CONTROLS ON THE VARIANCE IN CHEMISTRY OF THREE LAKES IN THE FLAT TOPS WILDERNESS AREA, COLORADO

by John T. Turk

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Multiply SI units	*By*	*To obtain inch-pound units*
meter (m)	3.281	feet
kilometer	0.6214	miles
millimeter (mm)	0.03937	inches

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ABSTRACT

The chemistry of three dilute lakes in the Flat Tops Wilderness Area, Colorado, can be divided into three principal components: (1) Biologically controlled characteristics or constituents that vary as a function of growing conditions, (2) constituents with concentrations that are determined by the degree of chemical weathering, and (3) constituents with concentrations that result from solubility controls, or a steady-state concentration resulting from relatively constant sources. pH is an example of a biologically controlled characteristic; calcium is an example of a chemical-weathering controlled constituent; aluminum is an example of a constituent that may be controlled by the solubility of a mineral (gibbsite), whereas sulfate is an example of a constituent controlled by precipitation.

Although quite variable during the ice-free season, pH can be predicted from processes that regulate photosynthesis. The use of simple models relating pH to controls on light intensity (cloud cover and time-of-day), and to stage during the growing season (julian date), explains as much as 63 percent of the variance in pH. Thus, the detection of trends in pH resulting from changes in precipitation chemistry can be greatly simplified by the use of these models.

Most chemical constituents measured in this study seem to vary in concentration about a mean value, with little or no trend during the ice-free season. Mineral solubility may control the concentration of some constituents, and tend to keep that concentration constant, barring major changes in watershed chemistry.

Other constituents have concentrations that probably result from the averaging-effect of snowpack accumulation on atmospheric sources. Thus, changes of average concentrations in these lakes could be detected by statistically different mean values in the future. If the same changes are measured in precipitation, then the importance of the atmospheric source to lake chemistry will be documented.

INTRODUCTION

The development of mineral and energy resources in the western United States will increase the release of atmospheric emissions upwind of areas sensitive to acidic deposition. The Flat Tops Wilderness Area in northwestern Colorado contains lakes having alkalinity values less than 100 µeq/L (Turk and Adams, 1983). The area is located downwind from present and projected sources of acidic, atmospheric emissions. These sources include coal-fired, electric-generation powerplants; oil-shale retorts; sulfide-ore smelters; and projected population centers related to energy development.

Description of Area

The Flat Tops Wilderness Area (fig. 1) is composed of thick deposits of upper Tertiary basalt that form a large mesa overlying the Leadville Limestone (Mississippian) and dolomite of the Dotsero Formation (Cambrian). In a few areas, Precambrian granite is exposed (Bass and Northop, 1963; Tweto, 1979). Topographic relief is great; the generally flat-lying basalt cap of the mesa has an altitude of about 3,350 m, remnant basalt plugs form major peaks at about 3,650 m, and deeply incised stream valleys have their bases at about 2,900 m within a few kilometers of their headwaters. Bedrock is exposed or covered with a few centimeters to a few tenths of a meter of soil at the higher altitudes of the mesa, whereas thick mantles of Quaternary glacial drift occur in the stream valleys. Massive landslide deposits occur at the base of the vertical basalt walls forming the valleys. Average annual precipitation in northwestern Colorado ranges from approximately 250 mm in areas of present and proposed energy development, to as much as 1,200 mm in the higher altitudes of the Flat Tops Wilderness Area. The Flat Tops Wilderness Area is the first major orographic barrier to air masses resulting from the predominant southwest winds over the Piceance basin and from the north-northeast winds common near Craig, Colorado, in the Yampa River valley. Thus, emissions from the major local sources of energy development may be precipitated or deposited from air masses crossing the Flat Tops Wilderness Area before effective dispersion has occurred.

Purpose and Scope

The purpose of this report is to evaluate the sources of variability in chemical data that define the acidification status of lakes in the Flat Tops Wilderness Area. Such information not only increases our knowledge of the biogeochemical controls important to watersheds sensitive to acidification, but also provides a reliable data base to define future changes. Because of the concerns over possible acidification of lakes in the area, emphasis is on lakes with water containing especially small alkalinity values.

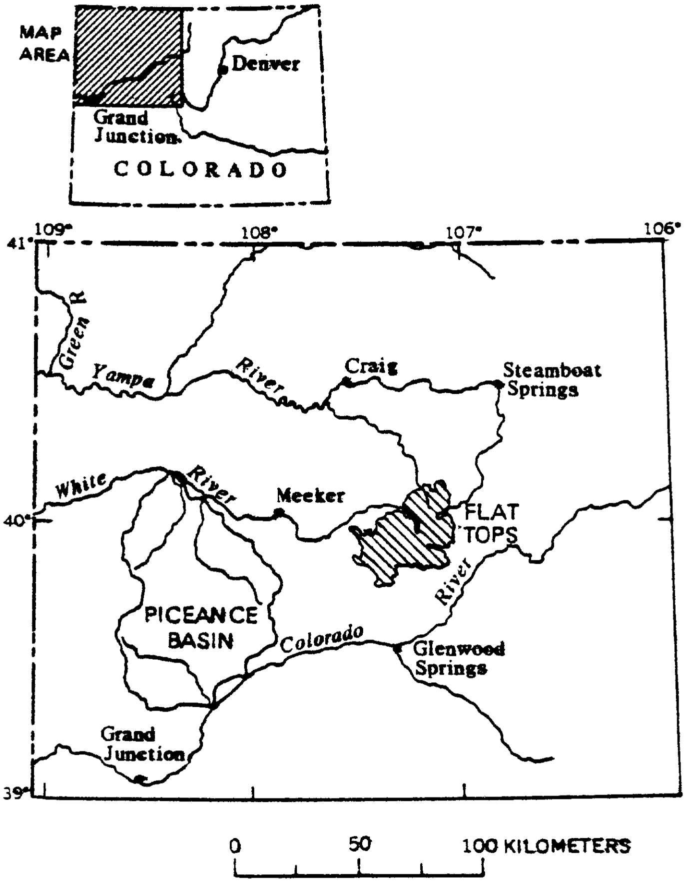

Figure 1.--Location of the Flat Tops Wilderness Area.

Acknowledgments

This study was funded by the U.S. Environmental Protection Agency under Interagency Agreement No. AD-14-F2A262 and by the U.S. Geological Survey Oil Shale Hydrology and Acid Rain programs. The data were collected with the assistance of Robert Boulger, Linda Britton, Donald Campbell, Johnnie Gibbs, Larry Jones, Martha Mustard, Caleb Reed, and Norman Spahr of the U.S. Geological Survey. Their willingness and ability to perform meticulous measurements under extremely adverse conditions, including wind, rain, hail, snow, lightning, and mud should be an inspiration for all scientists.

