35		0.04
average				2.13	
stdev			0.17		
max			2.35		
min			1.94		
August	casc 31	94216	1.95		0.2
	casc 32	94221	2.33		0.03
	casc 33	94228	2.09		0.01
	casc 34	94235	1.26		0.1
	casc 35	94242	1.96		0.09
average				1.92	
stdev			0.40		
max			2.33		
min			1.26		
Sept	casc 36	94249	2.06		0.19
	casc 37	94256	2.19		0.08
	casc 38	94263	2.44		0.01
	casc 39	94270	1.21		0.05
average		1.97			
stdev			0.53		
max			2.44		
min			1.21		
Oct	casc 40	94277	2.56		0.05
	casc 41	94284	2.31		0.09
	casc 42	94291	2.40		0.18
	casc 43	94298	2.54		0.04
	casc 44	94305	2.29		0.3
average		2.42			
stdev			0.13		
max			2.56		
min			2.29		
Nov	casc 45	94312	2.67		0.06
	casc 46	94319	2.12		0.04
	casc 47	94326	2.41		0.02
	casc 48	94333	2.07		0.01
average		2.32			

stdev			0.28	
max			2.67	
min			2.07	
Dec	casc 49	94340	1.95	0.01
	casc 50	94347	2.28	0.04
	casc 51	94354	1.99	0.05
	casc 52	94361	2.35	0.03
average		2.14		
stdev			0.21	
max			2.35	
min			1.95	
annual average		2.17		
stdev			0.36	
max			3.12	
min			1.21	

* of replicate sample tests

Appendix D

Mineral Springs Brook chloride concentrations sampled weekly- 1994

Sample	date	ppm Cl-	stdev *
Jan	msb 01	94004	3.07	0.06
	msb 02	94011	2.75	0.06
	msb 03	94018	2.70	0.1
	msb 04	94025	2.79	0.08
	msb 05	94032	2.96	0.11
average		2.85		
stdev			0.15	
max			3.07	
min			2.70	
Feb	msb 06	94039	2.97	0.09
	msb 07	94046	2.50	0.07
	msb 08	94053	2.20	0.02
	msb 09	94060	2.56	0.16
average		2.56		
stdev			0.32	
max			2.97	
min			2.20	
March	msb 10	94067	2.13	0.05
	msb 11	94074	1.97	0.07
	msb 12	94081	1.91	0.11

average			1.92		
stdev				0.19	
max				2.13	
min				1.68	
April	msb 14	94095		2.00	0.22
	msb 15	94102		1.67	0.05
	msb 16	94109		1.72	0.04
	msb 17	94116		1.64	0.07
average			1.76		
stdev				0.16	
max				2.00	
min				1.64	
May	msb 18	94123		2.06	0.09
	msb 19	94130		1.95	0.06
	msb 20	94137		1.86	0.03
	msb 21	94144		1.72	0.02
	msb 22	94151		2.43	0.04
average			2.01		
stdev				0.27	
max				2.43	
min				1.72	
June	msb 23	94158		1.87	0.11
	msb 24	94165		1.87	0.02
	msb 25	94172		2.20	0.08
	msb 26	94179		2.00	0.07
average			1.99		
stdev				0.16	
max				2.20	
min				1.87	
July	msb 27	94186		1.82	0.08
	msb 28	94193		1.99	0.03
	msb 29	94200		1.86	0.04
	msb 30	94207		2.09	0.11
average			1.94		
stdev				0.12	
max				2.09	
min				1.82	
August	msb 31	94216		2.41	0.05
	msb 32	94221		2.39	0.05
	msb 33	94228		2.22	0.06
	msb 34	94235		1.19	0.15
	msb 35	94242		1.96	0.07
average			2.03		
stdev				0.50	
max				2.41	
min				1.19	
Sept	msb 36	94249		1.97	0.03
	msb 37	94256		2.16	0.06

	msb 38	94263		2.34	0.12
	msb 39	94270		1.77	0.03
average				2.06	
stdev					0.25
max					2.34
min					1.77
Oct	msb 40	94277		1.92	0.07
	msb 41	94284		2.11	0.01
	msb 42	94291		2.25	0.05
	msb 43	94298		4.01	0.22
	msb 44	94305		2.77	0.02
average			2.61		
stdev				0.84	
max				4.01	
min				1.92	
Nov	msb 45	94312		2.51	0.05
	msb 46	94319		2.27	0.03
	msb 47	94326		2.73	0.01
	msb 48	94333		2.33	0.12
average			2.46		
stdev				0.21	
max				2.73	
min				2.27	
Dec	msb 49	94340		2.18	0.13
	msb 50	94347		2.01	0.05
	msb 51	94354		2.03	0.06
	msb 52	94361		1.91	0.03
average			2.03		
stdev				0.11	
max				2.18	
min				1.91	
annual average			2.22		
stdev				0.50	
max				4.01	
min				1.19	

* of replicate sample tests

Appendix E

Black Rock Brook sulfate concentrations sampled weekly- 1994					
	Sample	Date		ppm	stdev
Jan	brb 1	94004		13.70	0
	brb 2	94011		13.90	0
	brb 3	94018		13.70	0.14
	brb 4	94025		13.90	0.42
	brb 5	94032		13.30	0.00
average			13.70		
stdev				0.24	
max				13.90	
min				13.30	
Feb	brb 6	94039		13.95	0.21
	brb 9	94060		13.30	0.00
average			13.63		
stdev				0.46	
max				13.95	
min				13.30	
March	brb 11	94074		13.10	0
	brb 12	94081		12.40	0
	brb 13	94088		10.40	0
average			11.97		
stdev				1.40	
max				13.10	
min				10.40	
April	brb 14	94095		10.15	0.07
	brb 15	94102		10.35	0.21
	brb 16	94109		9.90	0
	brb 17	94116		10.20	0
average			10.15		
stdev				0.19	
max				10.35	
min				9.90	
May	brb 18	94123		10.20	0
	brb 19	94130		10.05	0.08
	brb 20	94137		9.99	0.00
	brb 21	94144		9.90	0.11
	brb 22	94151		9.74	0
average			9.98		
stdev				0.17	
max				10.20	
min				9.74	
June	brb 23	94158		10.20	0
	brb 24	94165		9.90	0

