

APPENDIX B

Trends in Dissolved Chloride, Sulfate and Nitrate in Cascade and Canterbury Brooks at Black Rock Forest

1. INTRODUCTION

Weekly samples of surface waters from several watersheds in Black Rock Forest have been collected since the early 1990s. Chemical compositions of these samples offer opportunities to estimate the integrated effects of precipitation and dry fallout influxes of a number of ions. They can also provide insights about integrated effects of chemical weathering and biological processes occurring in this temperate forested ecosystem. Here we discuss a few aspects of anion chemical compositions in Cascade and Canterbury Brooks sampled during calendar year 1994. Cascade Brook lies in the southern part of BRF and has an appreciable area of forested wetlands between the headwaters and the point of sample collection, which has been selected as the site of a new discharge gauging station. This catchment is not part of the watershed for the Village of Cornwall and contains no natural ponds or artificial reservoirs. Soils and glacial tills are thin and rocky. In contrast, Canterbury Brook drains to the north, and has much thicker glacial tills. There are no appreciable natural wetlands, ponds or artificial reservoirs in the catchment of Canterbury Brook upstream of the sampling location.

2. INTERLABORATORY COMPARISON OF CHLORIDE CONCENTRATIONS

Samples of Cascade and Canterbury Brooks from calendar year 1994 have now been measured for chloride concentrations independently in two laboratories: Lamont-Doherty Earth Observatory (LDEO) of Columbia University (Palisades, NY) and the Institute of Ecosystem Studies (IES) in Millbrook, NY. The analytical method at LDEO was coulometric titration using a silver electrode. At IES, the water samples were analyzed by ion chromatography.

The range of chloride concentrations for these two streams was 1 to 5 ppm, with most values between 1.5 and 3 ppm (Fig 1A, 1B). Both sets of analytical results show appreciable decline in Cl^- from the beginning of January through the end of March and then nearly constant values through the remainder of the year, with the exception to a few large week-to-

week excursions during late summer and autumn. One sample from Cascade Brook (week 44) showed appreciable deviation between results from the two labs, but there were no other large differences in this group of approximately 100 samples. There appears to be a slight bias towards systematically lower concentrations in LDEO chloride results for Canterbury Brook (Fig 1B), but not for Cascade Brook (Fig 1A).

These same data can be examined with scatter plots of LDEO vs IES results (Figs 2A,2B). A least-squares linear regression for all data from Cascade Brook yields a slope of only 0.80, primarily due to the large discrepancy for data from week 44, where the LDEO value was appreciably lower than for IES (Fig 2A). The equivalent regression slope for Canterbury Brook was 0.94 (Fig 2B), consistent with the slight offset evident in the time series plots. Percentage differences of IES minus LDEO Cl concentrations for Canterbury Brook show no significant trend with time during 1994, and cover a range of analytical differences of about $\pm 7\%$ (Fig 3).

3. CHLORIDE AND SULFATE IN CASCADE AND CANTERBURY BROOKS

The concentrations of chloride in both streams were quite similar throughout most of 1994 (Fig 4A), with the exception of two samples in October, where values reported for Canterbury Brook showed appreciable deviation from the general trend. The concentrations for the first three months of the year were about 30% higher than during the subsequent six months. Week-to-week changes tended to be quite small compared to those typically observed for precipitation at West Point, indicating that the forested soils of the Hudson Highlands provide a significant buffer to rapid changes in stream compositions, even for ions such as chloride with little or no influence by biological processes.

The temporal patterns for sulfate were somewhat different from chloride, however (Fig 4B). Week-to-week concentrations were relatively stable in both streams as observed for chloride, but Cascade Brook was systematically lower in sulfate than Canterbury Brook. The deviation between the two streams was especially large during the period June - September, when Cascade Brook was up to 50% lower in sulfate. The ratios of sulfate to chloride in weekly samples from the two streams were quite similar from January through May (Fig 4C), and then decreased appreciably in Cascade Brook until approximately the beginning of November. These data indicate that a substantial fraction of sulfate

supplied by precipitation and dry fallout to Black Rock Forest has been removed from Cascade Brook during the warmer half of the year, but little removal is evident for Canterbury Brook. If chloride is assumed to be approximately conservative within the soils of BRF (ie. no significant sources other than atmospheric delivery and no storage in the biota or soils), there appears to be an appreciable sink for sulfate in the Cascade Brook catchment.

4. PRECIPITATION CHLORIDE AND SULFATE IN THE HUDSON HIGHLANDS

4.1 Bulk Precipitation Chloride and Sulfate at BRF in 1994

Samples of bulk precipitation were collected at the BRF headquarters site through most of 1994. The funnel used to collect the weekly samples was exposed continuously to the atmosphere and thus also includes contributions from any dry fallout which may have impacted on the collector prior to the last precipitation episode of the composite sample. Chloride concentrations were unusually high during a few weeks of 1994 (Fig 5A), especially during winter and early spring, but for most of the year were relatively constant and low. Sulfate had more frequent large week-to-week fluctuations than chloride, and was generally higher during the warm half of the year (Fig 5B). Ratios of sulfate to chloride were thus highest during late spring through autumn (Fig 5C). The seasons of highest sulfate to chloride ratio in 1994 precipitation at BRF were also those with the lowest values of this ratio in Cascade Brook samples. The seasonal trend in precipitation concentrations of chloride and sulfate would tend to offset the effects of any sink for sulfate in the soils. Clearly there must be important removal processes for sulfate in the Cascade Brook drainage basin.

4.2 Monthly Precipitation Chloride and Sulfate at West Point (1985-95)

Samples of precipitation from the West Point NADP collection site are for wet-only deposition. The collector opening is covered except during episodes of rain or snow and does not receive inputs from accumulated aerosol deposition on the collector between events. Monthly mean concentrations of sodium and chloride for the period 1985-1995 were lowest during May through August, and highest during September through May (Fig 6A). Sulfate and nitrate were highest from April through September (Fig 6B), opposite to the seasonal pattern for chloride.

4.3 Annual Chloride and Sulfate at West Point (1980-1991)

Amount-weighted mean annual concentrations of chloride and sulfate experienced appreciable variations from 1980 through 1991 (Table1), especially during the first four years (Fig 6C). The ratio of sulfate to chloride in these mean annual values for West Point averaged about 4.2 (equivalents units) (Fig 6D), appreciable greater than observed in Cascade Brook during warm months of the year.

5. NITRATE BEHAVIOR IN CASCADE AND CANTERBURY BROOKS

Nitrate concentrations in both streams were $< 8\mu\text{Eq/L}$ throughout 1994 (Fig 7A), with the highest values in Canterbury Brook during the first five months of the year. Although there were appreciable week-to-week variations in both catchments, the most significant aspect of the stream nitrate concentrations were their consistently low values.

Precipitation nitrate at the BRF headquarters site during 1994 showed considerable weekly fluctuations, with several samples exceeding $100\mu\text{Eq/L}$ (Fig 7B). Values were generally highest for warm season precipitation, as characterized the seasonal pattern of sulfate concentrations. When precipitation and stream nitrate concentrations are plotted on the same scale (Fig 7C), the dramatic removal of nitrate from precipitation when it reaches the soils of the Hudson Highlands is evident.

Nitrate and sulfate concentrations in weekly composite bulk precipitation at BRF during 1994 (Fig 8A) were strongly correlated ($r = 0.91$). Although there is clearly some removal of sulfate in the catchment of Cascade Brook, the magnitude of this sink is minor compared to that for nitrate. Scatter plots of nitrate vs sulfate for Cascade Brook (Fig 8B) and Canterbury Brook (Fig 8C), with a line representing the least squares slope for BRF precipitation, illustrate the very small fraction of precipitation nitrate which is exported from these catchments in streams. If the nitrate and sulfate data from 1994 for these two streams are examined together, Cascade Brook appears to have lower average concentrations of both ions than Canterbury Brook as occurred for sulfate, but the covariation of dissolved concentrations of this pair of ions in the two streams is not strong (Fig 8D).

