

**ELEMENTAL ANALYSIS OF
BOUNDARY WATERS CANOE AREA LICHENS
OF THE
SUPERIOR NATIONAL FOREST**

Final Report

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by

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ABSTRACT

In the final report on the lichens and air quality in the Boundary Waters Canoe Area (Wetmore, 1987) it was recommended that a restudy of the elemental analysis of lichens be done every five years. This report is on the first restudy done in 1992.

In this study four species of lichens were collected during June, 1992 at the same localities as the previous study. The methods used were the same as in the previous study.

The results of this study showed some increase in five elements (Al, Fe, Cu, Cr and K) in lichens. These elements may come from airborne dust or their increase may be due to random changes. ANOVA and pairwise comparisons by statistical analysis showed a significant increase in the element group {Al, Fe, Cr, S} in all species at most localities but a decrease in {B} at all localities. The Trap Lake locality was more frequently at the low end of the accumulation scale and Lac La Croix was more frequently at the high end. It is concluded that there probably has been no important change in the air quality in the wilderness. The recommendation is made that the periodic five-year restudy of elemental analysis be continued.

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INTRODUCTION

Lichens are able to accumulate chemical elements in the excess of their metabolic needs depending on the levels in the substrate and air and, since lichens are slow growing and long lived, they serve as good summarizers of the environmental conditions in which they are growing. Chemical analysis of the thallus of lichens growing in areas of high fallout of certain elements will show elevated levels in the thallus. Toxic substances (such as sulfur) are also accumulated and determination of the levels of these toxic elements can provide indications of sub-lethal but elevated levels in the air (Wetmore, 1987).

During 1986 a complete study of lichens and air quality was done in the Boundary Waters Canoe Area (BWCA), including a species list and elemental analysis of three species at six localities. The report showed no elevated accumulation of elements at any locality. The report recommended that a restudy of elemental analysis be done every five years.

During June, 1992 all six of the elemental analysis localities used in the earlier study were revisited for new collections. One lichen species was added in the study for a better comparison with other regional studies (Wetmore, 1985, 1988a, 1988b, 1988c).

METHODS

Methods used in the present study were the same as those of the original study (Wetmore, 1987). All six of the previous localities were again sampled in June, 1992. At

each locality a bag of each species was collected from branches of conifers. Lichens were cleaned but not washed. Three replicates were obtained from each bag of each species for each locality. Multi-element analysis was by ICP and sulfur by infra red absorption. In the original study three species were analyzed (Cladina rangiferina, Evernia mesomorpha, and Hypogymnia physodes). In the present study Parmelia sulcata was added to the three species previously used to provide a better comparison with other regional studies.

Total fluoride content was studied in two species (Evernia mesomorpha and Hypogymnia physodes) at two localities. Analyses were done with two replicates of the 1986 collections and also two of the 1992 collections. Samples were prepared by grinding and digestion with 0.05 N sulfuric acid and one drop of Brij-35 wetting solution in a 50 ml polypropylene tube for 15 minutes. Sodium hydroxide was then added and the sample shaken for 15 minutes. Fluoride was determined using the Orion combination electrode with continuous stirring after addition of 5 ml of 3 M NaOAc and 10 ml of 0.5 M Na Citrate buffers to control the interfering ions, particularly aluminum ions. Standards were also included with the unknowns.

RESULTS AND DISCUSSION

Table 1 gives the results of the analysis for all replicates arranged by species. Table 2 gives the means and standard deviations for each set of replicates. All reported values were above the lower detection limits of the instruments. Analytical splits were made from some samples and are indicated by "@" in the tables. In these analytical splits the lichens were ground and mixed before being divided into replicates to determine the instrument error. Table 3 gives the values from the 1986 study and the 1992 study arranged by species and locality.

One additional species (Parmelia sulcata) was included in the present study because it has been used in other regional studies at Isle Royale National Park (Wetmore, 1985), Voyageurs National Park (Wetmore, 1984), and Grand Portage National Monument (Wetmore, 1992). Mean values for this species from these other areas is included in Table 3.