DATA COLLECTION

The lakes sampled in this study are: Ned Wilson, Upper Island, and Oyster. These lakes were selected based on a previous study (Turk and Adams, 1983). Selection was based on their small alkalinity values, geographic distribution, presence of organisms sensitive to acidification, and representativeness of the watershed characteristics of these lakes. Watershed characteristics of the selected lakes are presented elsewhere (Turk and Adams, 1983).

The data collected in this study include: diurnal measurement of pH, air and water temperature, and dissolved oxygen; determination of algal primary productivity; and determination of major-ion, nutrient, and trace-metal concentrations. Diurnal measurements were made on samples collected from shore at Ned Wilson Lake; diurnal measurements and all chemical sampling were done from a raft at the other two lakes. Rapid increase in depth, lack of thermal stratification, and lack of rooted vegetation make the near-shore samples at Ned Wilson Lake representative of mid-lake conditions. Samples for chemical analysis were collected from mid-depth or mid-stratum in stratified systems. Primary productivity was determined by the carbon-14 method described by Janzer and others (1973). Chemical concentrations were determined by the U.S. Geological Survey laboratory in Denver, Colorado, by methods described elsewhere (Skougstad and others, 1979).

RESULTS AND DISCUSSION

The different types of information collected in this study require separate treatment because of differences in controlling mechanisms, sampling frequencies, and conditions under which these data likely will be used in future studies. For example, it may be useful to decide whether changes in pH have occurred long before detailed investigations of trace metals are desired.

Measurements of pH and Related Data

Several characteristics of lakes are known to change during periods of 24 hours or less. In this study pH, percent cloud cover, air and water temperature, and dissolved oxygen were determined with sufficient frequency to address such diurnal variations. The diurnal data for the lakes in this study are presented in table 1.

Table 1.--*Diurnal data*

[N, Ned Wilson Lake; O,Oyster Lake; I,Upper Island Lake. Air and water temperatures are in degrees Celsius. pH 1, 2, and 3 were measured in replicate. Dissolved oxygen is in milligrams per liter]

Lake	Month	Day	Year	Time	Percent cloud cover	Temperature		pH1	pH2	pH3	Dissolved oxygen
						Air	Water				
N	07	20	82	1745	10	16.0	13.0	7.1	7.1	7.1	---
N	07	20	82	1850	5	13.0	12.5	6.75	7.0	7.0	---
N	07	20	82	2030	---	10.0	12.0	6.8	7.05	7.1	---
N	07	20	82	2340	---	8.0	11.5	6.85	7.05	7.1	---
N	07	21	82	0245	---	.5	10.0	6.50	6.95	7.10	---
N	07	21	82	0545	0	7.0	10.0	6.65	7.05	7.05	---
N	07	21	82	0845	0	16.0	12.5	6.8	7.0	7.0	---
N	07	21	82	1140	45	18.0	12.5	6.50	6.90	6.95	---
N	07	21	82	1505	60	16.0	14.0	6.8	7.0	6.99	---
N	07	21	82	1741	50	12.0	14.5	6.80	7.05	7.10	---
N	08	03	82	1240	90	----	15.4	7.1	7.20	7.20	5.1
N	08	03	82	1450	60	15.0	16.0	7.35	7.30	7.30	7.3
N	08	03	82	1830	80	14.0	16.0	7.30	7.22	7.22	6.5
N	08	03	82	2025	50	9.0	15.3	7.40	7.25	7.20	6.7
N	08	03	82	2400	40	5.5	14.8	7.45	7.30	7.25	6.4
N	08	04	82	0603	60	6.0	14.3	7.20	7.03	7.00	6.5
N	08	04	82	0855	50	9.5	15.5	7.20	7.10	7.02	6.6
N	08	04	82	1240	70	20.5	16.3	7.30	7.20	7.10	7.3
N	08	04	82	1505	40	20.5	16.3	7.35	7.25	7.15	7.3
N	08	04	82	1800	0	19.0	16.6	7.6	7.38	7.25	6.7
N	08	16	82	1755	50	13.5	15.2	7.6	7.40	7.50	6.3
N	08	16	82	2050	90	10.0	14.6	7.40	7.15	7.25	6.5
N	08	17	82	0010	0	6.0	14.3	7.6	7.22	7.32	6.4
N	08	17	82	0605	0	5.0	13.9	7.40	7.06	7.10	6.4
N	08	17	82	0850	60	9.0	14.7	7.30	7.20	7.30	6.5
N	08	17	82	1140	70	15.5	15.0	7.30	7.25	7.22	6.0
N	08	17	82	1440	90	17.0	15.3	7.40	7.32	7.25	6.3
N	08	17	82	1740	100	17.0	15.6	7.50	7.50	7.30	6.6
O	08	18	82	1550	60	22.0	18.7	9.18	9.28	9.22	7.3
O	08	18	82	1800	50	16.5	18.4	9.18	9.20	9.22	7.1

Table 1.--*Diurnal data*--Continued

Lake	Month	Day	Year	Time	Percent cloud cover	Temperature		pH1	pH2	pH3	Dis-solved oxygen
						Air	Water				
O	08	18	82	2040	0	9.0	17.1	9.20	9.25	9.30	7.1
O	08	18	82	2400	0	5.0	16.4	9.20	9.22	9.30	7.2
O	08	19	82	0625	10	4.0	15.9	9.12	9.18	9.22	6.8
I	08	21	82	0810	10	----	13.0	7.30	7.22	7.30	6.2
N	08	31	82	1835	40	12.0	14.4	7.8	7.46	7.48	6.8
N	08	31	82	2055	5	5.5	14.0	7.40	7.28	7.15	6.8
N	08	31	82	2400	5	6.5	13.8	8.00	7.35	7.35	6.6
N	09	01	82	0605	5	.0	13.1	7.65	7.38	7.30	6.3
N	09	01	82	1045	2	15.0	14.8	7.75	7.50	7.40	6.2
N	09	01	82	1200	3	15.5	14.6	8.40	8.01	7.50	6.0
N	09	01	82	1500	5	12.5	14.9	7.52	7.39	7.31	6.5
N	09	01	82	1800	1	11.5	15.3	7.71	7.43	7.40	6.7
N	10	02	82	1740	0	.0	6.2	7.80	7.69	7.70	8.2
N	10	02	82	2025	0	-4.0	5.7	7.80	7.80	7.70	7.9
N	10	03	82	0645	5	-4.0	4.5	7.50	7.35	7.45	8.0
N	10	03	82	0855	15	3.0	5.1	7.70	7.40	7.50	8.0
N	10	03	82	1215	60	8.0	6.0	7.60	7.52	7.60	7.9
N	10	03	82	1505	80	7.0	5.9	7.65	7.50	7.50	7.9
N	10	03	82	1800	40	2.0	5.6	7.55	7.50	7.51	7.8
N	07	19	83	1900	15	14.5	13.5	----	----	----	7.4
N	07	19	83	2100	7	10.0	12.5	7.15	7.03	7.02	6.7
N	07	19	83	2400	3	9.0	12.0	7.12	7.01	7.00	6.6
N	07	20	83	0615	100	6.0	11.0	----	----	----	6.1
N	07	20	83	1510	30	20.0	14.0	6.83	6.90	6.89	8.7
N	07	20	83	1800	100	10.0	15.0	6.86	6.74	6.82	5.5
N	07	20	83	2100	100	7.0	13.0	7.10	7.05	7.06	5.6
N	07	20	83	2400	85	7.0	13.0	7.05	7.01	6.96	6.0
N	07	21	83	0600	10	7.0	12.0	7.16	7.13	7.11	5.8
N	07	21	83	0900	20	9.5	13.0	7.12	7.16	7.13	6.2
N	07	21	83	1100	40	15.0	14.0	7.21	7.20	7.20	6.2
N	07	28	83	2027	75	10.5	13.5	7.32	7.19	7.39	7.0
N	07	28	83	2350	0	6.0	13.9	7.21	7.20	7.19	6.95
N	07	29	83	0553	0	4.0	13.0	7.11	7.10	7.12	6.9
N	07	29	83	0900	0	12.5	13.2	7.12	7.16	7.25	6.7
N	07	29	83	1200	50	15.0	14.0	7.22	7.26	7.22	6.9
N	07	29	83	1500	85	17.0	15.2	7.19	7.31	7.18	7.0
N	07	29	83	1803	1	16.0	15.5	7.26	7.27	7.29	6.65
N	07	29	83	2100	95	12.0	15.0	7.01	7.09	7.08	6.7
I	08	09	83	1830	100	----	17.0	7.67	7.69	7.70	6.5
I	08	09	83	2100	20	16.0	16.5	7.78	7.75	7.73	6.7