Amount-weighted annual concentrations of nitrate and ammonia in West Point precipitation (1980-1991) have tended to vary together over

this 12 year period (Fig 9E), resulting in a relatively constant ratio of nitrate to ammonia delivered to BRF in precipitation (Fig 9F).

6. BUDGETS OF CHLORIDE, SULFATE AND NITRATE AT BRF

Data from Cascade and Canterbury Brooks in 1994 can be used as representative of stream discharge concentrations at BRF for comparison with precipitation concentrations at the West Point NADP station. Mean annual amount-weighted concentrations from West Point (1980-1991) are considered here as representative of wet-only deposition to BRF. Chloride is assumed to be conservative in the ecosystem, with influxes from the atmosphere exactly balanced by stream discharge (Table 2). Mean annual chloride concentration in Cascade Brook in 1994 (63 uEq/L) is 5.3 times West Point precipitation (11.8 uEq/L for 1980-1991). The equivalent ratio for Canterbury Brook is $67 \text{ uEq/L} / 11.8 \text{ uEq/L} = 5.7$. If annual discharge of water (mm/yr) from these two catchments is 50% of precipitation influx (mm/yr), then the expected concentration of chloride in the streams would be 2.0 times that of precipitation (Table 2). The "extra" chloride observed in the streams is assumed to be derived primarily from dry fallout, which includes impaction of aerosols plus gas-phase reactions with leaves and other parts of the ecosystem. The magnitude of the dry fallout component is estimated by difference, and then represented in terms of a multiple times mean annual precipitation concentration. For Cascade and Canterbury Brooks, these influxes are estimated, respectively, as 1.65 and 1.85 times West Point precipitation concentration (Table 2).

The same mean annual budget approach can be used for nitrate and sulfate, assuming the dry fallout influx relative to precipitation influx for sulfate and nitrate to be the same as for chloride (Table 2). The dry fallout component for these two ions cannot be estimated by difference, as for chloride, since they are clearly not conservative within the BRF ecosystem. The resultant stream discharge fractions estimated for sulfate by Cascade and Canterbury Brooks are 73% and 86%, respectively. The balance of 27% and 14% are assumed to be either stored in the soils and/or biota, or lost to the atmosphere by formation of gas phases such as H_2S . For nitrate the fractions exported as dissolved ions by the streams are very small (<5%), indicating that the BRF ecosystem is very efficient in retaining or returning to the atmosphere the fixed nitrogen influxes delivered by precipitation plus dry fallout.

7. CONCLUSIONS

Data for chloride, sulfate and nitrate in stream samples from Black Rock Forest in 1994, precipitation samples from BRF during the same year, and precipitation samples over a number of years from the NADP collection site at West Point have been examined to assess first order chemical budgets for these ions in two small forested watersheds. The following conclusions are based on these data:

- 1) Analytical results for chloride from approximately 100 water samples obtained in 1994 from Cascade and Canterbury Brooks and measured at LDEO by coulometric titration and IES by ion chromatography were in good agreement (range of $\pm 7\%$ for all but a few samples), with no significant systematic differences.
- 2) Chloride and sulfate concentration variations in both streams were relatively smooth through much of the year, with a few large weekly excursions, and somewhat higher values during the winter months of 1994.
- 3) Sulfate concentrations and sulfate to chloride ratios in Cascade Brook were significantly lower than Canterbury Brook during warm season months, indicating a substantial sink for sulfate in this catchment relative to that for Canterbury Brook. Sulfate reduction in the forested wetlands of Cascade Brook may be a plausible explanation for this difference.
- 4) Chloride concentrations in precipitation from BRF during 1994 were generally higher during cold months, while sulfate had the opposite seasonal pattern. These trends would tend to lead to higher sulfate to chloride ratios during warm month stream discharge, opposite to that observed in Cascade Brook.
- 5) Monthly patterns of wet-only precipitation samples from West Point (1985-1995) show higher chloride during cold months, plus higher sulfate and nitrate during warm months, as observed in the bulk precipitation data for BRF.
- 6) Nitrate concentrations in both streams were low throughout the year ($< 8 \mu\text{Eq/L}$), equivalent to a small fraction of that observed for

precipitation at both West Point and BRF.

7) Nitrate to sulfate ratios in both streams were much lower than in precipitation, consistent with removal of a large fraction of fixed nitrogen influxes by the biota, including possible losses to the atmosphere of N gases.

8) Dry fallout influx of chloride to BRF, estimated by differences between observed chloride concentrations for 1994 in Cascade and Canterbury Brooks and mean annual precipitation over 12 years at West Point (1980-1991), appear to be at least as large as precipitation influxes.

9) Losses of sulfate in the catchments of Cascade and Canterbury Brooks, probably due largely to sulfate reduction in wetlands during warm seasons, represented 14-27% of annual atmospheric influxes.

10) Losses of nitrate in the catchments of Cascade and Canterbury Brooks, probably due largely to uptake by the ecosystem biota, represented >95% of annual atmospheric influxes.

11) Choice of Cascade Brook as a site for continuous discharge gauging and chemical monitoring appears to offer good opportunities for assessing magnitudes of biological perturbations of both the sulfur and nitrogen cycles in forested ecosystems.