Table 1. Analysis of BWCA Lichens

Values in ppm of thallus dry weight

Species	P	K	Ca	Mg	Al	Fe	Na	Mn	Zn	Cu	B	Pb	Ni	Cr	Cd	S	Locality
<u>C. rangiferina</u>	579	1549	843	340	386	378	14.8	91.6	15.8	1.5	1.3	2.1	0.5	0.5	0.1	331	Saganaga
<u>C. rangiferina</u>	541	1418	731	319	360	346	14.9	79.5	14.9	1.5	1.3	2.2	0.5	0.6	0.1	391	Saganaga
<u>C. rangiferina</u>	505	1367	689	306	331	331	18.2	79.3	13.4	1.5	1.3	2.3	0.6	0.6	0.1	396	Saganaga
<u>C. rangiferina</u>	517	1359	721	312	276	264	15.3	82.7	13.1	1.5	1.2	2.3	0.5	0.6	0.2	426	Saganaga@
<u>C. rangiferina</u>	559	1459	700	320	298	289	16	77.4	14.1	1.6	1.2	2.2	0.6	0.6	0.2	418	Saganaga@
<u>C. rangiferina</u>	550	1413	700	315	285	273	15.3	79	14.1	1.5	1.1	2	0.5	0.5	0.2	445	Saganaga@
<u>C. rangiferina</u>	634	1707	1144	428	314	281	18.7	52.5	22.7	1.9	1.2	1.9	0.5	0.6	0.2	429	Trap Lake
<u>C. rangiferina</u>	506	1518	934	342	307	275	17.3	43.3	20.6	1.9	1	2.4	0.6	0.6	0.2	488	Trap Lake
<u>C. rangiferina</u>	495	1333	1015	401	309	276	16.1	46.4	19.3	1.8	1.1	2.3	0.6	0.6	0.2	482	Trap Lake
<u>C. rangiferina</u>	624	1610	1101	365	294	262	15.4	52.5	23.6	1.9	1	2	0.5	0.5	0.2	474	Trap Lake@
<u>C. rangiferina</u>	616	1580	1097	365	299	265	15.8	50.2	23.6	1.8	0.9	1.8	0.5	0.5	0.2	471	Trap Lake@
<u>C. rangiferina</u>	653	1643	1073	363	307	278	17.3	51.6	23.8	2	1.2	2.2	0.5	0.5	0.2	521	Trap Lake@
<u>C. rangiferina</u>	303	958	607	267	260	337	15.9	93.9	14.4	1.5	1.1	2.1	0.5	0.5	0.2	289	Basswood L
<u>C. rangiferina</u>	319	1038	662	274	235	283	14.4	82.6	14.1	1.5	1.1	2.1	0.5	0.5	0.2	293	Basswood L
<u>C. rangiferina</u>	358	1078	734	295	290	381	18.3	96.3	14.7	1.5	1.4	2	0.5	0.6	0.2	250	Basswood L
<u>C. rangiferina</u>	324	923	694	273	252	331	14.4	85.6	13.9	1.4	1.2	2.1	0.5	0.5	0.2	303	Basswood L@
<u>C. rangiferina</u>	353	1022	687	282	261	334	15.6	85.7	14	1.4	1.2	2	0.5	0.6	0.2	289	Basswood L@
<u>C. rangiferina</u>	362	1046	700	289	251	300	16.3	90.5	14.7	1.5	1.3	1.9	0.5	0.5	0.2	317	Basswood L@
<u>C. rangiferina</u>	285	982	396	243	410	565	36.6	15.5	11.6	1.5	1.1	2.5	0.7	0.7	0.2	443	Lac La Croix
<u>C. rangiferina</u>	288	950	381	231	413	568	35.1	14.5	11.2	1.6	1.3	2.9	0.8	0.8	0.2	400	Lac La Croix
<u>C. rangiferina</u>	309	1063	419	241	342	496	35.9	15.3	11.4	1.8	1.4	3.2	0.8	0.7	0.2	385	Lac La Croix
<u>C. rangiferina</u>	306	1038	416	248	387	533	33.2	15.4	11.3	1.8	1.4	3	0.8	0.8	0.2	406	Lac La Croix@
<u>C. rangiferina</u>	321	1071	418	256	384	522	34	15.9	11.3	1.8	1.3	3.2	0.8	0.7	0.2	464	Lac La Croix@
<u>C. rangiferina</u>	331	1102	441	260	385	518	36.4	16.5	11.5	1.9	1.5	3.2	0.8	0.9	0.2	446	Lac La Croix@
<u>C. rangiferina</u>	386	1890	643	370	449	898	29.5	31.7	30.1	1.9	1.4	1.8	0.7	0.6	0.1	782	Trout Lake
<u>C. rangiferina</u>	368	1892	657	381	419	883	28.2	35.9	28.6	1.8	1.5	1.4	0.6	0.5	0.1	808	Trout Lake
<u>C. rangiferina</u>	395	1903	673	390	486	1051	31.7	34.4	29.5	1.9	1.6	2	0.7	0.7	0.1	792	Trout Lake
<u>C. rangiferina</u>	425	1132	885	452	276	247	12.8	33.3	16.2	1.4	0.8	1.6	0.4	0.5	0.1	388	Isabella L
<u>C. rangiferina</u>	497	1268	1026	525	285	257	13	41.3	18.6	1.6	1	1.9	0.5	0.5	0.1	357	Isabella L
<u>C. rangiferina</u>	590	1414	1219	618	268	236	13.8	47.8	21	1.7	1.2	1.7	0.5	0.5	0.2	332	Isabella L
<u>E. mesomorpha</u>	491	2061	1241	320	599	726	28.8	24.2	31.3	2.4	3.2	4.5	0.8	1.1	0.1	1100	Saganaga
<u>E. mesomorpha</u>	596	2324	1499	362	605	727	32.5	30	33.4	2.5	3.8	4.7	0.8	1.1	0.1	1230	Saganaga
<u>E. mesomorpha</u>	680	2781	1994	433	584	717	33.8	42.6	42.3	2.9	4.4	4	1	1.1	0.2	982	Saganaga
<u>E. mesomorpha</u>	614	2319	899	352	471	510	37.1	25.5	37.4	3.3	2.5	4.3	1	1.2	0.3	992	Trap Lake
<u>E. mesomorpha</u>	524	2253	931	316	421	450	30.1	28.5	40.3	3.2	2.2	3.7	0.7	0.9	0.3	969	Trap Lake
<u>E. mesomorpha</u>	523	2227	1070	323	488	535	28.5	30.3	38.8	3.2	2.2	3.9	0.8	1	0.3	1010	Trap Lake
<u>E. mesomorpha</u>	511	2146	699	370	661	1172	44.5	28.2	34.6	3.6	2.9	4.5	1.1	1.5	0.2	1190	Basswood L
<u>E. mesomorpha</u>	489	1949	646	343	654	1206	42.8	25.4	33.4	3.6	2.9	4.7	1.1	1.4	0.2	1090	Basswood L
<u>E. mesomorpha</u>	498	2068	742	397	786	1486	51.2	30.4	44.4	4	3.4	5.2	1.3	1.7	0.2	1160	Basswood L