	brb 25	94172		9.90	0
	brb 26	94179		9.42	0
average			9.86		
stdev				0.32	
max				10.20	
min				9.42	
July	brb 27	94186		8.61	0.00
	brb 28	94193		8.61	0
	brb 29	94200		8.16	0.13
	brb 30	94207		8.77	0.23
average			8.54		
stdev				0.26	
max				8.16	
min				8.77	
August	brb 31	94214		7.33	0.00
	brb 32	94221		7.43	0.26
	brb 33	94228		7.15	0.00
	brb 34	94235		7.79	0.00
	brb 35	94242		8.12	0.06
average			7.56		
stdev				0.39	
max				8.12	
min				7.15	
Sept	brb 36	94249		8.12	0.06
	brb 37	94256		8.07	0.00
	brb 38	94263		8.07	0.00
	brb 39	94270		7.93	0.06
average			8.05		
stdev				0.08	
max				8.12	
min				7.93	
Oct	brb 40	94277		8.02	0.07
	brb 41	94284		8.07	0.13
	brb 42	94291		8.43	0.25
	brb 43	94298		9.16	0.00
	brb 44	94305		9.53	0.00
average			8.64		
stdev				0.67	
max				9.53	
min				8.02	
Nov	brb 45	94312		8.57	0.06
	brb 46	94319		8.43	0.00
	brb 47	94326		8.68	0.25
	brb 48	94333		8.64	0.06
average			8.58		
stdev				0.11	
max				8.68	
min				8.43	

Dec	brb 49	94340	9.09	0.06
	brb 50	94347	9.18	0.06
	brb 51	94354	9.23	0.13
	brb 52	94361	9.41	0.00
averageaverage		9.22		
stdev	stdev		0.14	
max			9.41	
min			9.18	
annual				
average		9.80		
stdev			1.97	
max			13.95	
min			7.15	

* stdev of replicate samples

APPENDIX F

Table : Cl- & SO4--: a comparison of 1994 stream chemistry

	Sample	Date	ppm Cl-	ppm SO4--
Jan	brb 1	94004	16.06	13.70
	brb 2	94011	16.15	13.90
	brb 3	94018	16.12	13.70
	brb 4	94025	16.13	13.90
	brb 5	94032	22.65	13.30
average		17.42	13.70	
stdev			2.92	0.24
max			22.65	13.90
min			16.06	13.30
Feb	brb 6	94039	27.63	13.95
	brb 9	94060	3.13	13.30
average		15.38	13.63	
stdev			17.33	0.46
max			27.63	13.95
min			3.13	13.30
March	brb 11	94074	2.88	13.10
	brb 12	94081	2.68	12.40
	brb 13	94088	2.09	10.40
average		2.55	11.97	
stdev			0.41	1.40
max			2.88	13.10
min			2.09	10.40
April	brb 14	94095	1.97	10.15
	brb 15	94102	1.99	10.35
	brb 16	94109	2.11	9.90
	brb 17	94116	1.79	10.20
average		1.97	10.15	
stdev			0.13	0.19
max			2.11	10.35
min			1.79	9.90
May	brb 18	94123	2.14	10.20
	brb 19	94130	1.88	10.05
	brb 20	94137	1.81	9.99
	brb 21	94144	1.96	9.90
	brb 22	94151	1.83	9.74
average		1.92	9.98	
stdev			0.13	0.17
max			2.14	10.20

min				1.81		9.74
June	brb 23	94158		1.85		10.20
	brb 24	94165		1.65		9.90
	brb 25	94172		1.86		9.90
	brb 26	94179		1.58		9.42
average			1.74		9.86	
stdev				0.14		0.32
max				1.86		10.20
min				1.58		9.42
July	brb 27	94186		1.31		8.61
	brb 28	94193		1.97		8.61
	brb 29	94200		1.77		8.16
	brb 30	94207		1.62		8.77
average			1.67		8.54	
stdev				0.28		0.26
max				1.97		8.16
min		1.31		8.77		
August	brb 31	94214		1.78		7.33
	brb 32	94221		1.96		7.43
	brb 33	94228		1.85		7.15
	brb 34	94235		1.64		7.79
	brb 35	94242		1.85		8.12
average			1.81		7.56	
stdev				0.12		0.39
max				1.96		8.12
min				1.64		7.15
Sept	brb 36	94249		1.62		8.12
	brb 37	94256		1.68		8.07
	brb 38	94263		1.71		8.07
	brb 39	94270		1.76		7.93
average			1.69		8.05	
stdev				0.06		0.08
max				1.76		8.12
min				1.62		7.93
Oct	brb 40	94277		1.51		8.02
	brb 41	94284		1.90		8.07
	brb 42	94291		1.90		8.43
	brb 43	94298		2.03		9.16
	brb 44	94305		2.24		9.53
average			1.91		8.64	
stdev				0.26		0.67
max				2.24		9.53
min				1.51		8.02
Nov	brb 45	94312		1.94		8.57
	brb 46	94319		1.94		8.43
	brb 47	94326		2.10		8.68
	brb 48	94333		1.88		8.64
average			1.96		8.58	

stdev				0.10		0.11
max				2.10		8.68
min				1.88		8.43
Dec	brb 49	94340		1.99		9.09
	brb 50	94347		1.82		9.18
	brb 51	94354		2.01		9.23
	brb 52	94361		1.85		9.41
average			1.91		9.22	
stdev				0.10		0.14
max				2.01		9.41
min				1.82		9.18
annual	averagew/highs		4.03		9.80	
	stdev			5.92		1.97
	averagew/o highs		1.93		13.95	
	stdev			0.33		7.15
	max	w/highs		27.63		
	min			1.31		
	max	w/o highs		3.13		