TABLE 1

West Point NADP Station 1980-1991 Annual Means of Precipitation Chemistry

Stat Code	Year	Ca (mg/l)	Mg (mg/l)	K (mg/l)	Na (mg/l)	NH4 (mg/l)	NO3 (mg/l)	Cl (mg/l)	SO4 (mg/l)	pH	Conduct (uS/cm)	Ppt (cm)	
51	1980	0.12	0.039	0.020	0.274	0.18	1.67	0.38	2.81	4.21	28.3	108.40	
51	1981	0.15	0.088	0.030	0.468	0.22	1.72	0.88	2.86	4.21	35.1	117.68	
51	1982	0.11	0.037	0.016	0.135	0.16	1.41	0.25	2.29	4.32	27.0	115.67	
51	1983	0.08	0.047	0.023	0.271	0.12	1.16	0.48	1.83	4.40	22.3	184.90	
99	1984	0.10	0.047	0.034	0.215	0.17	1.51	0.42	2.11	4.32	26.1	137.59	
99	1985	0.10	0.044	0.017	0.145	0.22	1.89	0.34	2.55	4.22	31.5	108.09	
99	1986	0.09	0.036	0.016	0.142	0.20	2.04	0.36	2.74	4.22	31.7	123.10	
99	1987	0.07	0.033	0.018	0.170	0.15	1.51	0.38	2.28	4.27	27.5	128.30	
99	1988	0.10	0.030	0.012	0.147	0.13	1.53	0.34	2.38	4.26	26.8	108.59	
99	1989	0.06	0.029	0.022	0.160	0.23	1.69	0.41	2.25	4.27	28.1	144.70	
99	1990	0.07	0.036	0.016	0.226	0.21	1.45	0.49	2.23	4.28	27.4	147.99	
99	1991	0.11	0.025	0.042	0.128	0.22	1.59	0.31	2.51	4.24	29.5	121.11	
51+99	'80-'91	0.10	0.041	0.022	0.207	0.18	1.60	0.42	2.40	4.27	28.4	128.84	
51	1980	(ueq/l) 6.00	(ueq/l) 3.20	(ueq/l) 0.51	(ueq/l) 11.91	(ueq/l) 10.00	(ueq/l) 26.94	(ueq/l) 10.70	(ueq/l) 58.54	(ueq/l) 61.65	sum pos 93.27	sum neg 96.18	net +,- -2.91
51	1981	(ueq/l) 7.50	(ueq/l) 7.21	(ueq/l) 0.77	(ueq/l) 20.35	(ueq/l) 12.22	(ueq/l) 27.74	(ueq/l) 24.79	(ueq/l) 59.58	(ueq/l) 61.65	sum pos 109.70	sum neg 112.11	net +,- -2.41
51	1982	(ueq/l) 5.50	(ueq/l) 3.03	(ueq/l) 0.41	(ueq/l) 5.87	(ueq/l) 8.89	(ueq/l) 22.74	(ueq/l) 7.04	(ueq/l) 47.71	(ueq/l) 47.86	sum pos 71.56	sum neg 77.49	net +,- -5.93
51	1983	(ueq/l) 4.00	(ueq/l) 3.85	(ueq/l) 0.59	(ueq/l) 11.78	(ueq/l) 6.67	(ueq/l) 18.71	(ueq/l) 13.52	(ueq/l) 38.13	(ueq/l) 39.81	sum pos 66.70	sum neg 70.36	net +,- -3.66
99	1984	(ueq/l) 5.00	(ueq/l) 3.85	(ueq/l) 0.87	(ueq/l) 9.35	(ueq/l) 9.44	(ueq/l) 24.35	(ueq/l) 11.83	(ueq/l) 43.96	(ueq/l) 47.86	sum pos 76.37	sum neg 80.14	net +,- -3.77
99	1985	(ueq/l) 5.00	(ueq/l) 3.61	(ueq/l) 0.43	(ueq/l) 6.30	(ueq/l) 12.22	(ueq/l) 30.48	(ueq/l) 9.58	(ueq/l) 53.13	(ueq/l) 60.26	sum pos 87.83	sum neg 93.19	net +,- -5.36
99	1986	(ueq/l) 4.50	(ueq/l) 2.95	(ueq/l) 0.41	(ueq/l) 6.17	(ueq/l) 11.11	(ueq/l) 32.90	(ueq/l) 10.14	(ueq/l) 57.08	(ueq/l) 60.26	sum pos 85.41	sum neg 100.13	net +,- -14.72
99	1987	(ueq/l) 3.50	(ueq/l) 2.70	(ueq/l) 0.46	(ueq/l) 7.39	(ueq/l) 8.33	(ueq/l) 24.35	(ueq/l) 10.70	(ueq/l) 47.50	(ueq/l) 53.70	sum pos 76.09	sum neg 82.56	net +,- -6.47
99	1988	(ueq/l) 5.00	(ueq/l) 2.46	(ueq/l) 0.31	(ueq/l) 6.39	(ueq/l) 7.22	(ueq/l) 24.68	(ueq/l) 9.58	(ueq/l) 49.58	(ueq/l) 54.95	sum pos 76.33	sum neg 83.84	net +,- -7.51
99	1989	(ueq/l) 3.00	(ueq/l) 2.38	(ueq/l) 0.56	(ueq/l) 6.96	(ueq/l) 12.78	(ueq/l) 27.26	(ueq/l) 11.55	(ueq/l) 46.88	(ueq/l) 53.70	sum pos 79.37	sum neg 85.68	net +,- -6.31
99	1990	(ueq/l) 3.50	(ueq/l) 2.95	(ueq/l) 0.41	(ueq/l) 9.83	(ueq/l) 11.67	(ueq/l) 23.39	(ueq/l) 13.80	(ueq/l) 46.46	(ueq/l) 52.48	sum pos 80.83	sum neg 83.65	net +,- -2.82
99	1991	(ueq/l) 5.50	(ueq/l) 2.05	(ueq/l) 1.07	(ueq/l) 5.57	(ueq/l) 12.22	(ueq/l) 25.65	(ueq/l) 8.73	(ueq/l) 52.29	(ueq/l) 57.54	sum pos 83.95	sum neg 86.67	net +,- -2.72
51+99	'80-'91	4.83	3.35	0.57	8.99	10.23	25.77	11.83	50.07	53.70	81.67	87.67	-5.99

TABLE 2

Black Rock Forest Concentrations of Chloride, Sulfate and Nitrate
 [Derived from first-order precipitation-stream composition budgets]

Budget Parameter	Chloride ($\mu\text{Eq/L}$)	Sulfate ($\mu\text{Eq/L}$)	Nitrate ($\mu\text{Eq/L}$)	SO ₄ /Cl	NO ₃ /Cl
West Point Precip ('80-'91)	11.8	50.1	25.8	4.25	0.51
Cascade Brook ('94) - observed	63	194	1.9	3.08	0.01
Canterbury Brook ('94) - observed	67	245	2.6	3.65	0.01
Cascade Brook ('94) - conservative*	63	266	137		
Canterbury Brook ('94) - conservative*	67	286	147		
Cascade Bk/WP Precip - observed	5.3	3.9	0.07		
Canterbury Bk/WP Precip - observed	5.7	4.9	0.10		
Expected Stream/Precip concentration [assuming $Q = 0.5 \times P(\text{mm/yr})$]	2.0	2.0	2.0		
Cascade Bk Dry Fallout (K x P concn)	1.65	1.65	1.65		
Canterbury Bk Dry Fallout (K x P concn.)	1.85	1.85	1.85		
Cascade Bk stream anion discharge	100%	73%	1.4%		
Cascade Bk basin storage + atm loss	0%	27%	98.6%		
Canterbury Bk stream anion discharge	100%	86%	1.8%		
Canterbury Bk basin storage + atm loss	0%	14%	98.2%		