Table 2. Summary of Analysis of BWCA Lichens

Values in ppm of thallus dry weight

Cladina rangiferina

	P	K	Ca	Mg	Al	Fe	Na	Mn	Zn	Cu	B	Pb	Ni	Cr	Cd	S	Locality
Mean	541	1445	754	322	359	352	16	83.5	14.7	1.5	1.3	2.2	0.5	0.6	0.1	373	Saganaga
St.Dev.	37	94	80	17	28	24	1.9	7	1.2	<.1	<.1	0.1	<.1	<.1	<.1	36	Saganaga
Mean	542	1410	707	316	286	275	15.5	79.7	13.8	1.5	1.2	2.2	0.5	0.6	0.2	430	Saganaga@
St.Dev.	22	50	12	4	11	13	0.4	2.7	0.6	<.1	0.1	0.1	<.1	<.1	<.1	14	Saganaga@
Mean	545	1519	1031	390	310	277	17.4	47.4	20.9	1.9	1.1	2.2	0.6	0.6	0.2	466	Trap Lake
St.Dev.	77	187	105	44	4	4	1.3	4.7	1.7	<.1	0.1	0.3	<.1	<.1	<.1	32	Trap Lake
Mean	631	1611	1090	364	300	268	16.1	51.4	23.7	1.9	1	2	0.5	0.5	0.2	489	Trap Lake@
St.Dev.	20	31	15	1	6	8	1	1.1	0.1	0.1	0.1	0.2	<.1	<.1	<.1	28	Trap Lake@
Mean	327	1025	668	279	262	334	16.2	90.9	14.4	1.5	1.2	2	0.5	0.5	0.2	277	Basswood L
St.Dev.	28	61	64	15	28	49	2	7.3	0.3	<.1	0.2	<.1	<.1	0.1	<.1	24	Basswood L
Mean	346	997	694	282	255	322	15.4	87.3	14.2	1.5	1.2	2	0.5	0.5	0.2	303	Basswood L@
St.Dev.	20	65	6	8	6	19	1	2.8	0.4	<.1	0.1	0.1	<.1	<.1	<.1	14	Basswood L@
Mean	294	998	399	238	388	543	35.9	15.1	11.4	1.6	1.3	2.9	0.8	0.7	0.2	409	Lac La Croix
St.Dev.	13	58	19	6	40	41	0.7	0.5	0.2	0.2	0.1	0.4	0.1	0.1	<.1	30	Lac La Croix
Mean	320	1070	425	255	386	524	34.6	15.9	11.4	1.8	1.4	3.1	0.8	0.8	0.2	439	Lac La Croix@
St.Dev.	13	32	14	6	2	8	1.6	0.5	0.1	<.1	0.1	0.1	<.1	0.1	<.1	30	Lac La Croix@
Mean	383	1895	658	380	451	944	29.8	34	29.4	1.9	1.5	1.7	0.6	0.6	0.1	794	Trout L
St.Dev.	14	7	15	10	34	93	1.8	2.2	0.8	0.1	0.1	0.3	0.1	0.1	<.1	13	Trout L
Mean	504	1271	1043	532	276	247	13.2	40.8	18.6	1.6	1	1.7	0.4	0.5	0.2	359	Isabella L
St.Dev.	83	141	167	83	9	11	0.5	7.3	2.4	0.2	0.2	0.2	<.1	<.1	<.1	28	Isabella L

Evernia mesomorpha

	P	K	Ca	Mg	Al	Fe	Na	Mn	Zn	Cu	B	Pb	Ni	Cr	Cd	S	Locality
Mean	589	2389	1578	372	596	723	31.7	32.3	35.7	2.6	3.8	4.4	0.9	1.1	0.2	1104	Saganaga
St.Dev.	95	364	383	57	11	6	2.6	9.4	5.9	0.3	0.6	0.3	0.1	<.1	<.1	124	Saganaga
Mean	554	2267	967	330	460	498	31.9	28.1	38.8	3.2	2.3	4	0.8	1	0.3	990	Trap Lake
St.Dev.	52	47	91	19	35	44	4.6	2.4	1.5	0.1	0.1	0.3	0.1	0.1	<.1	21	Trap Lake
Mean	499	2054	696	370	700	1288	46.2	28	37.5	3.8	3.1	4.8	1.2	1.5	0.2	1147	Basswood L
St.Dev.	11	100	48	27	74	172	4.5	2.5	6	0.2	0.3	0.4	0.1	0.1	<.1	51	Basswood L
Mean	700	2550	1058	438	860	1344	76.5	38.6	39	3.6	3.7	5.6	1.6	2	0.4	1143	Lac La Croix
St.Dev.	26	97	132	20	58	137	12.1	3.8	4.9	0.1	0.4	0.8	0.2	0.4	<.1	99	Lac La Croix
Mean	528	2123	997	367	633	1390	45.6	33.9	33.9	3.1	3.3	4.7	1.1	1.3	0.2	1173	Trout L
St.Dev.	28	159	136	18	31	104	1.3	2.4	2.5	0.2	0.1	0.2	0.1	0.1	<.1	104	Trout L
Mean	560	2346	644	368	762	902	41.8	20.8	38.9	4.8	2.6	10.1	1.6	1.7	0.4	1273	Isabella L
St.Dev.	30	145	19	15	33	45	1.9	1.3	5.3	0.2	0.1	0.6	0.1	0.1	<.1	25	Isabella L