APPENDIX G

West Point Precipitation 12 Year Annual Averages 1979-1992				
	Year	Cl mg/l	SO4 mg/l	Ppt cm
jun	1979	0.75	3.9	1.4
jul	1979	0.18	6.32	5.21
aug	1979	0.14	3.52	13.34
sep	1979	1.27	1.68	20.45
oct	1979	0.28	2.8	12.57
nov	1979	0.82	2.38	17.15
dec	1979	0.31	1.61	5.97
jan	1980	--	--	5.72
feb	1980	0.32	2.02	2.49
mar	1980	0.43	1.71	24.01
apr	1980	0.55	1.67	19.41
may	1980	0.28	5.17	6.61
ave		0.49	2.98	11.19
stdev		0.34	1.59	7.66
max		1.27	6.32	24.01
min		0.14	1.61	1.4
june	1980	0.34	4.86	9.78
jul	1980	0.21	4.28	8
aug	1980	0.22	6.49	4.7
sep	1980	0.34	3.78	4.7
oct	1980	0.46	2.26	9.88
nov	1980	0.25	1.65	11.25
dec	1980	0.41	2.82	1.85
jan	1981	1.82	1.72	7.62
feb	1981	2.47	1.86	22.71
mar	1981	1.1	4.3	2.77
apr	1981	0.3	3.81	9.35
may	1981	0.48	2.52	18.49
ave		0.7	3.36	9.26
stdev		0.73	1.48	6.13
max		2.47	6.49	22.71
min		0.21	1.65	1.85
jun	1981	0.22	7.63	6.27
jul	1981	0.41	2.24	11.2
aug	1981	0.3	5.22	2.79
sep	1981	0.19	2.99	7.09
oct	1981	0.16	2.73	13.08
nov	1981	0.45	3.66	3.4
dec	1981	0.14	1.88	12.9
jan	1982	0.38	1.49	13.39
feb	1982	0.43	1.27	6.54
mar	1982	0.28	3.4	5.77
apr	1982	0.41	2.42	13.54

may	1982	0.11	2.47	7.03
ave		0.29	3.12	8.58
stdev		0.12	1.77	4
max		0.45	7.63	13.54
min		0.11	1.27	2.79
jun	1982	0.06	1.46	17.32
jul	1982	0.11	4.13	16.29
aug	1982	0.04	2.7	12.17
sep	1982	0.3	2.72	6.3
oct	1982	0.43	2.87	3.28
nov	1982	0.24	0.88	10.72
dec	1982	1.29	1.56	3.33
jan	1983	0.29	1.06	10.08
feb	1983	1.07	1.6	12.4
mar	1983	0.37	1.24	33.38
apr	1983	0.21	1.76	30.96
may	1983	0.25	3.27	12.01
ave		0.39	2.10	14.02
stdev		0.39	1.01	9.55
max		1.29	4.13	33.38
min		0.04	0.88	3.28
jun	1983	0.16	2.91	4.86
jul	1983	0.08	4.02	10.19
aug	1983	0.28	3.35	7.57
sep	1983	0.38	1.39	9.07
oct	1983	0.36	1.1	15.24
nov	1983	0.42	1.74	15.77
dec	1983	1.18	1.37	23.37
jan	1984	0.61	1.69	3.53
feb	1984	1.57	1.71	10.62
mar	1984	0.12	1.25	16.92
apr	1984	0.28	1.53	20.32
may	1984	0.25	2.31	14.22
ave		0.47	2.03	12.64
stdev		0.45	0.93	6.06
max		1.57	4.02	23.37
min		0.08	1.1	3.53
jun	1984	0.19	1.86	21.87
jul	1984	0.16	2.71	17.55
aug	1984	0.13	2.91	12.51
sep	1984	0.15	2.34	1.65
oct	1984	0.28	3.12	3
nov	1984	1.03	1.4	8.26
dec	1984	0.34	2.42	5.92
jan	1985	0.36	2.35	2.21
feb	1985	0.61	1.12	5.72
mar	1985	0.41	2.89	5.97
apr	1985	0.52	3.92	3.19
may	1985	0.17	2.22	17.75
ave		0.36	2.44	8.8
stdev		0.26	0.76	6.92
max		1.03	3.92	21.87

min		0.13	1.12	1.65
jun	1985	0.15	2.68	10.9
jul	1985	0.13	3.49	12.35
aug	1985	0.26	3.78	8.46
sep	1985	0.61	2.18	14.91
oct	1985	0.5	3.36	3.96
nov	1985	0.19	1.86	18.49
dec	1985	0.7	3.16	4.19
jan	1986	0.54	1.61	13.23
feb	1986	0.22	1.96	8.15
mar	1986	0.46	2.56	6.48
apr	1986	0.38	4.06	9.97
may	1986	0.33	6.71	5.51
ave		0.38	3.12	9.72
stdev		0.19	1.38	4.48
max		0.7	6.71	18.49
min		0.13	1.61	3.96
jun	1986	0.16	3.69	15.24
jul	1986	0.43	3.76	15.24
aug	1986	0.18	4.41	9.65
sep	1986	0.34	6.37	3.48
oct	1986	0.19	2.73	6.02
nov	1986	0.31	1.23	16.1
dec	1986	0.66	1.16	14.02
jan	1987	0.38	1.38	12.42
feb	1987	0.49	1.43	4.75
mar	1987	0.64	1.57	7.52
apr	1987	0.5	1.53	20.66
may	1987	0.13	4.28	7.32
ave		0.37	2.80	11.04
stdev		0.18	1.69	5.35
max		0.66	6.37	20.66
min		0.13	1.16	3.48
jun	1987	0.23	5.4	7.09
jul	1987	0.24	4.95	8.13
aug	1987	0.18	4.36	11.51
sep	1987	0.28	1.65	18.85
oct	1987	0.2	1.42	16.79
nov	1987	0.98	1.6	8.79
dec	1987	0.35	2.77	4.5
jan	1988	0.28	1.23	7.01
feb	1988	0.45	1.72	8.89
mar	1988	0.21	2.76	5.59
apr	1988	0.33	3.41	6.02
may	1988	0.19	3.38	10.95
ave		0.33	2.89	9.51
stdev		0.22	1.44	4.41
max		0.98	5.4	18.85
min		0.18	1.23	4.5
jun	1988	0.32	4.02	1.47
jul	1988	0.14	4.34	18.24