Table 1.--*Diurnal data*--Continued

Lake	Month	Day	Year	Time	Percent cloud cover	Temperature		pH1	pH2	pH3	Dis-solved oxygen
						Air	Water				
I	08	09	83	2400	0	9.5	16.0	7.38	7.35	7.34	6.7
I	08	10	83	0600	0	8.0	14.0	7.40	7.38	7.38	7.3
I	08	10	83	0900	0	----	14.5	7.55	7.52	7.54	6.6
I	08	10	83	1200	0	17.0	16.0	7.62	7.59	7.61	5.8
I	08	10	83	1500	1	18.0	16.0	7.50	7.67	7.69	6.3
I	08	10	83	1800	10	14.5	17.0	8.01	7.81	7.82	6.8
N	08	11	83	1715	98	12.5	16.0	7.36	7.31	7.31	6.3
N	08	11	83	2100	98	9.5	16.0	7.25	7.20	7.17	6.1
N	08	11	83	2348	100	8.5	15.5	7.16	7.11	7.14	6.6
N	08	12	83	0548	100	8.5	15.0	7.14	7.11	7.09	6.5
N	08	12	83	0823	80	12.5	15.5	7.21	7.21	7.21	6.2
N	08	12	83	1200	100	13.0	16.0	7.28	7.26	7.25	6.0
N	08	12	83	1500	99	11.0	16.0	7.20	7.15	7.12	6.5
N	08	12	83	1900	90	9.0	15.5	6.82	6.90	6.95	6.4
N	08	16	83	1800	---	17.0	18.0	6.89	6.93	6.96	6.4
N	08	16	83	2100	---	10.5	15.0	7.35	7.31	7.27	6.4
N	08	16	83	2400	---	11.0	16.0	7.13	7.03	7.05	6.4
N	08	17	83	0615	100	10.5	16.0	7.15	7.17	7.19	6.4
N	08	17	83	0930	---	15.0	17.0	7.55	7.46	7.39	6.4
N	08	17	83	1200	---	14.5	18.0	7.36	7.37	7.37	6.4
N	08	17	83	1500	70	18.0	18.0	7.30	7.32	7.30	6.4
N	08	17	83	1800	7	17.0	18.5	7.55	7.47	7.47	6.2
O	08	18	83	1800	50	13.0	19.0	7.98	8.01	8.02	6.1
O	08	18	83	2100	50	6.0	19.5	8.16	8.16	8.04	6.6
O	08	18	83	2400	100	8.5	19.0	8.20	8.22	8.19	6.2
O	08	19	83	0600	0	5.0	18.0	7.94	8.00	8.25	6.1
O	08	19	83	0930	2	15.0	18.0	8.04	8.02	7.98	5.9
O	08	19	83	1200	65	20.0	19.0	8.08	7.96	8.01	6.0
O	08	19	83	1500	10	18.0	19.5	8.43	8.42	8.40	6.4
O	08	19	83	1800	100	14.0	19.5	8.46	8.17	8.13	6.7
I	08	23	83	1800	5	16.0	15.0	7.63	7.62	7.61	6.5
I	08	23	83	2100	0	9.0	15.0	7.63	7.55	7.50	6.5
I	08	23	83	2400	60	7.0	15.0	7.60	7.64	7.65	6.2
I	08	24	83	0600	0	4.0	14.6	7.57	7.51	7.47	6.2
I	08	24	83	0900	0	12.0	14.5	7.59	7.59	7.54	6.2
I	08	24	83	1200	45	12.5	15.0	7.60	7.60	7.61	6.5
I	08	24	83	1500	90	12.0	15.0	7.66	7.73	7.61	6.5
I	08	24	83	1800	100	11.0	14.0	7.79	7.75	7.82	6.4
N	08	29	83	1800	80	10.0	15.5	7.34	7.32	7.29	5.9
N	08	29	83	2100	---	5.0	14.8	7.31	7.35	7.23	6.0