*assumes no net ecosystem storage or loss to atmosphere

Fig. 1

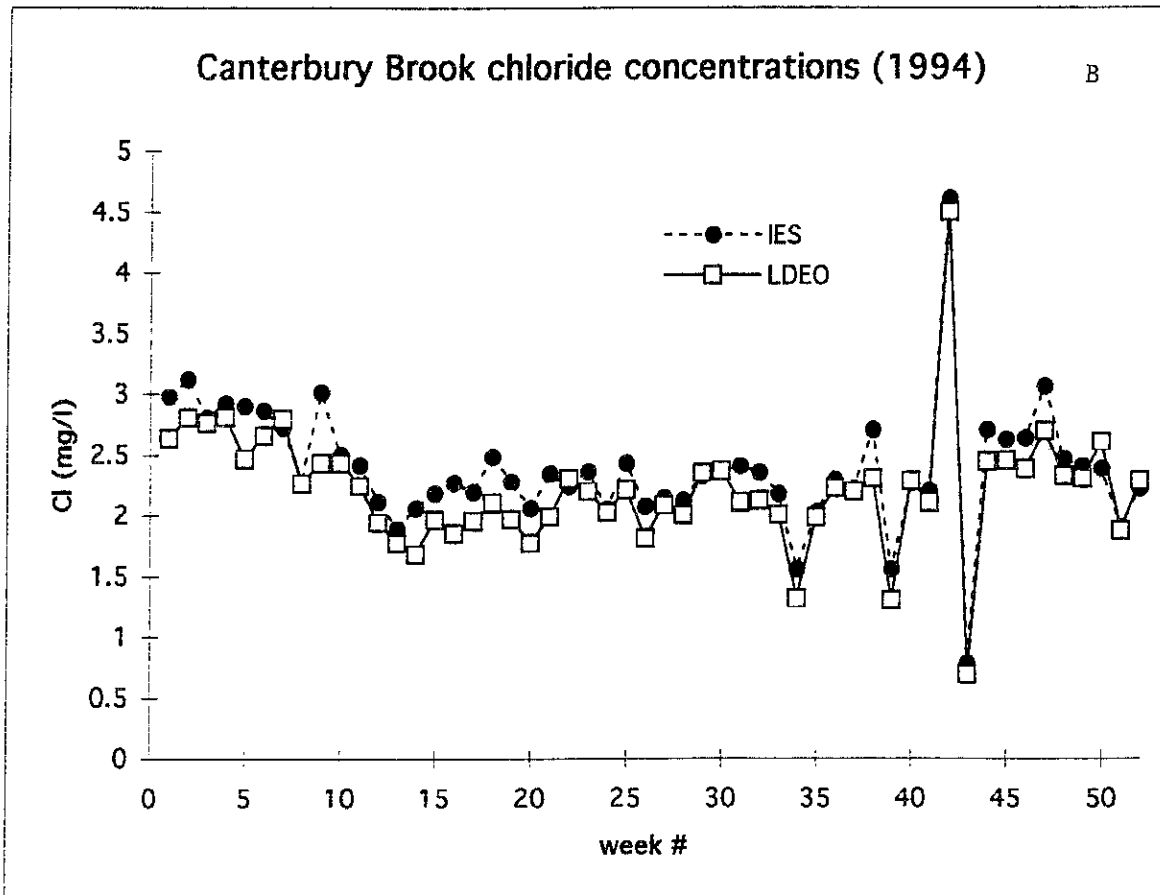
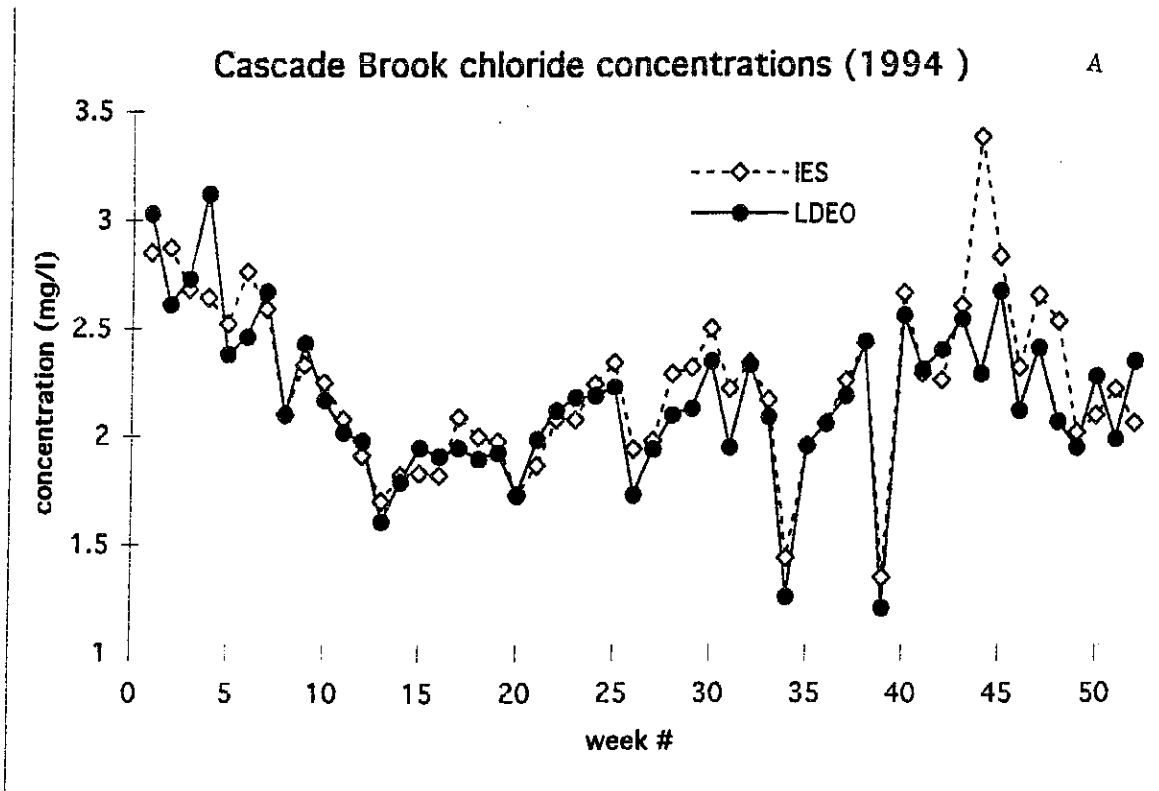
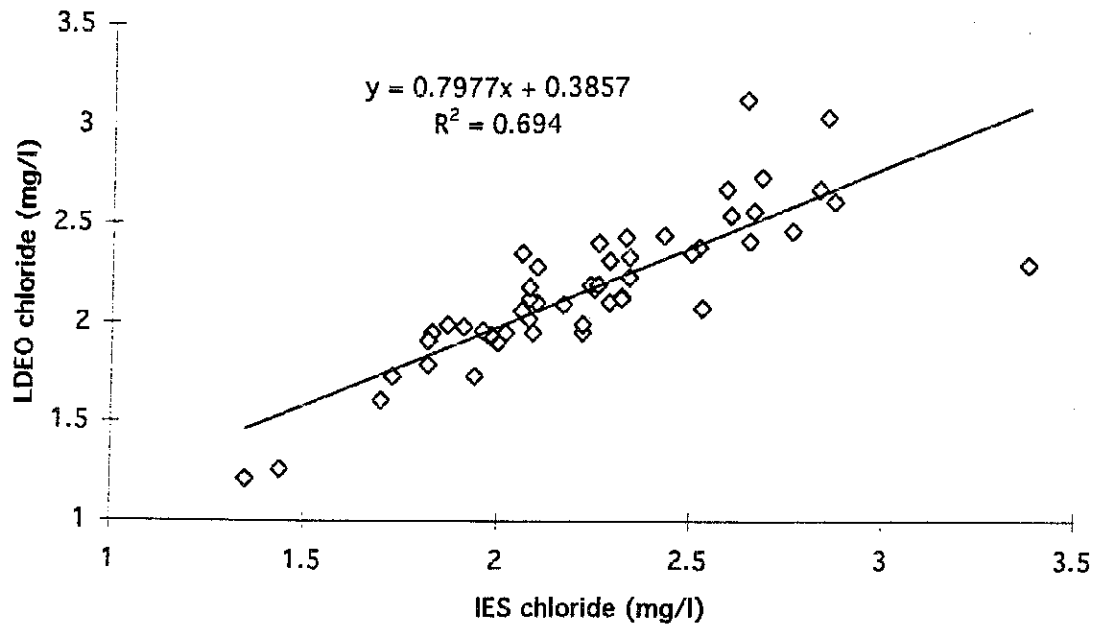


Fig. 2

Correlation of IES and LDEO chloride measurements
(Cascade Brook 1994)

A



Correlation of IES and LDEO chloride measurements
(Canterbury Brook 1994)