aug	1988	0.49	2.4	10.9
sep	1988	0.23	1.53	8.56
oct	1988	0.53	1.46	6.53
nov	1988	0.42	1.07	22.33
dec	1988	0.91	2.93	2.11
jan	1989	0.88	2.85	3.66
feb	1989	0.51	3.12	5.33
mar	1989	0.32	2.37	9.22
apr	1989	0.28	2.72	9.98
may	1989	0.25	2.13	27.51
ave		0.44	2.58	10.49
stdev		0.24	0.98	8.18
max		0.91	4.34	27.51
min		0.14	1.07	1.47
jun	1989	0.31	3.33	24.26
jul	1989	0.39	3.13	6.81
aug	1989	0.22	1.3	9.04
sep	1989	0.99	1.72	18.9
oct	1989	0.29	1.28	16.69
nov	1989	0.47	1.49	9.7
dec	1989	0.49	1.59	3.6
jan	1990	0.41	1.48	11.94
feb	1990	0.38	2.54	8.53
mar	1990	0.3	2.35	10.11
apr	1990	0.32	2.46	6.2
may	1990	0.3	2.23	13.49
ave		0.41	2.08	11.61
stdev		0.2	0.70	5.89
max		0.99	3.33	24.26
min		0.22	1.28	3.6
jun	1990	0.15	4	13.82
jul	1990	0.21	2.82	9.79
aug	1990	0.17	2.56	24.56
sep	1990	0.29	2.6	4.29
oct	1990	0.87	1.24	16.33
nov	1990	1.32	1.58	18.7
dec	1990	0.68	1.55	10.24
jan	1991	0.4	0.71	4.65
feb	1991	0.47	3.2	4.72
mar	1991	0.57	1.52	13.18
apr	1991	0.33	1.91	8.9
may	1991	0.19	3.68	12.57
ave		0.47	2.28	11.81
stdev		0.35	1.02	6.11
max		1.32	4	24.56
min		0.15	0.71	4.29
jun	1991	0.16	1.77	8.92
jul	1991	0.23	4.57	13.16
aug	1991	0.22	2.26	11.75
sep	1991	0.12	2.22	15.06
oct	1991	0.65	2.79	10.95
nov	1991	0.25	1.44	12.12

dec	1991	0.26	1.63	5.13
jan	1992	0.66	1.44	6.81
feb	1992	0.4	2.55	5.36
mar	1992	0.88	1.76	13.11
apr	1992	0.51	4.43	7.75
may	1992	0.6	2.32	12.67
ave		0.41	2.43	10.23
stdev		0.24	1.06	3.33
max		0.88	4.57	15.06
min		0.12	1.44	5.13
annual average		0.42	2.63	10.68
stdev		0.34	1.28	56.18
max		2.47	7.63	33.38
min		0.04	0.71	1.4

APPENDIX H

West Point Precipitation Monthly averages

Summary Period	Year	Cl	SO4 mg/l	Ppt mg/l	cm
jan	1980		--	--	5.72
jan	1981		1.82	1.72	7.62
jan	1982		0.38	1.49	13.39
jan	1983		0.29	1.06	10.08
jan	1984		0.61	1.69	3.53
jan	1984		0.89	2.22	3.56
jan	1985		0.36	2.35	2.21
jan	1986		0.54	1.61	13.23
jan	1987		0.38	1.38	12.42
jan	1988		0.28	1.23	7.01
jan	1989		0.88	2.85	3.66
jan	1990		0.41	1.48	11.94
jan	1991		0.4	0.71	4.65
jan	1992		0.66	1.44	6.81
average		0.608	1.633	7.559	
stdev			0.417	0.566	3.962
feb	1980		0.32	2.02	2.49
feb	1981		2.47	1.86	22.71
feb	1982		0.43	1.27	6.54
feb	1983		1.07	1.6	12.4
feb	1984		1.57	1.71	10.62
feb	1984		1.64	1.95	11.38
feb	1985		0.61	1.12	5.72
feb	1986		0.22	1.96	8.15
feb	1987		0.49	1.43	4.75
feb	1988		0.45	1.72	8.89
feb	1989		0.51	3.12	5.33
feb	1990		0.38	2.54	8.53
feb	1991		0.47	3.2	4.72
feb	1992		0.4	2.55	5.36
average		0.788	2.004	8.399	
stdev			0.659	0.637	5.008
mar	1980		0.43	1.71	24.01
mar	1981		1.1	4.3	2.77
mar	1982		0.28	3.4	5.77
mar	1983		0.37	1.24	33.38
mar	1984		0.12	1.25	16.92
mar	1984		0.21	1.32	16.15
mar	1985		0.41	2.89	5.97
mar	1986		0.46	2.56	6.48
mar	1987		0.64	1.57	7.52
mar	1988		0.21	2.76	5.59
mar	1989		0.32	2.37	9.22
mar	1990		0.3	2.35	10.11
mar	1991		0.57	1.52	13.18
mar	1992		0.88	1.76	13.11