Table 1.--*Diurnal data*--Continued

Lake	Month	Day	Year	Time	Percent cloud cover	Temperature		pH1	pH2	pH3	Dis-solved oxygen
						Air	Water				
N	08	29	83	2400	80	3.0	14.8	7.46	7.34	7.23	6.0
N	08	30	83	0600	90	3.0	14.2	7.36	7.35	7.30	5.9
N	08	30	83	0900	10	13.0	14.7	7.39	7.42	7.40	5.7
N	08	30	83	1200	100	13.5	15.1	7.36	7.32	7.36	5.8
N	08	30	83	1530	40	9.5	15.5	7.58	7.53	7.51	5.9
N	08	30	83	1800	0	10.0	15.5	7.75	7.63	7.59	6.1
O	08	31	83	1800	0	13.0	17.0	8.87	8.92	8.95	6.5
O	08	31	83	2100	0	5.5	16.5	8.96	9.00	8.98	6.4
O	08	31	83	2400	0	3.5	15.8	8.89	8.92	8.94	5.9
O	09	01	83	0600	0	2.0	15.0	8.75	8.75	8.73	5.8
O	09	01	83	0900	---	16.0	15.0	8.89	8.91	8.90	5.8
O	09	01	83	1200	40	16.5	16.0	8.81	8.83	8.81	5.8
O	09	01	83	1500	50	19.0	17.0	8.70	8.76	8.76	5.8
O	09	01	83	1800	30	15.5	16.5	9.00	8.98	8.97	6.0
I	09	07	83	1800	55	14.0	13.0	8.83	8.72	8.63	6.7
I	09	07	83	2100	100	10.5	12.5	8.63	8.61	8.69	6.8
I	09	07	83	2400	100	7.0	12.5	8.64	8.67	8.60	6.8
I	09	08	83	0600	100	5.0	13.5	7.77	7.75	7.68	6.4
I	09	08	83	0900	100	6.5	13.0	7.81	7.66	7.55	6.4
I	09	08	83	1200	80	10.0	12.5	8.29	8.27	8.22	6.6
I	09	08	83	1500	40	13.0	12.5	8.12	8.12	8.13	6.6
I	09	08	83	1800	35	10.0	13.0	8.65	8.65	8.68	6.8
N	09	09	83	1800	35	12.5	14.0	7.42	7.48	7.37	6.2
N	09	09	83	2100	5	9.0	3.5	7.43	7.41	7.38	6.0
N	09	09	83	2400	80	7.5	13.5	7.21	7.34	7.31	6.0
N	09	10	83	0600	80	3.0	13.0	7.43	7.29	7.14	6.9
N	09	10	83	0900	50	9.5	13.5	7.34	7.29	7.14	6.0
N	09	10	83	1200	2	12.0	14.5	7.47	7.42	7.41	5.95
N	09	10	83	1500	25	12.0	15.0	7.46	7.42	7.44	5.9
N	09	10	83	1800	5	11.0	15.0	7.46	7.37	7.41	6.0
I	09	20	83	1800	0	-1.5	9.5	7.61	7.52	7.52	6.9
I	09	20	83	2100	0	-4.0	9.2	7.70	7.73	7.70	7.0
I	09	20	83	2400	0	-4.0	8.9	7.49	7.47	7.47	6.9
I	09	21	83	0700	0	-4.0	7.2	7.37	7.34	7.42	6.9
I	09	21	83	0900	0	1.0	8.5	7.49	7.45	7.42	6.9
I	09	21	83	1200	0	5.0	8.5	7.53	7.44	7.47	6.6
I	09	21	83	1500	0	7.0	9.0	7.49	7.42	7.42	7.0
N	09	27	83	1800	5	6.5	9.0	7.73	7.70	7.67	7.1
N	09	27	83	2100	30	4.5	8.0	7.42	7.21	7.33	7.1
N	09	27	83	2400	0	3.0	7.5	7.58	7.48	7.47	7.1
N	09	28	83	0600	20	2.0	7.5	7.45	7.40	7.29	7.0

Table 1.--*Diurnal data*--Continued

Lake	Month	Day	Year	Time	Percent cloud cover	Temperature		pH1	pH2	pH3	Dis-solved oxygen
						Air	Water				
N	09	28	83	0900	60	4.0	8.0	7.39	7.32	7.25	7.1
N	09	28	83	1200	65	7.5	9.5	7.41	7.38	7.33	7.1
N	09	28	83	1500	25	9.0	9.0	7.57	7.55	7.49	7.2
N	09	28	83	1800	85	7.5	9.0	7.80	7.75	7.70	7.2
O	09	29	83	1800	100	7.0	10.0	7.75	7.72	7.66	7.3
O	09	29	83	2100	45	3.0	9.0	7.48	7.44	7.42	7.5
O	09	29	83	2400	15	3.0	9.0	7.78	7.72	7.67	7.1
O	09	30	83	0600	80	3.0	8.0	7.84	7.76	7.70	6.8
O	09	30	83	0900	35	7.0	9.0	7.60	7.62	7.62	6.5
O	09	30	83	1200	60	10.0	12.0	7.75	7.72	7.69	6.2
O	09	30	83	1500	100	5.0	9.5	7.92	7.87	7.85	7.1
O	09	30	83	1800	100	2.0	8.5	8.04	7.96	7.90	7.3

Of the diurnal data presented here, only those for pH will be described in detail. The data for percent cloud cover, air and water temperature, and dissolved-oxygen concentration are presented as ancillary data useful in explaining processes controlling the pH.

Quality Assurance of pH Data

Determination of the principal controls affecting pH is one of the primary objectives of this study. To determine the degree of change in pH that is caused by biogeochemical processes, it is first necessary to evaluate the precision of the pH measurement itself. All pH measurements were made in triplicate to allow evaluation of instrument drift and measurement precision. Because the lakes sampled here are so dilute, minor changes in sample chemistry caused by sampling may alter the pH. In particular, residual effects of the calibration buffers on the electrode could produce a systematic bias of the pH in the direction of the pH of the last calibration buffer used prior to sample measurement. To evaluate whether the measurement procedure adequately prevented this and other sources of drift, a comparison was made of the difference in pH between the first and second, second and third, and first and third pH measurements of each triplicate set.

The mean differences in pH between each of the measurements among all triplicate sets are summarized in table 2. The 95-percent confidence intervals of the measurement differences overlap zero, indicating that there is no significant drift to the measurements. The variance in pH of these measurements was compared to the mean pH for each triplicate set by linear regression. There was no significant ($P=0.05$) correlation between variance and pH. The data were subsequently combined and used to estimate the mean variance in pH due to measurement precision of 0.005.

Table 2.--*Difference in pH, expressed as microequivalents per liter, between determinations in triplicate sets*

Determinations used	Number of samples	Mean difference	Standard error of mean
Second minus first----------	161	-0.0013	0.0023
Third minus second----------	161	.0008	.0006
Third minus first-----------	161	-.0005	.0026

Determination of pH Controls

The variations in pH measured during this study result from the combined effects of many biological and geochemical processes on water chemistry. For example, photosynthesis and respiration affect pH by decreasing or increasing the concentration of carbon dioxide, a weak acid in water. Photosynthesis and respiration are affected by sunlight intensity, air and water temperature, abundance of nutrients, photosynthesizing biomass, quantity and type of organic detritus, and other factors that may be difficult to quantify. Geochemical processes, such as weathering of rock minerals, generally neutralize acidity. These processes may affect the pH in a lake directly as lake water reacts with suspended or deposited minerals. Mineral weathering may affect lake pH if alkaline ground water, resulting from long periods of reaction with rock minerals, mixes with dilute and more acidic lake water from snowmelt that has had minimal reaction with rock minerals. Because of the remote setting of the lakes studied, indirect evaluation of some controlling mechanisms is necessary. Thus, multivariate regression is used here as a first approximation of the relative importance of several processes in controlling pH. This approach also allows the lake pH to be predicted from data such as time of year, making possible the comparison of data collected under various conditions and at various times.