B

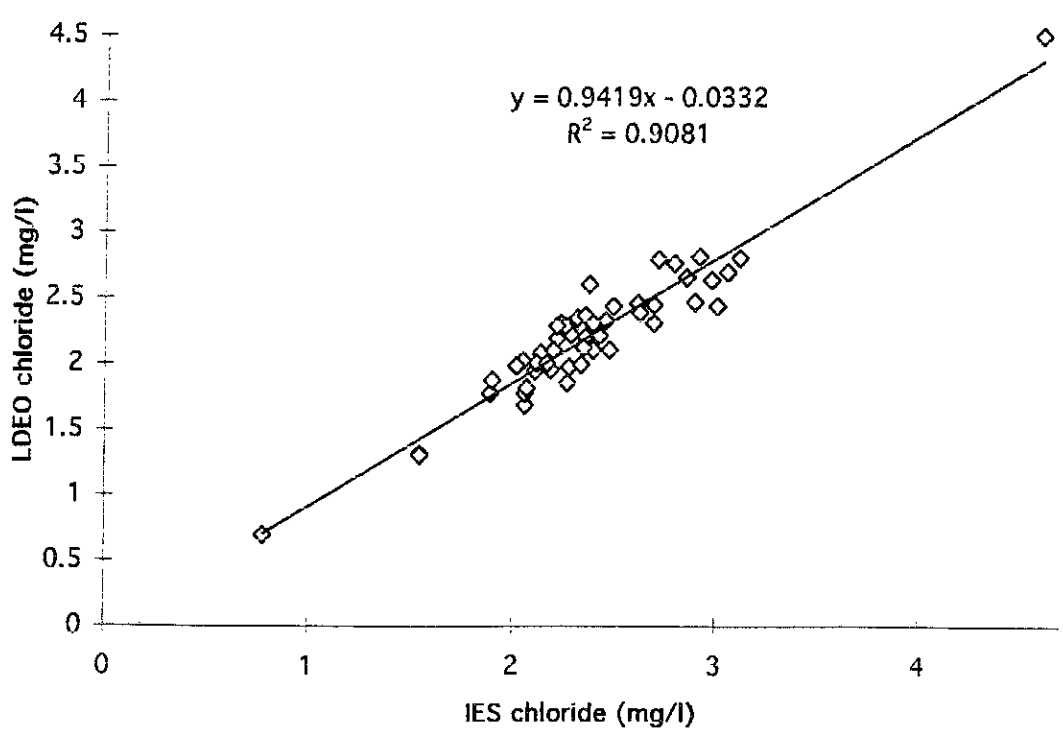
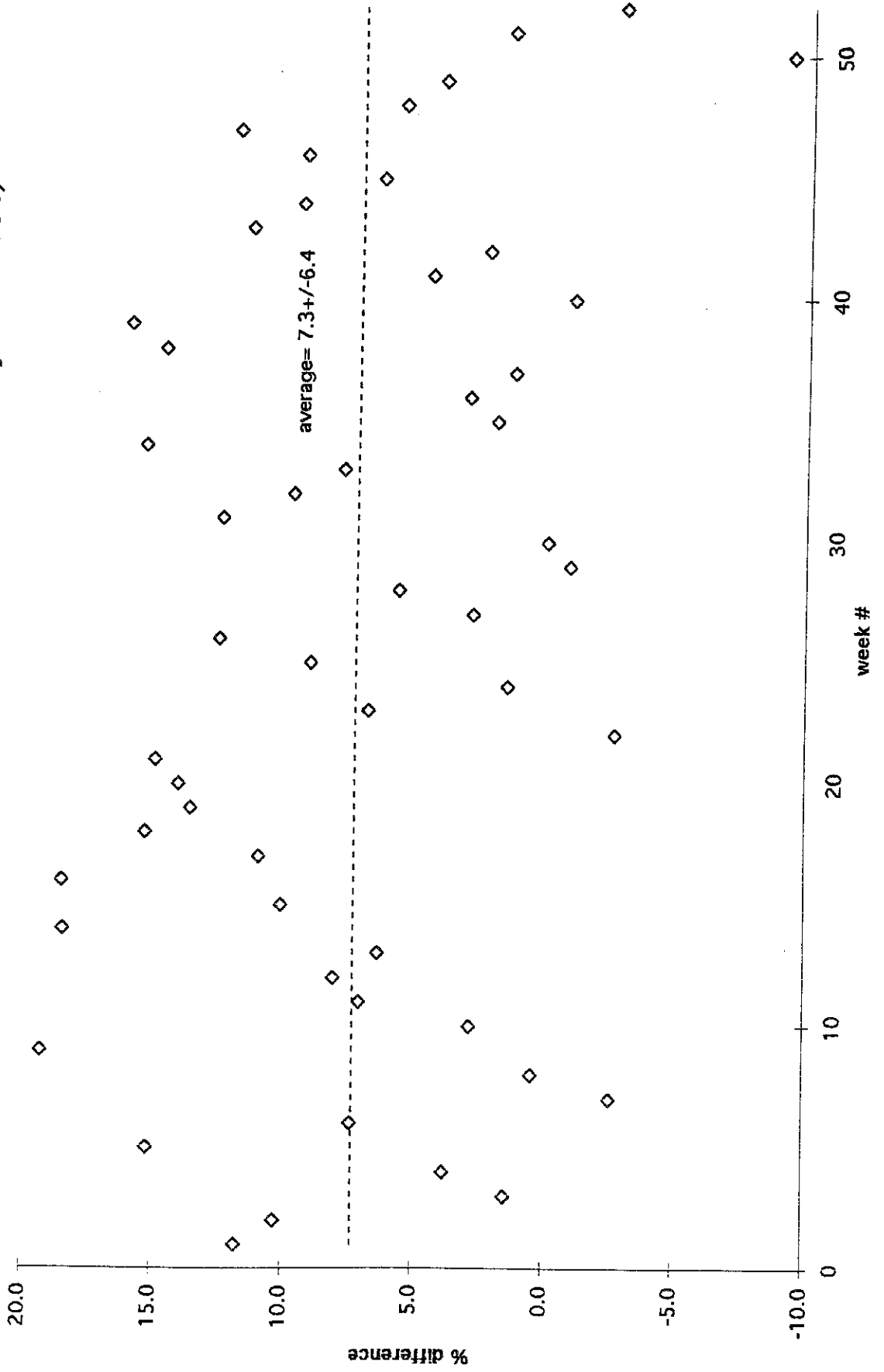
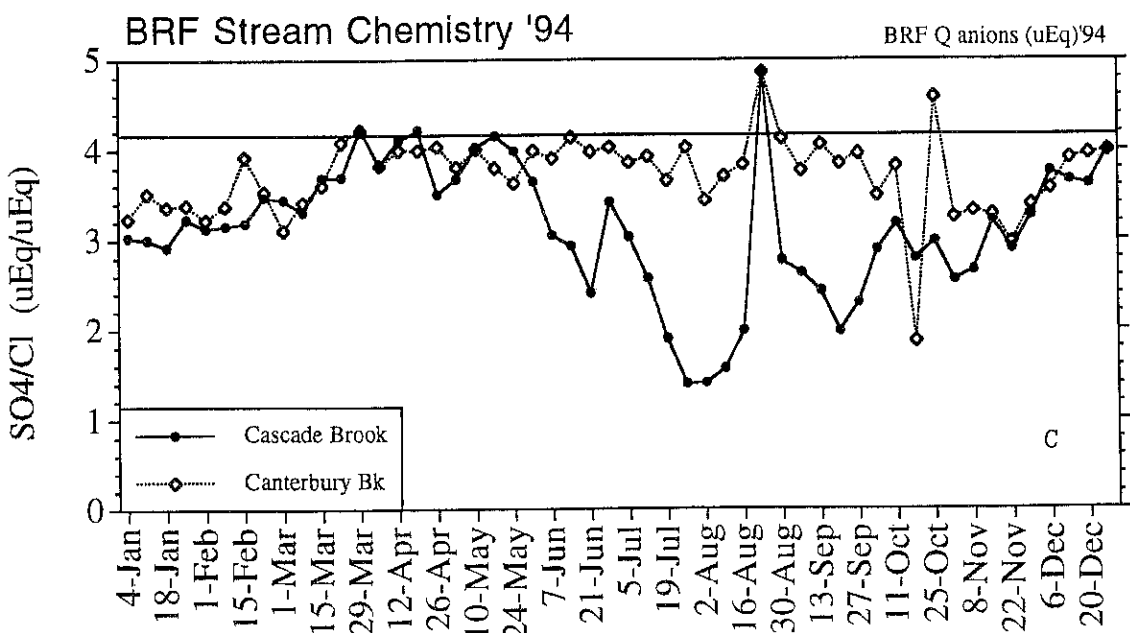
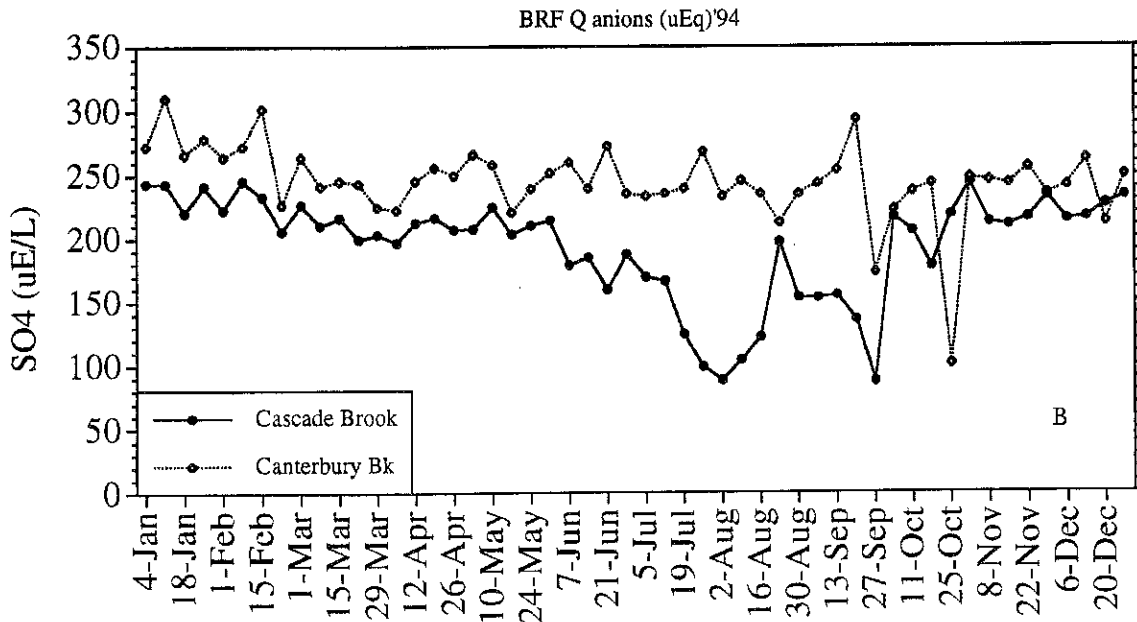
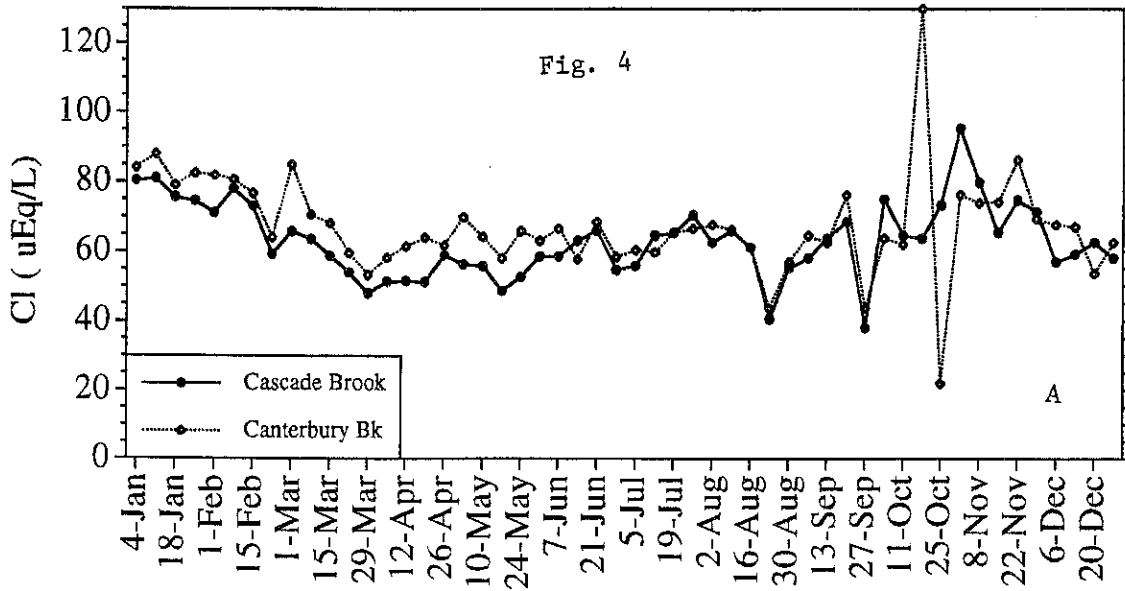