Table 2, Continued. Summary of Analysis of BWCA Lichens

Hypogymnia physodes

	P	K	Ca	Mg	Al	Fe	Na	Mn	Zn	Cu	B	Pb	Ni	Cr	Cd	S	Locality
Mean	648	2519	18562	653	821	989	29.6	182.4	71.7	4.5	3.2	18	1.7	1.4	0.6	875	Saganaga
St.Dev.	100	263	3076	45	51	62	1.8	64.4	2.8	0.1	0.2	1.6	0.1	0.1	0.1	31	Saganaga
Mean	705	2898	13434	598	619	693	20.3	107.5	74.9	4.7	2.3	15.1	1.3	0.8	0.7	922	Trap Lake
St.Dev.	74	186	1479	17	16	12	3.5	5.1	1.9	0.1	0.2	0.5	0.2	0.2	<.1	26	Trap Lake
Mean	712	3003	15934	737	852	1380	26	143	69	4.3	2.7	13.6	1.5	1.3	1	942	Basswood L
St.Dev.	117	176	961	35	47	154	1.8	9.1	3	0.4	0.1	0.5	<.1	0.1	0.1	56	Basswood L
Mean	733	3106	22106	855	781	1234	31.1	222.7	72.2	4.2	2.8	11.5	1.6	1.2	1.3	934	Lac La Croix
St.Dev.	62	50	2629	26	40	52	1.9	39.2	2.2	0.3	0.1	1.4	0.1	0.1	0.1	57	Lac La Croix
Mean	641	2684	23902	692	676	1515	27.3	181.8	71.8	3.9	2.6	9.3	1.4	1.1	0.5	966	Trout L
St.Dev.	45	148	4253	26	32	147	2.9	19	9.1	0.2	0.1	0.2	<.1	0.1	0.1	117	Trout L
Mean	683	2693	19237	793	604	681	21.6	111.9	72.5	5.5	1.9	16.1	1	0.9	1	752	Isabella L
St.Dev.	48	114	264	76	42	51	2.2	29.6	2.8	0.4	0.1	0.7	0.1	0.1	<.1	26	Isabella L

Parmelia sulcata

	P	K	Ca	Mg	Al	Fe	Na	Mn	Zn	Cu	B	Pb	Ni	Cr	Cd	S	Locality
Mean	1150	3143	3452	564	1153	1197	25.9	199.3	85.2	4.4	4.7	16.9	1.6	1.4	0.4	1080	Saganaga
St.Dev.	118	126	370	16	109	127	2.2	59.2	2.1	0.1	0.5	2.3	0.2	0.2	<.1	56	Saganaga
Mean	1440	3271	2931	633	883	818	20.7	97.6	107.6	5.9	4.5	23.6	1.4	1.1	0.5	1032	Trap Lake
St.Dev.	90	94	403	25	50	36	2.1	1.2	5.5	0.2	0.4	7.1	0.1	0.1	0.1	25	Trap Lake
Mean	998	2907	2540	512	1203	1455	29	94.7	77.2	5.4	4.1	14.8	1.6	1.5	0.5	1147	Basswood L
St.Dev.	55	113	119	23	69	125	1.7	4.3	3.9	0.2	0.3	0.6	0.1	0.1	<.1	84	Basswood L
Mean	1232	3401	2646	618	1056	1369	38.1	109.4	73.6	4.4	3.9	13.3	1.8	1.3	0.5	1217	Lac La Croix
St.Dev.	81	155	159	38	133	185	0.8	6.7	5.2	0.1	0.2	0.2	0.2	0.2	0.1	25	Lac La Croix
Mean	1286	3239	4381	648	1036	1867	33.4	137.9	83.1	4.1	5.1	15.5	2	1.5	0.4	1062	Trout L
St.Dev.	264	371	281	61	24	111	6.4	18.2	5	0.1	0.2	0.2	0.1	0.1	<.1	14	Trout L
Mean	895	2698	4463	552	871	910	27.6	103.9	86.7	6.9	3.5	19.5	1.7	1.4	0.6	999	Isabella L
St.Dev.	114	184	449	26	56	56	2.1	21.2	11.2	0.2	0.2	3.2	0.1	<.1	<.1	45	Isabella L

Cladonia stellaris

	P	K	Ca	Mg	Al	Fe	Na	Mn	Zn	Cu	B	Pb	Ni	Cr	Cd	S	Locality
Mean	198	658	231	286	453	564	80.7	20.1	17.8	2.6	1.3	14.6	1.3	1.1	0.2	431	Lichen std.
St.Dev.	4	33	7	6	14	20	0.8	0.7	0.5	0.1	<.1	0.3	0.1	0.1	<.1	5	Lichen std.

NBS Peach

	P	K	Ca	Mg	Al	Fe	Na	Mn	Zn	Cu	B	Pb	Ni	Cr	Cd	S	Locality
Mean	1223	3747	4391	1210	481	169	16.2	691.9	69	3.2	18	12.4	2.1	2.3	0.3	NA	NBS-Peach
St.Dev.	32	59	55	17	4	2	1.4	8	1.4	0.1	0.3	0.4	<.1	0.2	<.1	NA	NBS-Peach