Temporal sources of pH variance

Although time is not normally considered a controlling mechanism of pH, it is most conveniently treated as an independent variable. Natural variations of pH with time make it difficult to determine whether differences between measurements are caused by changes in the chemistry of the system. For example, if energy development occurs near the lakes described here, future measurements of pH may be different from some measurement before development. This hypothetical change in pH could be caused by the effects of emissions from energy development on the chemistry of the lakes. Alternatively, the change in pH merely could be a result of the natural fluctuation in pH. By treating time as an independent variable, it is possible to determine the variation in pH that can be attributed to natural processes operating both before, and, presumably, after energy development. Variations in pH in excess of those variations that can be attributed to natural processes then can be attributed to other mechanisms, such as possible effect of emissions from energy development.

Natural variations in pH with time logically can be separated into several classes. Diurnal variations are caused by processes that differ in rate as a function of the available sunlight, for example, photosynthesis. Seasonal variations are caused by processes that differ as a function of the temperature or hydrology of the system, for example, the accumulation of biomass during the growing season, or the seasonal influx of dilute snowmelt. Annual variations are caused by processes linked to the natural eutrophication of the system, or to fluctuations in climate, for example, drought years. Each of these classes can affect the difference in pH that needs to be measured for the difference to be statistically significant.

Diurnal.--Diurnal variations in pH are presented in table 3. The individual measurements were converted to hydrogen-ion activities, averaged, and converted back to a mean pH for each triplicate set of measurements.

Table 3.--*Diurnal variations in mean pH and the carbon-14 primary productivity rate, in milligrams of carbon per square meter per day*

Name of lake	Date	Minimum	Maximum	Range	Carbon-14
Ned Wilson------	07/20/82	6.73	6.99	0.26	---
"	08/03/82	7.07	7.39	.32	53
"	08/16/82	7.16	7.49	.33	---
"	08/31/82	7.26	7.82	.56	30
"	10/02/82	7.43	7.76	.33	---
"	07/19/83	6.80	7.20	.40	---
"	07/28/83	7.06	7.29	.23	24
"	08/11/83	6.89	7.33	.44	47
"	08/16/83	6.95	7.50	.55	20
"	08/29/83	7.29	7.65	.36	45
"	09/09/83	7.25	7.44	.19	39
"	09/27/83	7.31	7.75	.44	---
Upper Island----	08/09/83	7.36	7.87	.51	210
"	08/23/83	7.51	7.79	.27	180
"	09/07/83	7.66	8.72	1.05	140
"	09/20/83	7.38	7.71	.33	---
Oyster----------	08/18/82	9.17	9.25	.08	---
"	08/18/83	8.00	8.42	.41	30
"	08/31/83	8.74	8.98	.24	31
"	09/29/83	7.45	7.96	.52	---

The range in mean pH for Ned Wilson Lake was from 6.73 to 7.82, with a mean range per diurnal cycle of 0.37; the range in pH for Upper Island Lake was from 7.36 to 8.72, with a mean range per diurnal cycle of 0.54; and the range in pH for Oyster Lake was from 7.45 to 9.25, with a mean range per diurnal cycle of 0.31. Thus the natural diurnal variation in pH was much greater than the precision limits of replicate measurements. This diurnal variation needs to be considered in determining whether measurements made at different times are significantly different from one another, even if the measurements are made on the same day of the year.

Diurnal variation in pH complicates the determination of whether two measurements of pH are significantly different. By increasing the natural variation in pH, anthropogenic changes in pH become more difficult to detect. It is possible to partially correct for this natural variation if it can be modeled; then corrections can be applied to one pH value to make it more directly comparable to a previous value. Because natural diurnal variation is mostly the result of photosynthesis and respiration, readily measured variables related to these mechanisms are used here to partially account for the diurnal variation in pH.

Photosynthesis is dependent on the diurnal cycle of sunlight. Because direct measurement of sunlight intensity is not routinely available for wilderness lakes it will be approximated by a harmonic function:

$$\text{HARMONIC} = \text{SINE}[(6.28 \times \text{TIME}/1440) + \text{PHASEANGLE}] \qquad (1)$$

Equation 1 transforms 24-hour time into a harmonic function, where time is in minutes past midnight and phaseangle is a constant between 0 and 2 pi. The data from this study were transformed by equation 1 and regressed against pH. Phaseangle was selected from the best fit of data from this study; it equaled 1.0 pi. The effect of this phase-angle value was to produce an equation with a minimum value corresponding to 0600 hours and a maximum value corresponding to 1800 hours. The amplitude of the harmonic function varies with time of year, cloud cover, and other mechanisms affecting photosynthesis. Thus, equation 1 most accurately models the pH if it is evaluated for each diurnal set of data. Such evaluation of the data in this study indicated that equation 1 explained an average of 35 percent of the variance in pH. Unfortunately, the small number of data points available for each diurnal set (average n = 8) increases the error and decreases the statistical significance of this approach. An average fit of the data will be presented in the section on seasonal variations.

Seasonal.--Seasonal variations in pH include diurnal variations, plus variations that are caused by mechanisms that slowly vary in rate during the annual cycle. During an entire annual cycle, seasonal variations might be a harmonic function; however, access to the lakes described here restricts the present data to the summer. Thus, a linear regression of pH on julian date is used to evaluate the importance of seasonal variance. Such a regression explains only 3 percent of the variance in pH for Upper Island Lake; however, it explains 59 percent for Ned Wilson Lake and 39 percent for Oyster Lake. The regression characteristics for these data are summarized in table 4.

Table 4.--*Regression characteristics, by lake, of pH on julian date*

Lake	Intercept	Slope	n	R-square	P>F
Ned Wilson--------	5.58	0.007	100	0.59	0.0001
Upper Island------	6.66	.004	32	.03	.34
Oyster------------	13.5	-.021	29	.39	.0003

It should be noted that these data were measured during parts of 2 years. The regressions are markedly different between Ned Wilson Lake and Oyster Lake, having opposite slope and significantly different intercepts. These equations are only valid for the part of the year represented by the data here. For example, the regression data for Oyster Lake indicate impossibly large values of pH for small values of julian time. The regression data for Ned Wilson Lake may not be unrealistic at such times; however, access makes it difficult to obtain sufficiently accurate pH data to evaluate the validity of the regressions during the winter.

By combining those variables important to the diurnal variance in pH with julian date, a model can be constructed that is applicable to pH measurements made any time during the season. The regression characteristics using all independent variables significant in diurnal or seasonal variance in pH are summarized in table 5.