Fig. 3

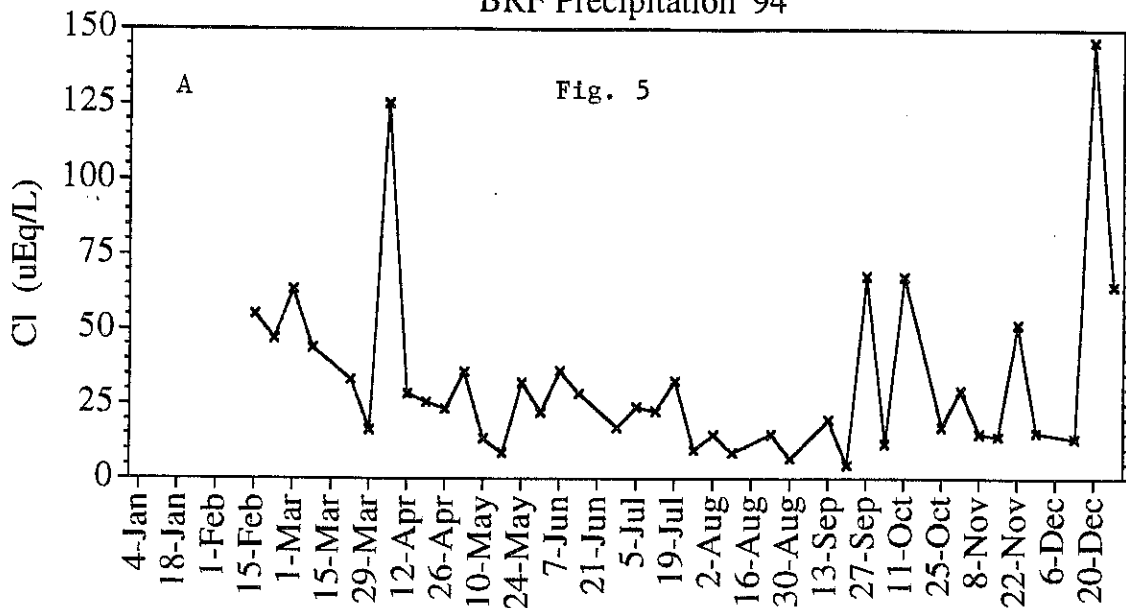
% difference in LDEO and IES chloride measurements (Canterbury Brook 1994)