average		0.45	2.214	12.16	
stdev			0.272	0.908	8.359
apr	1980		0.55	1.67	19.41
apr	1981		0.3	3.81	9.35
apr	1982		0.41	2.42	13.54
apr	1983		0.21	1.76	30.96
apr	1984		0.28	1.53	20.32
apr	1984		0.38	1.74	21.63
apr	1985		0.52	3.92	3.19
apr	1986		0.38	4.06	9.97
apr	1987		0.5	1.53	20.66
apr	1988		0.33	3.41	6.02
apr	1989		0.28	2.72	9.98
apr	1990		0.32	2.46	6.2
apr	1991		0.33	1.91	8.9
apr	1992		0.51	4.43	7.75
average		0.379	2.669	13.42	
stdev			0.105	1.053	7.92
may	1980		0.28	5.17	6.61
may	1981		0.48	2.52	18.49
may	1982		0.11	2.47	7.03
may	1983		0.25	3.27	12.01
may	1984		0.25	2.31	14.22
may	1984		0.26	2.51	14.12
may	1985		0.17	2.22	17.75
may	1986		0.33	6.71	5.51
may	1987		0.13	4.28	7.32
may	1988		0.19	3.38	10.95
may	1989		0.25	2.13	27.51
may	1990		0.3	2.23	13.49
may	1991		0.19	3.68	12.57
may	1992		0.6	2.32	12.67
average		0.271	3.229	12.88	
stdev			0.132	1.35	5.793
jun	1979		0.75	3.9	1.4
jun	1980		0.34	4.86	9.78
jun	1981		0.22	7.63	6.27
jun	1982		0.06	1.46	17.32
jun	1983		0.16	2.91	4.86
jun	1984		0.12	1.71	24.18
jun	1984		0.19	1.86	21.87
jun	1985		0.15	2.68	10.9
jun	1986		0.16	3.69	15.24
jun	1987		0.23	5.4	7.09
jun	1988		0.32	4.02	1.47
jun	1989		0.31	3.33	24.26
jun	1990		0.15	4	13.82
jun	1991		0.16	1.77	8.92
average		0.237	3.516	11.96	
stdev			0.168	1.694	7.77
jul	1979		0.18	6.32	5.21
jul	1980		0.21	4.28	8
jul	1981		0.41	2.24	11.2
jul	1982		0.11	4.13	16.29
jul	1983		0.08	4.02	10.19

jul	1984		0.16	2.44	17.35
jul	1984		0.16	2.71	17.55
jul	1985		0.13	3.49	12.35
jul	1986		0.43	3.76	15.24
jul	1987		0.24	4.95	8.13
jul	1988		0.14	4.34	18.24
jul	1989		0.39	3.13	6.81
jul	1990		0.21	2.82	9.79
jul	1991		0.23	4.57	13.16
average		0.22	3.8	12.11	
stdev			0.113	1.107	
aug	1979		0.14	3.52	13.34
aug	1980		0.22	6.49	4.7
aug	1981		0.3	5.22	2.79
aug	1982		0.04	2.7	12.17
aug	1983		0.28	3.35	7.57
aug	1984		0.16	3.19	11.41
aug	1984		0.13	2.91	12.51
aug	1985		0.26	3.78	8.46
aug	1986		0.18	4.41	9.65
aug	1987		0.18	4.36	11.51
aug	1988		0.49	2.4	10.9
aug	1989		0.22	1.3	9.04
aug	1990		0.17	2.56	24.56
aug	1991		0.22	2.26	11.75
average		0.214	3.461	10.74	
stdev			0.104	1.333	4.993
sep	1979		1.27	1.68	20.45
sep	1980		0.34	3.78	4.7
sep	1981		0.19	2.99	7.09
sep	1982		0.3	2.72	6.3
sep	1983		0.38	1.39	9.07
sep	1984		0.19	2.39	1.96
sep	1983		0.31	1.17	8
sep	1984		0.15	2.34	1.65
sep	1985		0.61	2.18	14.91
sep	1986		0.34	6.37	3.48
sep	1987		0.28	1.65	18.85
sep	1988		0.23	1.53	8.56
sep	1989		0.99	1.72	18.9
sep	1990		0.29	2.6	4.29
sep	1991		0.12	2.22	15.06
average		0.337	2.504	9.551	
stdev			0.223	1.313	5.902
oct	1979		0.28	2.8	12.57
oct	1980		0.46	2.26	9.88
oct	1981		0.16	2.73	13.08
oct	1982		0.43	2.87	3.28
oct	1983		0.36	1.1	15.24
oct	1983		0.36	1.04	15.01
oct	1984		0.28	3.12	3
oct	1985		0.5	3.36	3.96
oct	1986		0.19	2.73	6.02
oct	1987		0.2	1.42	16.79
oct	1988		0.53	1.46	6.53

oct	1989		0.29	1.28	16.69
oct	1990		0.87	1.24	16.33
oct	1991		0.65	2.79	10.95
average		0.65	2.79	10.67	
stdev			0.196	0.849	5.209
nov	1979		0.82	2.38	17.15
nov	1980		0.25	1.65	11.25
nov	1981		0.45	3.66	3.4
nov	1982		0.24	0.88	10.72
nov	1983		0.42	1.74	15.77
nov	1983		0.45	1.56	16.81
nov	1984		1.03	1.4	8.26
nov	1985		0.19	1.86	18.49
nov	1986		0.31	1.23	16.1
nov	1987		0.98	1.6	8.79
nov	1988		0.42	1.07	22.33
nov	1989		0.47	1.49	9.7
nov	1990		1.32	1.58	18.7
nov	1991		0.25	1.44	12.12
average		0.543	1.681	13.54	
stdev			0.351	0.672	5.165
dec	1980		0.41	2.82	1.85
dec	1981		0.14	1.88	12.9
dec	1982		1.29	1.56	3.33
dec	1983		1.18	1.37	23.37
dec	1983		1.13	1.24	23.49
dec	1984		0.34	2.42	5.92
dec	1985		0.7	3.16	4.19
dec	1986		0.66	1.16	14.02
dec	1987		0.35	2.77	4.5
dec	1988		0.91	2.93	2.11
dec	1989		0.49	1.59	3.6
dec	1990		0.68	1.55	10.24
dec	1991		0.26	1.63	5.13
average		0.629	1.896	8.891	
stdev			0.368	0.77	7.328