Table 5.--*Regression characteristics for pH against cloud cover (percent), harmonic function (defined by equation 1), and julian date. N is the number of data points used in the regression*

Parameter	Value	R-square	P>F
	<u>Ned Wilson Lake (n=91)</u>		
Intercept----------	5.72	----	------
Cloud Cover---------	.0009	0.06	0.0003
Harmonic------------	.040	.01	.010
Julian--------------	.007	.56	.0001
Model---------------	------	.63	.0001
	<u>Upper Island Lake (n=32)</u>		
Intercept----------	6.49	----	------
Cloud Cover---------	.005	0.30	0.0006
Harmonic------------	.174	.10	.032
Julian--------------	.005	.03	.232
Model---------------	-----	.43	.0011
	<u>Oyster Lake (n=28)</u>		
Intercept----------	12.6	----	------
Cloud Cover---------	-.005	0.22	0.003
Harmonic------------	.154	.06	.10
Julian--------------	-.016	.21	.004
Model---------------	------	.50	.0007

Annual.--Annual variations in pH include diurnal and seasonal variations, as well as variations caused by longer lasting changes in lake biology or chemistry. Such changes include climatic fluctuations and the introduction of significant anthropogenic emissions. Because only one visit was made to Upper Island Lake and Oyster Lake during 1982, an analysis of annual variations would be unreliable. Ned Wilson Lake was sampled during five diurnal cycles in 1982, and six in 1983. Annual variations in pH were tested for in the regression equation characterized in table 5. This was done by entering two additional variables into the equation: (1) A test of annual differences in the intercept was made by entering a variable equal to 0 in 1982 and 1 in 1983; and (2) a test of annual differences in the slope of the pH on julian date regression was made by entering a variable equal to the variable in item (1), multiplied by julian date. Thus, coefficients of these two variables significantly different from 0 would indicate significant annual differences in pH. In combination with one another, and the other parameters from table 5, the regression model is characterized in table 6.

Table 6.--*Regression characteristics for pH on cloud cover, harmonic function, julian date, and yearly differences in intercept (I-test) and pH/julian date slope (S-test)*

Ned Wilson Lake (n=91)

Parameter	Value	R-square	P>F
Intercept--------	5.45	----	------
Cloud Cover------	-.0009	0.06	0.0001
Harmonic---------	.063	.05	.0006
Julian-----------	.008	.55	.0001
I-test-----------	.494	.00	.4892
S-test-----------	-.002	.01	.0540
Model------------	------	.68	.0001

As can be seen from the data in table 6, more than one-half the variance in pH for Ned Wilson Lake is explained by the julian date. Cloud cover and the harmonic function, which both affect diurnal variations in sunlight, are significant; together, they explain 11 percent of the variance in pH. The fraction of variance in pH explained by cloud cover and the harmonic function for Upper Island Lake is 40 percent, and for Oyster Lake, it is 28 percent (table 5). Thus, comparison of pH data collected in one year with data from another year may not be valid for all lakes, even if the samples are collected on the same julian date. If only a single value of pH is available from a lake for one year, for example, a historical measurement from several decades ago, the most appropriate test for significant change would be against a model of the type in tables 5 and 6. Such a model can be developed for any lake of interest, and could provide estimates of the difference in pH necessary for a given probability of change. Examples of the problem of comparing historical pH values with recent values are related to the acidification of lakes. Burns and others (1981) and Lewis (1982) compare single measurements of pH made many years apart, assuming that short-term variations are random. Because cloud cover is affected by climatic differences among years, this source of short-term variation may not be random between years. Related differences in the hydrology of lakes as a function of climatic fluctuation further complicates comparison. Additional data collected in drought cycles is an obvious research need to supplement the results presented here.

Primary productivity as a source of pH variance

The regressions of pH on julian time indicate that mechanisms that vary through the summer are very important in controlling pH for some lakes. The only mechanism for which direct measurements were made is photosynthesis. The photosynthesis rates (table 3) do not seem correlated with pH, or with the diurnal range in pH. It is unclear whether this is because the carbon-14 method is too imprecise, or whether the carbon-14 method is not indicative of all photosynthesis. Photosynthesis by periphyton or rooted macrophytes may significantly affect pH, even though these mechanisms would not be determined by the carbon-14 algal-photosynthesis method used here. Also, the diurnal measurements usually were made during 2 days, whereas the primary-productivity determinations were made during about 6 hours that may not be representative of the entire diurnal period.

Cloud cover as a source of variance in pH

Photosynthesis varies as a function of the duration and intensity of sunlight, whether sunlight is controlled by the diurnal cycle or by cloud cover. The estimates of cloud cover in this study were regressed against pH for each diurnal set; the results explained an average of 24 percent of the variance in pH. The harmonic function alone explained an average of 35 percent of the variance in pH. In a regression against pH using both the harmonic function and cloud cover, 54 percent of the variance in pH was explained by these two sources of variability in sunlight. Thus, the percentage of variance in pH explained seems additive for these two variables. The same restrictions caused by few measurements per diurnal set apply as in the simple harmonic fit.

Relationship of dissolved-oxygen concentrations to pH

Photosynthesis produces oxygen as a byproduct, and oxygen is consumed by respiration. Thus, the diurnal cycle of dissolved oxygen may be a measure of the balance between these two mechanisms. The diurnal data for pH were regressed against dissolved-oxygen concentration, with only 22 percent of the variance in pH being explained by the dissolved-oxygen concentrations. This result is less explanatory than the results based on time, and does not significantly aid in explaining the variance in pH. The lack of correlation may result from the efficient exchange of oxygen between the atmosphere and lake in the windy environment of these lakes. Gains and losses of oxygen by this exchange mask the effects of photosynthesis and respiration on oxygen.

Measurements of Chemical Constituents

The diurnal measurements discussed in the preceding section indicate that variables, such as pH, change in response to both short-term and long-term controls. Other components, such as the dissolved minerals, may respond only to long-term controls, because changes require replacement of the lake water rather than internal shifts in chemical equilibria. Several classes of chemical components exist because of differences in sources, biological activity, and important chemical reactions.

Major Nutrients

Nutrients, for example, phosphorus and nitrogen species, may vary with the growth of algae and macrophytes. The expected pattern is a maximum in concentration early in the growing season, with a decrease in concentration through the summer. The data from this study were regressed against julian date, and the regression characteristics are presented in table 7.

Table 7.--*Regression characteristics of dissolved major nutrient species against julian date*

Species	Intercept	Slope	n	R-square	P>F
		Ned Wilson Lake			
Ammonia as N----	----	-------	14	0.03	0.55
Nitrite plus nitrate as N--	0.11	-0.0004	14	.29	.05
Orthophosphate--	----	-------	15	.002	.87
Silica---------	----	-------	13	.03	.60
		Upper Island Lake (Epilimnion)			
Ammonia as N----	----	-------	5	0.35	0.30
Nitrite plus nitrate as N--	----	-------	6	.01	.89
Orthophosphate--	----	-------	6	.13	.48
Silica---------	----	-------	6	.11	.51
		Upper Island Lake (Hypolimnion, unfiltered)			
Ammonia as N----	----	-------	6	0.22	0.34
Nitrite plus nitrate as N--	----	-------	6	.05	.67
Orthophosphate--	----	-------	6	.20	.37
		Oyster Lake			
Ammonia as N----	----	-------	4	.30	.45
Nitrite plus nitrate as N--	----	-------	4	.20	.55
Orthophosphate--	----	-------	4	.23	.52
Silica---------	----	-------	4	.64	.20

The results presented in table 7 indicate that the major nutrient species are not obviously related to julian date, a measure of stage in the algal-growth cycle. Much of the apparent lack of relationship may be the result of the few measurements for two of the lakes. Recycling of nutrients between the water and the lake bottom or dead plankton may keep nutrients at approximately constant concentrations. The only evidence for a seasonal trend is at Ned Wilson Lake, which has a decrease in nitrite plus nitrate as nitrogen as the growing season progresses. This decrease may result from the algal assimilation of inorganic nitrogen, with any recycling from dead algae being in the form of ammonia or organic nitrogen.