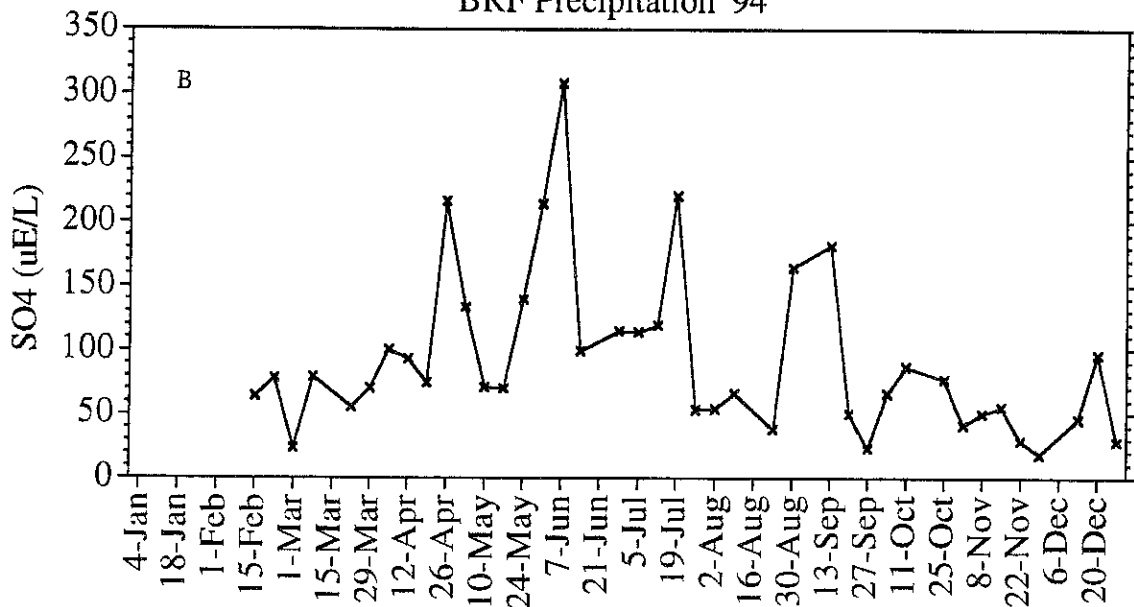
BRF Q anions (uEq)'94



BRF Precipitation '94



BRF Precipitation '94



BRF Precipitation '94

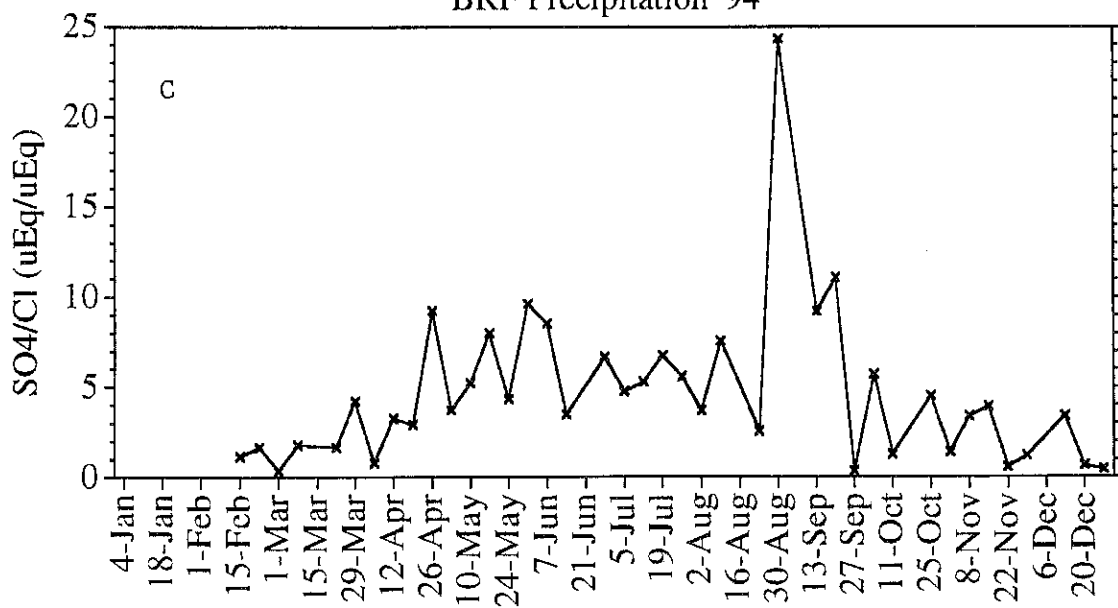
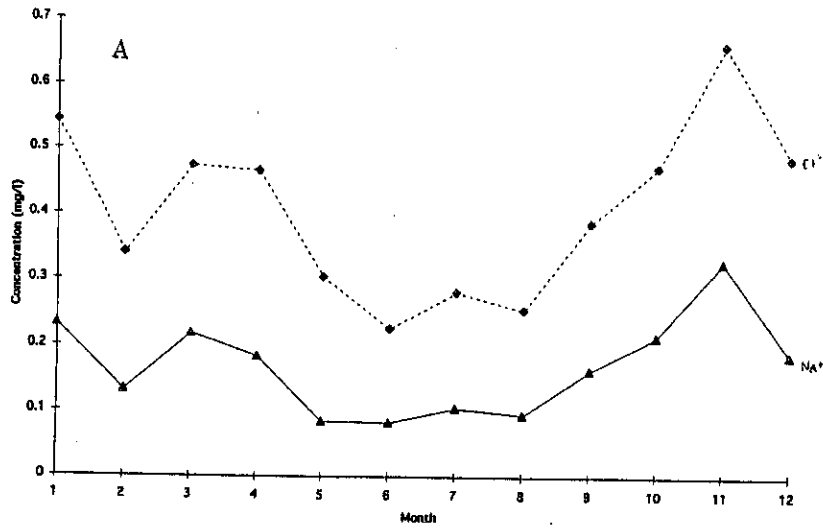
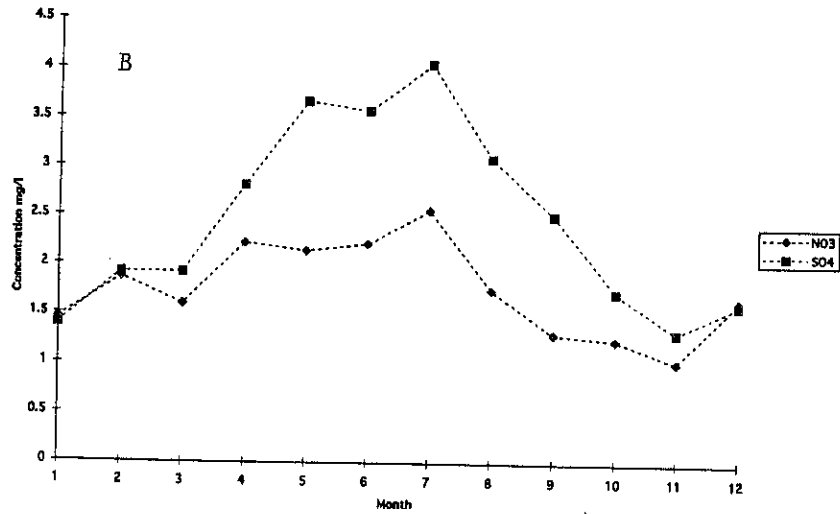


Fig. 6

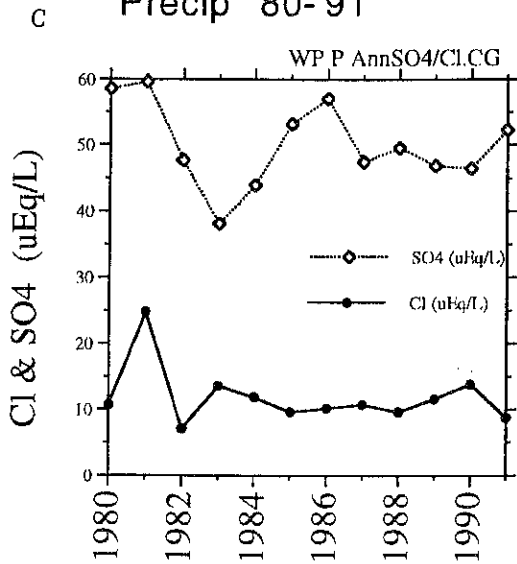
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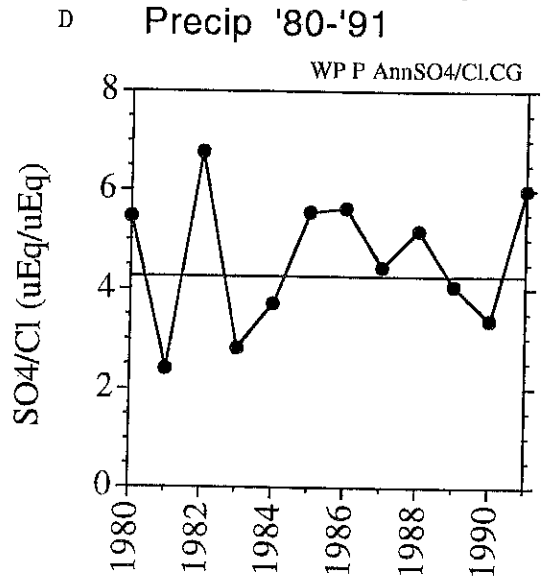
Seasonal Variations in Precipitation Nitrate and Sulfate