APPENDIX I
Calculation of Runoff Ratio

	ET m		Ppt m	Ppt m/m2		Runoff m	Runoff m/m2		Runoff Ratio
Jan	0.0150		0.0756	7.53E-09		0.0606	6.04E-09		0.80
Feb	0.0180		0.0840	8.37E-09		0.0660	6.57E-09		0.79
March	0.0280		0.1216	1.21E-08		0.0936	9.32E-09		0.77
April	0.0510		0.1342	1.34E-08		0.0832	8.29E-09		0.62
May	0.0810		0.1288	1.28E-08		0.0478	4.76E-09		0.37
June	0.1090		0.1196	1.19E-08		0.0106	1.05E-09		0.09
July	0.1320		0.1211	1.21E-08		-0.0109	-1.1E-09		
Aug	0.1190		0.1074	1.07E-08		-0.0116	-1.2E-09		
Sept	0.0860		0.0955	9.51E-09		0.0095	9.46E-10		0.10
Oct	0.0610		0.1067	1.06E-08		0.0457	4.55E-09		0.43
Nov	0.0360		0.1354	1.35E-08		0.0994	9.9E-09		0.73
Dec	0.0200		0.0889	8.86E-09		0.0689	6.86E-09		0.78
sum	0.7560		1.3187	1.09E-07		0.5852	5.83E-08		
average	0.0630	0.1099	1.09E-08		0.0585	5.83E-09		0.55	
stdev	0.0417		0.0201	2.18E-09		0.0310	3.09E-09		0.28
max	0.1320		0.0201	1.35E-08		0.0994	9.90E-09		0.80
min	0.0150		0.0756	0.00E+00		0.0000	0.00E+00		0.00

Runoff Ratio= Runoff/meter: Rainfall/meter
In this case Black Rock Forest is 10040000 m2.

APPENDIX J

calculation of average chloride concentration using a weighted approach

Month	Black Rock Brook ppm Cl-	Canterbury Brook ppm Cl-	Cascade Brook ppm Cl-	Mineral Springs Brook ppm Cl-	Unweighted Average
Jan	17.42	2.69	2.77	2.85	6.43
Feb	15.38	2.53	2.42	2.56	5.72
March	2.55	2.09	1.94	1.92	2.13
April	1.97	1.86	1.90	1.76	1.87
May	1.92	2.03	1.93	2.01	1.97
June	1.74	2.06	2.08	1.99	1.97
July	1.67	2.20	2.13	1.94	1.98
Aug	1.81	1.90	1.92	2.03	1.92
Sept	1.69	2.00	1.97	2.06	1.93
Oct	1.91	2.40	2.42	2.61	2.34
Nov	1.96	2.46	2.32	2.46	2.30
Dec	1.91	2.26	2.14	2.03	2.09
average	4.33	2.21	2.16	2.18	2.72
stdev	5.66	0.26	0.27	0.34	1.58
max	17.42	2.69	2.77	2.85	6.43
min	1.67	1.86	1.90	1.76	1.87

	BRB x .2928	Cant x .2649	Casc x .1345	MSB x .3078	Weighted Average	Weighted w/ highs
Jan	0.81171	0.71329	0.37292	0.87764	2.78	7.06
Feb	0.73257	0.67064	0.32515	0.78694	2.52	6.29
March	0.74729	0.55463	0.26138	0.59200	1.71	2.16
April	0.57560	0.49271	0.25555	0.54147	1.46	1.87
May	0.56354	0.53669	0.25985	0.61724	1.51	1.98
June	0.50801	0.54569	0.28021	0.61200	1.49	1.95
July	0.48800	0.58146	0.28660	0.59738	1.51	1.95
Aug	0.53142	0.50363	0.25802	0.62583	1.45	1.92
Sept	0.49511	0.53024	0.26545	0.63322	1.45	1.92
Oct	0.56064	0.63609	0.32554	0.80332	1.72	2.33
Nov	0.57425	0.65109	0.31137	0.75609	1.73	2.29
Dec	0.56060	0.59916	0.28791	0.62502	1.60	2.07
ave	0.60	0.58	0.29	0.67	1.74	2.82
stdev	0.11	0.07	0.04	0.10	0.44	1.82
max	0.81	0.71	0.37	0.88	2.78	7.06
min	0.49	0.49	0.26	0.54	1.45	1.87

	%
BRB	0.2928
Cant	0.2649
Casc	0.1345
MSB	0.3078

APPENDIX K

estimates of streamflow

	Cant	Casc	BRB	MSB	Total	Cant/Casc	cant/cascflow: cant/casc area
	m3/month						
Jan	578158	350244	677734	714870	2321006	1.65	0.84
Feb	327671	242477	416208	439014	1425371	1.35	0.69
March	451670	315293	559882	590561	1917406	1.43	0.73
April	443449	339322	571422	602733	1956926	1.31	0.66
May	359710	291992	475742	501811	1629255	1.23	0.63
June	124661	103407	166490	175612	570170	1.21	0.61
July	59709	44418	76012	80178	260317	1.34	0.68
Aug	234030	214301	327282	345215	1120829	1.09	0.56
Sept	267234	102610	269987	284780	924612	2.60	1.32
Oct	207525	175486	279598	294919	957529	1.18	0.60
Nov	462381	357526	598532	631328	2049767	1.29	0.66
Dec	405584	294176	510825	538816	1749401	1.38	0.70

m3/yr	sum	3921782	2831252	4929715	5199837	16882586	
m3/m	ave	326815	235938	4108104	333201	406882	1.42	0.72
	stdev	152742	107684	186976	197222	640330	0.40	0.20
m3/m	max	578158	357526	677734	714870	2321006	2.60	1.32
m3/m	min	59709	44418	76012	80178	260317	1.09	0.56