Table 3. Comparison of 1986 and 1992 BWCA Elemental Analysis

Values in ppm of thallus dry weight

Cladina rangiferina

	P	K	Ca	Mg	Al	Fe	Na	Mn	Zn	Cu	B	Pb	Ni	Cr	Cd	S	Locality
1986																	
Mean	392	1505	495	245	225	172	25.5	27.6	13.7	1.5	1.6	2.2	0.6	0.4	0.2	460	Saganaga
Std.Dev.	109	41	10	7	9	7	2.2	8.3	1.4	0.1	0.1	0.1	0.2	<.1	<.1	49	
1992																	
Mean	541	1445	754	322	359	352	16	83.5	14.7	1.5	1.3	2.2	0.5	0.6	0.1	373	Saganaga
St.Dev.	37	94	80	17	28	24	1.9	7	1.2	<.1	<.1	0.1	<.1	<.1	<.1	36	
1986																	
Mean	770	2328	740	346	210	156	36.4	52.4	20.2	2.1	1.7	1.2	0.6	0.4	0.2	513	Trap Lake
Std.Dev.	125	366	149	1	16	14	13.6	10.9	0.9	0.1	0.4	0.4	0.1	<.1	<.1	95	
1992																	
Mean	545	1519	1031	390	310	277	17.4	47.4	20.9	1.9	1.1	2.2	0.6	0.6	0.2	466	Trap Lake
St.Dev.	77	187	105	44	4	4	1.3	4.7	1.7	<.1	0.1	0.3	<.1	<.1	<.1	32	
1986																	
Mean	367	1496	455	230	256	210	24.5	59.5	14.2	1.4	1.3	1.5	0.7	0.4	0.1	435	Basswood Lake
Std.dev.	35	155	9	16	18	14	0.2	43	1.3	0.1	<.1	0.3	<.1	<.1	<.1	25	
1992																	
Mean	327	1025	668	279	262	334	16.2	90.9	14.4	1.5	1.2	2	0.5	0.5	0.2	277	Basswood Lake
St.Dev.	28	61	64	15	28	49	2	7.3	0.3	<.1	0.2	<.1	<.1	0.1	<.1	24	
1986																	
Mean	497	1822	529	315	256	213	27.5	26.7	12.5	1.4	1.9	1.1	0.6	0.4	0.1	462	Lac La Croix
Std.dev.	116	262	81	43	46	37	2.1	12.2	0.8	<.1	<.1	0.2	0.1	<.1	<.1	12	
1992																	
Mean	294	998	399	238	388	543	35.9	15.1	11.4	1.6	1.3	2.9	0.8	0.7	0.2	409	Lac La Croix
St.Dev.	13	58	19	6	40	41	0.7	0.5	0.2	0.2	0.1	0.4	0.1	0.1	<.1	30	
1986																	
Mean	639	2328	607	331	231	263	31.5	57.9	16.7	1.6	2	1	0.6	0.4	0.1	490	Trout Lake
Std.dev.	104	131	107	26	74	88	3.2	33.7	2.2	0.2	0.3	<.1	0.1	0.1	<.1	4	
1992																	
Mean	383	1895	658	380	451	944	29.8	34	29.4	1.9	1.5	1.7	0.6	0.6	0.1	794	Trout Lake
St.Dev.	14	7	15	10	34	93	1.8	2.2	0.8	0.1	0.1	0.3	0.1	0.1	<.1	13	
1986																	
Mean	335	1568	601	254	261	214	28	47.5	16.6	1.6	1.8	1.6	0.6	0.4	0.2	470	Isabella Lake
Std.dev.	22	105	5	22	42	30	5.4	1.3	1.5	0.1	<.1	0.6	0.4	<.1	<.1	42	
1992																	
Mean	504	1271	1043	532	276	247	13.2	40.8	18.6	1.6	1	1.7	0.4	0.5	0.2	359	Isabella Lake
St.Dev.	83	141	167	83	9	11	0.5	7.3	2.4	0.2	0.2	0.2	<.1	<.1	<.1	28	

Aluminum, iron, copper, potassium and chromium increased more often than the other elements. Boron decreased in all species at all localities and potassium decreased more often than it increased. The other elements showed mixed changes. No locality showed consistent increase or decrease in elemental levels. These increases may be due to random changes or they may indicate a trend that should be investigated. A comparison of the lichen standard from the two studies shows comparable values.

Table 4 gives the results of the analysis for fluorides (F) for the two species and two localities from collections made in 1986 and 1992. There is little difference between values for the two years.

Fluorides have been shown to be toxic to lichens (Nash, 1971, LeBlanc & Rao, 1971, Gilbert, 1971, and others). Fluoride literature has been summarized by Gilbert (1973) for the few studies done on lichens and fluorides. He states that the pattern of sensitivity to F is different than lichen sensitivity to sulfur dioxide. Fumigation studies have verified F damage at 5ppm F for 4 days (Nash, 1971) or 65 ppb for 12 hours (Comeau & LeBlanc, 1972).

Damage to the lichen is evident

Table 4. Fluorine analysis of BWCA Lichens
 Values in ppm of thallus dry weight

	1986	1992
<u>Evernia mesomorpha</u>		
Basswood Lake	2.6	3.2
Basswood Lake	2.0	2.8
Lac La Croix	1.5	1.3
Lac La Croix	1.5	0.8
Trout Lake	<.8	0.8
Trout Lake	<.8	0.8
 <u>Hypogymnia physodes</u>		
	1986	1992
Basswood Lake	1.4	1.7
Basswood Lake	1.1	2.3
Lac La Croix	1.6	0.9
Lac La Croix	1.5	1.1
Trout Lake	1.2	1.0
Trout Lake	1.0	1.1
Lichen standard <u>Cladina stellaris</u>	<.8	

by chlorotic spotting (Nash, 1971, Gilbert, 1973). The distance from the source where there is detectable accumulation in lichens seems to be restricted to about 7.5 miles (Gilbert, 1971). Nash (1971) reported levels in two lichens at 6000 meters from the source as 18-21ppm while levels 100m from the source were 174-220 ppm. There are very few literature reports on fluorides in lichens and the only one that reported F levels in either of the species analyzed in this study was Takala et al. (1978). They give accumulation values for Hypogymnia physodes in clean areas as 4.2-7.8 ppm while in polluted areas the levels reached 18.4-23.5 ppm. The levels in the BWCA for this species are below these levels for a clean locality. However, if the distance of detection is as short as 7.5 miles, as reported by Gilbert (1971), the BWCA localities may be too far away from any source to detect elevated levels. It may be concluded that the areas of the BWCA studied are not being damaged by fluorides from nearby iron mining.