West Point Monthly Precip '80-'91



West Point Monthly Precip '80-'91



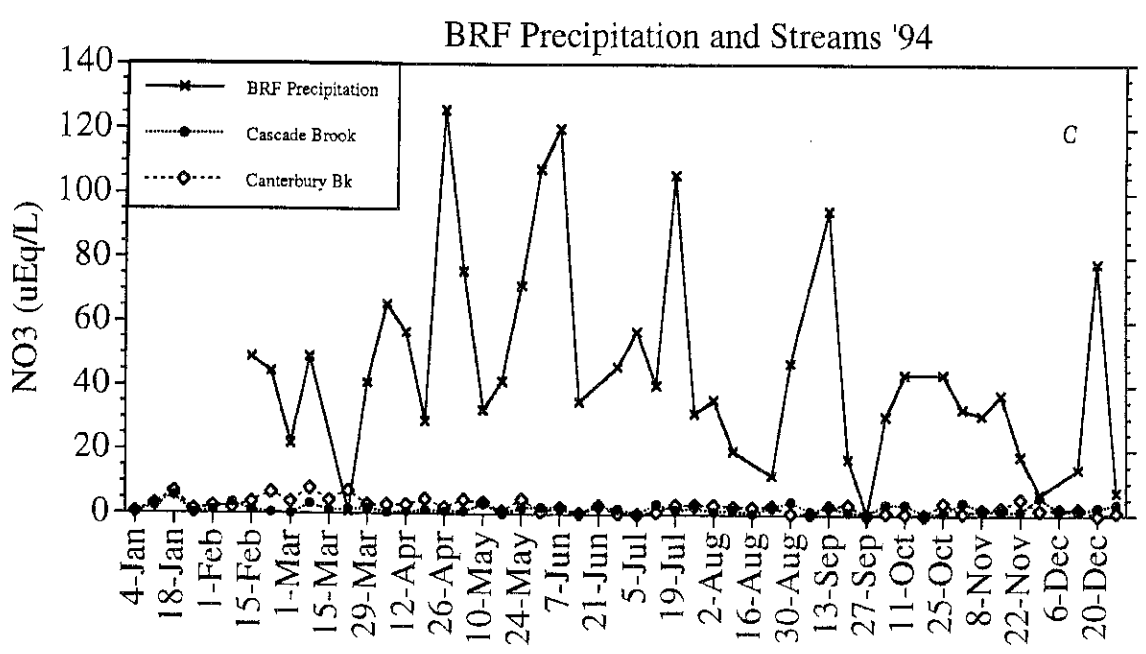
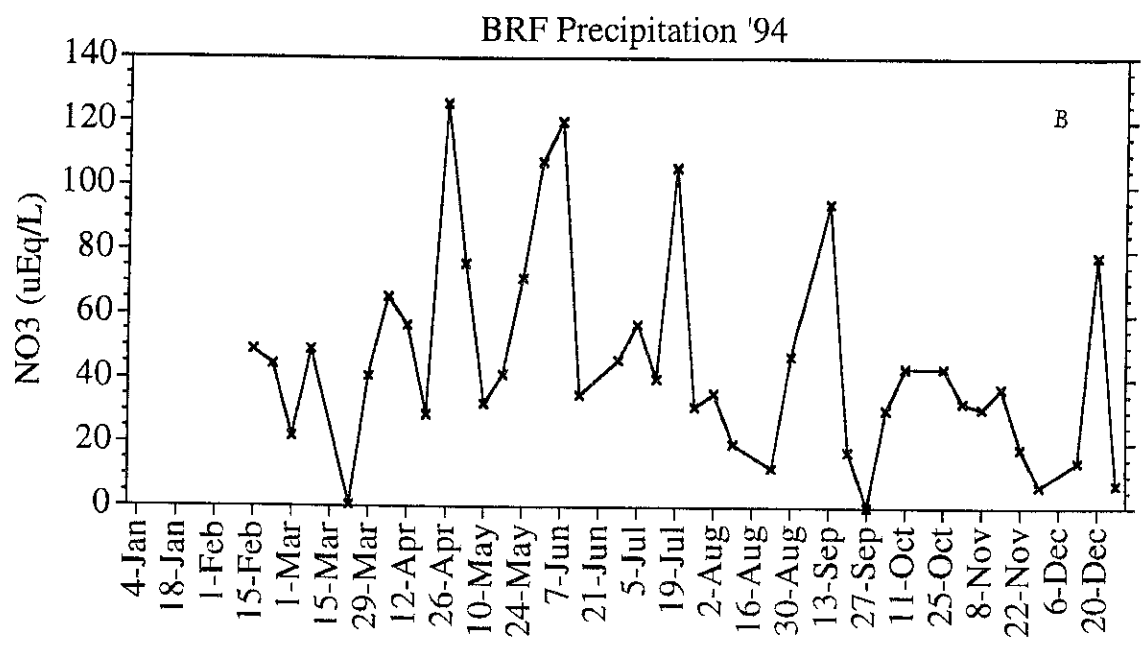
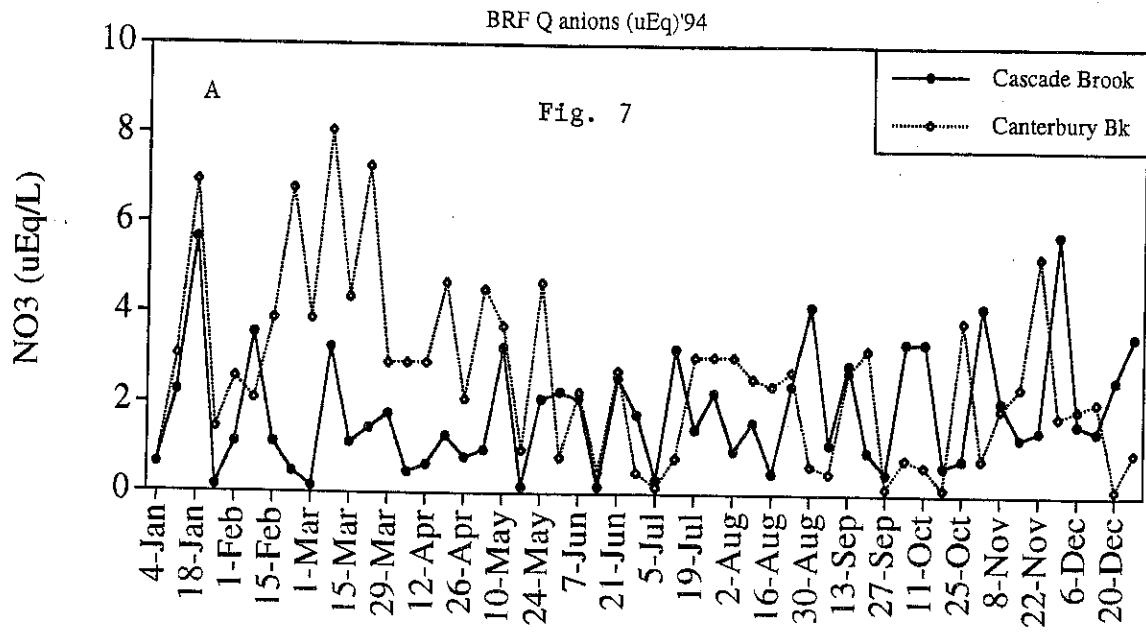


Fig. 8