Cant	Casc	BRB	MSB	BRF unweighted	BRFweighted
m3/month			flow estimate	flow estimate	
578158	350244	568761	599926	2321006	2097090
327671	242477	285940	301608	1425371	1157696
451670	315293	407755	430098	1917406	1604815
443449	339322	379651	400454	1956926	1562875
359710	291992	297955	314281	1629255	1263937
124661	103407	102038	107629	570169.6	437735
59709	44418	51947	54794	260316.7	210868
234030	214301	181704	191660	1120829	821696
267234	102610	357469	377056	924611.6	1104370
207525	175486	168096	177307	957528.6	728415
462381	357526	393528	415091	2049767	1628525
405584	294176	358048	377667	1749401	1435476
3921782	2831252	3552893	3747572	14053499	6101287
326815	235938	296074	312298	1171125	508441
152742	107684	147012	155067	545174	336869
578158	357526	568761	599926	2097090	998191
59709	44418	51947	54794	210868	95380

APPENDIX L

detemination of Chloride

Methods

The method used determines the chloride ion concentration by the coulometric titration of Cl- ions with Ag+ generated from a wire that sits in the sample. Coulometric analyses are based on the measurement of current and time needed to complete a chemical reaction. The Buchler-Cotlove instrument at Lamont automatically performs the titrations. The endpoint of the titration is determined amperometrically (by measurement of electric current). Detection limits are about .25 milliequivalents of Cl- and by adjusting sample volumes or the instruments sensitivity, the high range is 558.6 milliequivalents/L or the salinity of seawater. Precision is ±0.15% generally limited by pipetting errors.

Sample Collection

Samples were collected once each week and filtered, labelled and stored until analysis.

Sample Storage

Chloride samples should be stored in airtight , glass stoppered, impermeable glass bottles. Low-density plastic bottles should be avoided for long term storage. It is recommended that the samples be stored at room temperature and freezing or refrigeration is not recommended. If the samples containers are rinsed thoroughly with the sample, contamination is not a problem. Also, concentration by evaporation is the major source of error, therefore the airtight sample containers are needed.

General

The Buchler-Cotlove Chloridometer immerses two silver electrodes into the sample and passes an electrical current through the sample. Thus, silver cations are generated at the anode and the silver cations react with the chloride anions in the solution to cause silver chloride to precipitate out. Because silver cations are generated at a constant and known rate, the chloride anions are thus consumed at a known rate. When the chloride in solution has been removed, the endpoint has been reached. This is indicated by a quick rise in the current which is detected amperometrically by the silver sensing electrodes. A tiny switch detects the current and breaks the circuit. Therefore, the chloride anions in solution are proportional to the number of coulombs of current passed. The Buchler-Cotlove Chloridometer measures time.

Interferences

Ag+ titrations precipitate Br- and F- and thus measure total halides in each sample. Since Cl-, Br-, and F- in seawater are 558.6, .862, and .070 mmol/L the error due to Br- and F- amounts to less than .2%. Other more serious errors are incurred in samples containing sulfide or sulfhydryl groups. Some dissolved materials like organic compounds my complex Ag + and therefore interfere with the titration. Check for this by doing standard additions to several standards.

Ranges

Titrations are most accurate and precise if the titration times fall between 20-200 seconds. Therefore, adjusting the sample volume and/or generating current rate to fall within the prescribed range. If we have some idea before testing of what the chloride anion concentrations are going to be the procedure can be adjusted accordingly. If this is not the case, then the sample may have to be titrated more than once.

Materials

Buchler-Cotlove Chloridometer

Finn pipette for sample and standards

Pipetter tips

Reed pipettes for Cl- spike and reagent

tiny bulb pipette for gelatin 5ml?

Knox gelatin

Beaker for disposal of waste liquid

titration vials

Reagents

1. Pure H_2O free of Chloride anions- Double-deionized water is appropriate.

2. HNO_3 Reagent. To prepare the HNO_3 reagent add 6.4 milliliters of concentrated reagent grade HNO_3 to 900 milliliters of double-deionized water. Next, add 100 milliliters of regent-grade glacial acetic acid. Mix thoroughly and store in a glass bottle. Label and date.

3. NaCl Standard Note: 100mM/L=100meq/L. Dissolved 5.8450 g of dried, reagent-grade NaCl In double deionized water and dilute to 1L in a volumetric flask. This solution is used to check the calibration of the instrument. Store in tightly sealed bottles.

4. Gelatin- Add 1L of hot double distilled water to 6.2 grams of dry powder Knox Gelatin and heat to approximately 70-80°C and swirl until all of the powder is dissolved. Store the gelatin in a wide mouth glass bottle. Date and label. Store in the refrigerator. Enough gelatin for each days session should be spooned out of the refrigerated container into a glass beaker. Let the gelatin melt somewhat to soften it. Heating may be necessary. The dry powder consists of 60 grams of gelatin, 1 gram of thymel blue and 1 gram of thymel.

Procedure

1. Make sure the power switch is off. Clean the pair of sensing electrodes and the generating electrodes using silver polish. Make absolutely sure that the power switch is off whenever touching electrodes immersed in double distilled water.

2. To prepare a sample for testing, pipette in the desired amount of sample, then the chloride spike. Next add the HNO_3 reagent being sure to wash any of the chloride spike or sample

droplets that my have splashed onto the inside walls of the container. Last add 3 drops of gelatin. Whenever testing a new sample, be sure to fill the pipette with that sample and discard. Then repipette and use that sample. Pipetting skills are important and practice is the best way to get better. I practiced with my samples on a balance so I could rate my accuracy. Also, the tiniest drop hanging on the tip or clinging to the inside of the tip can ruin results. Change tips frequently and do not invert the pipetter. Keep it upright or horizontal when between samples.