STATISTICAL ANALYSIS

Introduction

Generally, one bag of lichens was collected from a site, cleaned, separated into groups (with different individuals in the groups), ground, and analyzed for chemical constituents. Occasionally, a composite sample was prepared and ground before being subsampled (these are noted in the data by an @ following the location name). The questions of interest are:

! is variability among independent samples larger than variability among composite subsamples?

! for a species, has there been a change in elemental composition from 1986 to 1992?

! within a year, and for a species, are there differences among locations? is there a geographical trend?

! are there differences between the BWCA and Rainbow Lake?

Variability

To answer this question the C. rangiferina data from 1992 was used -- the whole samples + average of subsamples as one data set, the subsamples as another -- since C. rangiferina was the only species with subsamples collected. The MSE was computed for each chemical element in each data set, and then compared using a F-test. Nine of the 16 elements showed significantly ($\alpha = .05$) higher variability among samples than among subsamples; for the other 7 elements there was no significant difference. Overall, these results provide strong evidence ($P < 0.00001$) that inter-sample variance is larger than within sample variance.

The variability due to instrument accuracy was lower than the variability due to population sampling. Individual lichen thalli will vary in accumulation depending on exposure and other factors. Perhaps a study should be done to examine different sampling methods to more accurately reflect the elemental accumulation at a locality. It may be that all thalli of a species at a locality should be cleaned and ground before dividing into replicates. The

resulting elemental levels would then represent an average for the locality.

Inter- and intra-year comparisons

Approach

Break elements into related groups using correlations. Reduce dimensionality through principal components analysis, using correlations to adjust for differing scales of the variables, with an aim of explaining at least 80% of the variability. Run analyses of variance.

The principal components analysis resulted in six groups of elements among the 16 elements measured: Group A = {K, Zn, Cu, Pb, Ni}, Group B = {Ca, Mg, Mn, Cd}, Group C = {Al, Fe, Cr, S}, Groups D-F = {P}, {Na}, {B}. Relative to the raw data, the analysis data for {P} have been multiplied by 0.10; the analysis data for {B} have been multiplied by 10.0.

Results -- 1986 vs. 1992

For all six analysis groups, the ANOVA showed a significant Yr*Species*Locality interaction ($\alpha = 0.05$), so these results are broken down by species. The element group {Al, Fe, Cr, S} showed an increase between 1986 and 1992 at a majority of the localities in all species, while the element {B} showed a decrease at all localities and species. All other element groups showed a mixed response.

1986 vs 1992

C. rangiferina

{K, Zn, Cu, Pb, Ni}

No between years differences.

{Ca, Mg, Mn, Cd}

Basswood 86 = 92 Isabella 86 < 92 La Croix 86 = 92 Saganaga 86 < 92 Trap 86 < 92 Trout 86 = 92

{Al, Fe, Cr, S}

Basswood 86 = 92 Isabella 86 = 92 La Croix 86 < 92 Saganaga 86 = 92 Trap 86 < 92 Trout 86 < 92

{P}

Basswood 86 = 92 Isabella 86 < 92 La Croix 86 > 92 Saganaga 86 < 92 Trap 86 > 92 Trout 86 > 92

{Na}

Basswood 86 > 92 Isabella 86 > 92 La Croix 86 < 92 Saganaga 86 > 92 Trap 86 > 92 Trout 86 = 92

{B}

1986 > 1992 for all localities; year effect is the same for all localities

E. mesomorpha

{K, Zn, Cu, Pb, Ni}

Basswood 86 = 92 Isabella 86 < 92 La Croix 86 = 92 Saganaga 86 = 92 Trap 86 < 92 Trout 86 < 92

{Ca, Mg, Mn, Cd}

No between years differences.

{Al, Fe, Cr, S}

Basswood 86 < 92 Isabella 86 < 92 La Croix 86 = 92 Saganaga 86 < 92 Trap 86 < 92 Trout 86 < 92

{P}

1986 < 1992 for all localities; year effect is the same for all localities

{Na}

Basswood 86 < 92 Isabella 86 < 92 La Croix 86 < 92 Saganaga 86 > 92 Trap 86 < 92 Trout 86 < 92

{B}

Basswood 86 > 92 Isabella 86 > 92 La Croix 86 > 92 Saganaga 86 > 92 Trap 86 > 92 Trout 86 > 92

H. physodes

{K, Zn, Cu, Pb, Ni}

Basswood 86 = 92 Isabella 86 > 92 La Croix 86 = 92 Saganaga 86 < 92 Trap 86 > 92 Trout 86 > 92

{Ca, Mg, Mn, Cd}

Basswood 86 < 92 Isabella 86 > 92 La Croix 86 < 92 Saganaga 86 > 92 Trap 86 = 92 Trout 86 = 92

{Al, Fe, Cr, S}

Basswood 86 < 92 Isabella 86 = 92 La Croix 86 < 92 Saganaga 86 < 92 Trap 86 < 92 Trout 86 < 92