Major Weathering Products

The major products of weathering, for example, calcium and alkalinity, may vary with the hydrologic cycle of a lake. Immediately after snowmelt, a lake may have small concentrations of these weathering products, because rapid transport of snowmelt into the lake allows little time for weathering of rock minerals. As the season progresses, ground water that has had a longer time in contact with rock minerals may contribute an increasing proportion of the lake water. Thus, major products of weathering may vary with julian date in the opposite direction of nutrients. The results of regressions of major weathering products against julian date are presented in table 8.

Additional evidence of weathering as a source of these constituents is their variation in concentration among the lakes (table 10 in the next section), with the variation being similar among the variables. Also, the concentrations in the lakes are much greater than in the snowpack. Samples collected from the snowpack in the drainage basin of Ned Wilson Lake prior to snowmelt indicate calcium concentrations of about 0.1 mg/L, and one-half this concentration, or less, for sodium, magnesium, and potassium. Potassium geochemistry may be complicated by uptake by vegetation or adsorption on clays, because its mean concentration does not vary similarly with the other likely weathering products.

The results presented in table 8 indicate that these lakes probably do not have differing hydrologic sources as a function of julian date. The two statistically significant regressions have extremely small slope coefficients, that predict a change of only 0.1-0.2 mg/L during the ice-free season.

Atmospherically Contributed Constituents

Constituents contributed to a lake mostly by precipitation may vary little if the lake receives most of its water from snowmelt. The accumulation of the snowpack averages out the normal storm-to-storm variation in chemical concentration. In these lakes, chloride, nitrate, and sulfate may be mostly contributed by precipitation; however, nitrate concentrations may be controlled by biological processes. The results of regression of these constituents against julian date are presented in table 9; these results indicate lack of seasonal variance.

Table 8.--*Regression characteristics of major weathering products against julian date*

Species	Intercept	Slope	n	R-square	P>F
Ned Wilson Lake					
Calcium	----	------	15	0.00	0.82
Magnesium	----	------	15	.02	.61
Sodium	----	------	15	.02	.60
Potassium	----	------	15	.04	.49
Alkalinity	----	------	20	.04	.37
Upper Island Lake (Epilimnion)					
Calcium	----	------	6	0.30	0.26
Magnesium	----	------	6	.11	.53
Sodium	----	------	6	.03	.73
Potassium	----	------	6	.14	.46
Alkalinity	----	------	6	.02	.77
Upper Island Lake (Hypolimnion)					
Calcium	----	------	6	0.06	0.64
Magnesium	0.47	-0.001	6	.70	.04
Sodium	----	------	6	.00	.90
Potassium	----	------	6	.22	.35
Alkalinity	----	------	6	.05	.66
Oyster Lake					
Calcium	----	------	5	0.05	0.71
Magnesium	----	------	5	.24	.40
Sodium	1.06	-0.002	5	.84	.03
Potassium	----	------	5	.26	.38
Alkalinity	----	------	5	.01	.85

Additional evidence of a precipitation source for chloride and sulfate is provided by the similarity of their mean concentrations (table 10), even though other major ions differ greatly in concentration. Also, these concentrations are similar to the concentration in the snowpack in the drainage basin of Ned Wilson Lake. Samples collected prior to snowmelt indicated chloride concentrations of 0.04-0.10 mg/L and sulfate concentrations of 0.33-0.74 mg/L.

The results presented in tables 7-9 indicate that these lakes are relatively constant in chemical concentration of most constituents reported here. This is an extremely useful finding for the purpose of monitoring changes in lake chemistry that may result from future changes in precipitation chemistry. In contrast to pH, which varies as a function of many factors that must be understood, most chemical constituents seem controlled by a steady source from internal recycling, weathering, and precipitation.

Table 9.--*Regression characteristics of atmospherically contributed constituents against julian date*

Species	n	R-square	P>F
		Ned Wilson Lake	
Chloride--------	15	0.01	0.74
Sulfate---------	15	.00	.84
		Upper Island Lake (Epilimnion)	
Chloride--------	6	.01	.84
Sulfate---------	6	.05	.66
		Upper Island Lake (Hypolimnion)	
Chloride--------	6	.01	.82
Sulfate---------	6	.33	.24
		Oyster Lake	
Chloride--------	5	.49	.19
Sulfate---------	5	.08	.64

Those constituents not having a significant correlation with julian date may be presented best as mean values. Such constituents may only appear to vary because of analytical-precision limits, or may actually vary because of shifting chemical equilibria or hydrologic fluctuations. The statistical characteristics of the means are summarized in table 10.

Trace Constituents

Mean values

Trace constituents may be contributed to a lake by rock weathering or precipitation. Their reactivity with the other chemical constituents and the biota may result in complex variations in concentration, or in only minor variation. Many of the possible chemical controls can be evaluated by determining whether solubility limits are equaled or exceeded, thus limiting the potential for increased concentrations. The statistical characteristics of the means are presented in table 11.

Table 10.--*Statistical characteristics of the mean for constituents not varying with julian date*

[concentrations in milligrams per liter except for alkalinity, which is in microequivalents per liter)

Variable	n	Minimum	Maximum	Mean	Standard Error
			Ned Wilson Lake		
Ammonia	14	0.003	0.09	0.04	0.01
Nitrite + nitrate	14	.01	.08	.02	.01
Orthophosphate	15	<.002	.007	.003	.0004
Silica	13	.7	1.2	1.2	.04
Calcium	15	.70	2.10	1.18	.11
Magnesium	15	.13	.27	.21	.01
Sodium	15	.13	.52	.22	.02
Potassium	15	.11	.34	.20	.01
Chloride	15	.01	.31	.11	.02
Fluoride	15	<.01	.09	.02	.01
Sulfate	15	.02	.82	.61	.05
Alkalinity	21	30	64	49	2.3
			Upper Island Lake (Epilimnion)		
Ammonia	5	0.003	0.11	0.03	0.02
Nitrite + nitrate	6	<.001	.02	.01	.003
Orthophosphate	6	.002	.003	.002	.0002
Silica	6	1.7	2.6	2.2	.14
Calcium	6	1.0	2.0	1.4	.15
Magnesium	6	.30	.34	.32	.01
Sodium	6	.31	.40	.33	.01
Potassium	6	.10	.35	.28	.04
Chloride	6	.09	.18	.12	.01
Fluoride	6	<.01	.02	.01	.004
Sulfate	6	.58	.84	.65	.04
Alkalinity	6	61	91	82	4.5
			Upper Island Lake (Hypolimnion)		
Ammonia	6	0.01	0.13	0.06	0.02
Nitrite + nitrate	6	.09	.22	.12	.02
Orthophosphate	6	<.01	.04	.01	.006
Silica	2	.9	1.5	1.2	.3
Calcium	6	1.0	2.2	1.3	.18
Magnesium	6	.29	.32	.31	.01
Sodium	6	.27	.35	.30	.01
Potassium	6	.10	.36	.27	.04
Chloride	6	.11	.16	.13	.01
Fluoride	6	.01	.03	.01	.003
Sulfate	6	.62	.94	.76	.05
Alkalinity	6	62	94	76	4.7