3. Condition the electrodes by running several replicate titrations until results agree and then discard those results. The initial current should be less than 3 μamp. If it is not the electrodes need to be recleaned and reconditioned.

4. Place the titration vial containing the sample on the machine and place in the raised position. Set the selector switch to OFF. Turn the titration switch to ADJUST. The stirring mechanism will start and the current indicator needle will fall to less than 3 μamps.

5. Reset the timer to 0.0 seconds and set the adjustable red current indicator needle to 10μamps above the indicator pointer.

- After turning the titration switch to ADJUST, avoid a further delay of more than 20 seconds before starting the titration. It is not necessary to allow current indicator to fall to 3μamps before starting the titration, only that it fall below the cut-off switch.

The delay before the baseline current is reached is due to incomplete mixing, to the reaction between added Cl- ions and excess Ag+ from the preceding titration, and to the response time of the indicator electrodes. The baseline current increases during sequential titrations in the same vial, and the current rise at the end point increases somewhat faster. The gelatin ensures the dispersion of the AgCl precipitate, and prevents either Ag+ or Cl- sorption onto the AgCl miccelles by swamping their surface sites.

6. Turn the switch to TITRATE. The timer will start instantaneously with the generation of Ag+.

7. When titration stops, record the time.

8. If the sample vial is full or if the initial baseline current is too high, or if a noticeable AgCl precipitate is clouding the vial, remove the sample vial and add another. Rinse the electrodes with double-deionized water to avoid cross contamination.

9. Polish the silver electrodes at least once every 100 titrations.

10. It is necessary to clip off the end of the silver anode if it becomes thinner than a pin.

The particular machine used is somewhat old and seems tempermental. Due to electricity in the Geochemistry building, I feel from my experience that the machines accuracy is subject to available power and sometimes there seem to be surges or shortages of electricity. Also, the stirring mechanism has a knob which seems to determine the stirring rate. I liked to check this at the end of every titration and adjust its tightness to a certain desirable level which is slightly less than completely tight to maximize consistency. The machine gets tired if used too long. On days when I ran 100 samples I was unhappy with the large drift. Keeping the sampling at 60 runs per session seemed to be the best procedure.

Reference Froelich, Philip N. Determination of Chloride in Seawater and Estuarine Waters

APPENDIX M
determination of Sulfate

Equipment:
Stopwatch with sweep second hand
One 10 or 20 ml glass pipet
50,100,500,1000 ul Eppendorf pipets
Eppendorf pipet tips
Several (3 per sample/standard)
125 ml erlnmeyer flasks
5 cm spectophotometer cells
500 ml wash bottle filled with deionized water
600 ml beaker for waste
kimwipes
Thermometer (-10 to +160 degrees Celsius)
One 1000 ml erlenmeyer
2 magnetic stirring bars
1 magnetic stirrer
Spectrophotometer
1 stirrer/hotplate
1 1 liter volumetric flask
15 50 ml volumetric flasks
2 1 gallon storage bottles

Reagents:
Stock sulfate solution (about 1000mg/L) Dissolve 1.8141 gm of K2SO4 in distilled water and dilute to one liter

1 N HCl: Add 85 ml conc. HCl to 300 ml distilled water and dilute to 1 liter.

Stock Gelatin Solution: Dissolve 1.5 gm Difco-Bacto Gelatin in 500 ml of hot (about 70 degrees Celsius) distilled water, cool and store at 4 degrees celsius for at least 16 hours before use. (Bring water to 70 degrees on the stirrer/hotplate, move flask to cold magnetic stirrer, add gelatin, stir 15 minutes, let stand at room temperature for 15 more minutes, then put in refrigerator).
Stable for 28 days if kept cold. Store 150 ml aliquots in 250 ml plastic bottles in the refrigerator.

Barium/Gelatin Reagent: Bring 150 ml of stock gelatin solution to room temperature (by leaving it on a bench- DON'T cook it on a hotplate).
Add 1.5 gm BaCl2 H2O and stir for 1 hour. Let stand one additional hour at room temperature and then put in the refrigerator. Stable for 7 days if kept cold.

Procedure: Charge triplicate 125 ml erlenmeyer flasks with 20 aliquots of each sample/standard. Add 1000 ul of 1.0 N HCl to each flask and swirl to mix. This is

only necessary if the gelatin is very low in sulfate. Spike the solution with 50 uM/L conc.. ex: .5 ml spike of 2050 uM/L diluted with 20 ml of sample/standard-would equal an addition of 50 uM/L

At 1 minute intervals add 1000 ul of the Ba/Gelatin reagent to each flask, swirl to mix, then let stand to allow formation of $BaSO_4$ colloid. Measure the absorbance of each solution at 420 nm in 5 cm cells EXACTLY 30 minutes after adding the Ba/Gelatin reagent.

Swirl solution gently just before transferring to cell

Notes

1. Measure absorbances against deionized water using double beam instrument if available.
2. Calibration standards

Dilute	50 ul	1000 mg SO_4^{--}/L	to	50 ml	to make	1 ppm SO_4^{--}
"	100 ul	"	"	"	2 ppm	"
"	250 ul	"	"	"	5 ppm	"
"	500 ul	"	"	"	10 ppm	"
"	1000ul	"	"	"	20 ppm	"

3. Run full calibration curve once each time a new reagent is used. At other times the Blank, 5 ppm, and 20 ppm standards will suffice.
4. Detection Limit due to blank is .10-.15 ppm SO_4^{--}. No advantage is gained by using 10 cm cells.
5. Top end is about 50 ppm SO_4^{--}. Samples over 20 ppm should be diluted and run again.
6. Rinse all glassware thoroughly with deionized water immediately after use.

Reference: Tabatabai, M.A. (1974) A Rapid Method for Determination of Sulfate in Water Samples, *Environ. Lett,* 7(3), 237-243.