{P}

Basswood 86 = 92 Isabella 86 < 92 La Croix 86 > 92 Saganaga 86 = 92 Trap 86 = 92 Trout 86 = 92

{Na}

1986 > 1992 for all localities; year effect is the same for all localities

{B}

Basswood 86 > 92 Isabella 86 > 92 La Croix 86 > 92 Saganaga 86 = 92 Trap 86 > 92 Trout 86 > 92

Results -- BWCA 1986

The results are summarized below using $\alpha = 0.05$. For all six analysis groups, the ANOVA showed a significant Species*Locality interaction, so these results are broken down by species. The error terms used for these comparisons were the same as those used for the Year differences above. The localities are arranged from low on the left to high on the right. Lac La Croix is the locality that is significantly isolated at the high end more frequently than any other locality. The Trap Lake locality is the most frequent isolated locality at the low end. There seems to be no other trend toward a geographical gradient from west to east for the intermediate localities.

Cladina rangiferina

{K, Zn, Cu, Pb, Ni}

Saganaga Basswood Lake Lac La Croix Isabella Lake Trout Lake Trap Lake
Lac La Croix Isabella Lake Trout Lake Trap Lake
Trout Lake Trap Lake

{Ca, Mg, Mn, Cd}

Saganaga Basswood Lake Lac La Croix Isabella Lake Trout Lake Trap Lake

{Al, Fe, Cr, S}

Saganaga Trap Lake Basswood Lake Isabella Lake Lac La Croix Trout Lake

{P}

Isabella Lake Basswood Lake Saganaga Lac La Croix Trout Lake Trap Lake
Basswood Lake Saganaga Lac La Croix Trout Lake Trap Lake
Trout Lake Trap Lake

{Na}

Basswood Lake Saganaga Lac La Croix Isabella Lake Trout Lake Trap Lake
Trout Lake Trap Lake

{B}

Basswood Lake Saganaga Trap Lake Isabella Lake Lac La Croix Trout Lake

Evernia mesomorpha

{K, Zn, Cu, Pb, Ni}

Trout Lake Isabella Lake Trap Lake Saganaga Basswood Lake Lac La Croix
Isabella Lake Trap Lake Saganaga Basswood Lake Lac La Croix
Basswood Lake Lac La Croix

{Ca, Mg, Mn, Cd}

Trap Lake Trout Lake Basswood Lake Isabella Lake Saganaga Lac La Croix

{Al, Fe, Cr, S}

	Trap Lake	<u>Saganaga</u>	<u>Isabella Lake</u>	<u>Trout Lake</u>	Basswood Lake	Lac La Croix
{P}				<u>Trout Lake</u>	<u>Basswood Lake</u>	Lac La Croix
	<u>Trout Lake</u>	<u>Isabella Lake</u>	<u>Basswood Lake</u>	<u>Saganaga</u>	<u>Trap Lake</u>	<u>Lac La Croix</u>
{Na}						
	<u>Isabella Lake</u>	<u>Trap Lake</u>	<u>Trout Lake</u>	<u>Basswood Lake</u>	<u>Saganaga</u>	Lac La Croix
					<u>Saganaga</u>	<u>Lac La Croix</u>
{B}						
	<u>Isabella Lake</u>	<u>Trout Lake</u>	<u>Trap Lake</u>	<u>Saganaga</u>	<u>Basswood Lake</u>	<u>Lac La Croix</u>

Hypogymnia physodes

{K, Zn, Cu, Pb, Ni}

	<u>Saganaga</u>	<u>Trout Lake</u>	<u>Basswood Lake</u>	<u>Lac La Croix</u>	Trap Lake	Isabella Lake
			<u>Basswood Lake</u>	<u>Lac La Croix</u>	<u>Trap Lake</u>	Isabella Lake

{Ca, Mg, Mn, Cd}

	<u>Basswood Lake</u>	<u>Trap Lake</u>	<u>Trout Lake</u>	Lac La Croix	Saganaga	Isabella Lake
			<u>Trout Lake</u>	<u>Lac La Croix</u>	<u>Saganaga</u>	Isabella Lake

{Al, Fe, Cr, S}

	Trap Lake	<u>Saganaga</u>	<u>Isabella Lake</u>	<u>Basswood Lake</u>	<u>Trout Lake</u>	<u>Lac La Croix</u>
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{P}

	<u>Isabella Lake</u>	<u>Basswood Lake</u>	Trout Lake	Trap Lake	Saganaga	Lac La Croix
		<u>Basswood Lake</u>	<u>Trout Lake</u>	<u>Trap Lake</u>	<u>Saganaga</u>	Lac La Croix

{Na}

	<u>Isabella Lake</u>	<u>Trap Lake</u>	Trout Lake	Basswood Lake	Lac La Croix	Saganaga
		<u>Trap Lake</u>	<u>Trout Lake</u>	<u>Basswood Lake</u>	<u>Lac La Croix</u>	Saganaga
				<u>Basswood Lake</u>	<u>Lac La Croix</u>	<u>Saganaga</u>

{B}

	<u>Saganaga</u>	<u>Trap Lake</u>	<u>Trout Lake</u>	<u>Basswood Lake</u>	Isabella Lake	Lac La Croix
		<u>Trap Lake</u>	<u>Trout Lake</u>	<u>Basswood Lake</u>	<u>Isabella Lake</u>	<u>Lac La Croix</u>

Results -- BWCA 1992

The results are and summarized below using a = 0.05. For all six analysis groups, the ANOVA showed a significant Species*Locality interaction, so these results are broken down by species. The error terms used for these comparisons were from new ANOVAs which included the P. sulcata data. The Trap Lake locality is most frequently isolated at the low end and Lac La Croix is most frequently isolated at the high end.