Table 10.--*Statistical characteristics of the mean for constituents not varying with julian date*--Continued

Variable	n	Minimum	Maximum	Mean	Standard Error
Oyster Lake					
Ammonia-------------	4	0.01	0.06	0.04	0.01
Nitrite + nitrate---	4	.01	.01	.01	.0002
Orthophosphate------	4	.002	.004	.002	.0005
Silica--------------	4	2.0	3.0	2.4	.2
Calcium-------------	5	2.1	3.0	2.5	.18
Magnesium-----------	5	.74	1.1	.95	.06
Sodium--------------	5	.58	.70	.63	.02
Potassium-----------	5	.19	.40	.26	.04
Chloride------------	5	.10	.25	.14	.03
Fluoride------------	5	<.01	.04	.01	.01
Sulfate-------------	5	.71	.85	.79	.03
Alkalinity----------	5	164	216	192	11

Mineral-solubility controls

To determine whether mineral-solubility controls may control concentrations of the trace constituents the data were analyzed with SOLMNEQ (Kharaka and Barnes, 1973), an equilibrium-solubility model. Although kinetics can determine whether potential solubility controls are important in controlling concentrations, several minerals seem to be likely controls in these lakes. This hypothesis is based on the consistent tendency for the analytical data to approximate calculated solubilities for these minerals. Aluminum may be controlled by the solubility of gibbsite, copper by copper oxide, and boron by borax. X-ray diffraction analyses did not indicate the presence of these three minerals in the soil of the drainage basin of Ned Wilson Lake. Lack of crystalline structure, and small concentrations relative to other minerals, could account for the apparent absence of these minerals. More detailed work is needed specifically designed to determine whether these minerals control lake chemistry. Many of the analyses indicated supersaturated conditions with several minerals that may not be effective controls because of kinetic constraints. Among these are: andalusite, apatite, chlorite, corundum, montmorillonite, and muscovite. Apatite, chlorite, and montmorillonite were identified by x-ray diffractograms.

Table 11.--*Statistical characteristics of the mean for trace constituents*

[Values of n differ, because some analyses for some constituents were less than detection limits (all concentrations in micrograms per liter)]

Trace Constituent	n	Minimum	Maximum	Mean	Standard error
			Ned Wilson Lake		
Aluminum----------	13	10	25	16	1
Arsenic-----------	4	.3	1	.6	.2
Boron-------------	13	7	12	10	.5
Cadmium-----------	6	.4	1	.7	.1
Chromium----------	2	1	1	1	---
Copper------------	7	1	7	3	.8
Iron--------------	12	3	14	6	.9
Lead--------------	10	1	3	2	.2
Manganese---------	12	1	6	2	.4
Nickel------------	3	1	11	5	3
Zinc--------------	9	1	6	3	.5
			Upper Island (Epilimnion)		
Aluminum----------	5	22	30	28	1
Arsenic-----------	1	----	--	.4	---
Boron-------------	5	5	13	9	1
Cadmium-----------	4	.4	1	.6	.1
Chromium----------	1	----	--	1	---
Copper------------	4	2	4	3	.4
Iron--------------	5	5	24	10	3
Lead--------------	3	1	3	2	.7
Manganese---------	3	.7	2	1	.2
Mercury-----------	1	----	--	1	---
Nickel------------	4	.5	4	2	.9
Zinc--------------	2	1	15	8	7
			Oyster Lake		
Aluminum----------	4	29	45	39	4
Arsenic-----------	2	.5	.6	.6	---
Boron-------------	4	9	13	11	.9
Cadmium-----------	4	.2	1.4	.8	.2
Chromium----------	1	----	----	1	---
Copper------------	3	2.5	3.5	3	.3
Iron--------------	4	17	26	23	2
Lead--------------	4	1	6	3	1
Manganese---------	2	.7	1.5	1	.4
Nickel------------	3	.5	1	.8	.2
Zinc--------------	3	1.3	10	6	3

SUMMARY

The chemistry of three dilute lakes in the Flat Tops Wilderness Area, Colorado, can be divided into three principal components: (1) Biologically controlled parameters that vary as a function of growing conditions; (2) constituents with concentrations that are determined by the degree of chemical weathering; and (3) constituents with concentrations that result from solubility controls, or a steady-state concentration resulting from relatively constant sources. pH is an example of a biologically controlled characteristic, calcium is an example of a chemical-weathering controlled constituent; aluminum is an example of a constituent that may be controlled by the solubility of the mineral gibbsite, whereas sulfate is an example of a constituent controlled by precipitation.

Although quite variable during the ice-free season, pH can be predicted from processes that regulate photosynthesis. The use of simple models relating pH to controls on light intensity (cloud cover and time-of-day), and to stage in the growing season (julian date), explains as much as 63 percent of the variance in pH. Thus, the detection of trends in pH resulting from changes in precipitation chemistry can be greatly simplified by the use of these models.

Most chemical constituents measured in this study seem to vary in concentration about a mean value, with little or no trend during the ice-free season. Mineral solubility may control the concentration of some constituents and may tend to keep the concentration constant, barring major changes in watershed chemistry. Other constituents have concentrations that probably result from the averaging effect of snowpack accumulation on atmospheric sources. Thus, changes in mean concentrations in precipitation could be detected by statistically different mean concentrations in the future, particularly if the same changes are measured in the precipitation.

By using the results presented here, future changes in lake chemistry can be detected more accurately and in less time than without these results. This would allow a rapid dissemination of information on the effects of economic development as it progresses. Predictions of changes in lake chemistry as a function of the quantity and location of atmospheric emissions can be readily verified or rejected, and our predictive models can be modified to more accurately describe the systems modeled. If this approach is used, it should be possible to develop measures to prevent significant deterioration of the lakes, while avoiding overly restrictive emissions controls. The results of this study also should be of value in determining the reliability of other studies that show apparent changes in lake pH, based on the comparison of single measurements of pH made many years apart.

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