Cladina rangiferina

{K, Zn, Cu, Pb, Ni}

Basswood Lake Isabella Lake Saganaga Lac La Croix Trap Lake Trout Lake
Isabella Lake Saganaga Lac La Croix Trap Lake Trout Lake
Saganaga Lac La Croix Trap Lake Trout Lake

{Ca, Mg, Mn, Cd}

Lac La Croix Trout Lake Basswood Lake Saganaga Trap Lake Isabella Lake
Trap Lake Isabella Lake

{Al, Fe, Cr, S}

Basswood Lake Isabella Lake Saganaga Trap Lake Lac La Croix Trout Lake
Basswood Lake Isabella Lake Saganaga Trap Lake Lac La Croix Trout Lake

{P}

Lac La Croix Basswood Lake Trout Lake Isabella Lake Saganaga Trap Lake
Trout Lake Isabella Lake Saganaga Trap Lake
Isabella Lake Saganaga Trap Lake

{Na}

Isabella Lake Saganaga Basswood Lake Trap Lake Trout Lake Lac La Croix

{B}

Basswood Lake Saganaga Trap Lake Isabella Lake Lac La Croix Trout Lake

Evernia mesomorpha

{K, Zn, Cu, Pb, Ni}

Saganaga Trap Lake Trout Lake Basswood Lake Lac La Croix Isabella Lake
Trout Lake Basswood Lake Lac La Croix Isabella Lake

{Ca, Mg, Mn, Cd}

Saganaga Trout Lake Trap Lake Basswood Lake Isabella Lake Lac La Croix

{Al, Fe, Cr, S}

Trap Lake Saganaga Trout Lake Basswood Lake Isabella Lake Lac La Croix

{P}

Basswood Lake Trout Lake Trap Lake Isabella Lake Saganaga Lac La Croix

{Na}

Saganaga Trap Lake Isabella Lake Trout Lake Basswood Lake Lac La Croix

{B}

Trap Lake Isabella Lake Basswood Lake Trout Lake Lac La Croix Saganaga

Hypogymnia physodes

{K, Zn, Cu, Pb, Ni}

Trout Lake Isabella Lake Basswood Lake Lac La Croix Trap Lake Saganaga
Basswood Lake Lac La Croix Trap Lake Saganaga

{Ca, Mg, Mn, Cd}

Trap Lake Saganaga Trout Lake Basswood Lake Isabella Lake Lac La Croix

Trout Lake Basswood Lake Isabella Lake Lac La Croix
Basswood Lake Isabella Lake Lac La Croix

{Al, Fe, Cr, S}

Isabella Lake Trap Lake Lac La Croix Saganaga Trout Lake Basswood Lake

{P}

Trout Lake Saganaga Isabella Lake Trap Lake Basswood Lake Lac La Croix

{Na}

Trap Lake Isabella Lake Basswood Lake Trout Lake Saganaga Lac La Croix
Isabella Lake Basswood Lake Trout Lake Saganaga Lac La Croix
Basswood Lake Trout Lake Saganaga Lac La Croix

{B}

Isabella Lake Trap Lake Trout Lake Basswood Lake Lac La Croix Saganaga
Trap Lake Trout Lake Basswood Lake Lac La Croix Saganaga
Trout Lake Basswood Lake Lac La Croix Saganaga

Parmelia sulcata

{K, Zn, Cu, Pb, Ni}

Lac La Croix Basswood Lake Saganaga Trout Lake Isabella Lake Trap Lake

{Ca, Mg, Mn, Cd}

Basswood Lake Trap Lake Lac La Croix Isabella Lake Trout Lake Saganaga
Isabella Lake Trout Lake Saganaga

{Al, Fe, Cr, S}

Trap Lake Isabella Lake Saganaga Lac La Croix Basswood Lake Trout Lake
Trap Lake Isabella Lake Saganaga Lac La Croix Basswood Lake Trout Lake

{P}

Isabella Lake Basswood Lake Saganaga Lac La Croix Trout Lake Trap Lake

{Na}

Trap Lake Saganaga Isabella Lake Basswood Lake Trout Lake Lac La Croix
Saganaga Isabella Lake Basswood Lake Trout Lake Lac La Croix
Basswood Lake Trout Lake Lac La Croix
Trout Lake Lac La Croix

{B}

Isabella Lake Lac La Croix Basswood Lake Trap Lake Saganaga Trout Lake

Discussion -- BWCA 1986 vs 1992

The reasons for the increase of the element group {Al, Fe, Cr, S} at most localities between 1986 and 1992 are unknown. All other groups except {B} had a mixed response with about as many localities increasing and decreasing. The element {B} decreased at all

localities over this time period. In both sample years the Trap Lake locality was most frequently isolated at the low end and the Lac La Croix locality was isolated at the high end. The Trap Lake locality is at the eastern end of the wilderness and Lac La Croix is in the northwestern part. This might indicate an air quality gradient, but the intermediate localities do not show any such trend from west to east.

Results -- BWCA 1992 vs. Rainbow Lake 1992

All four species were included in these comparisons. Data for each locality were averaged prior to analysis (note that this changes the error term from within location to between locations). There were no element groups for which the 1992 compositions from the BWCA and Rainbow Lake differed significantly ($\alpha = .05$).

CONCLUSIONS

Instrument variability is less than the variability of the lichen population at a locality.

An increase was noted in some elements, especially the group {Al, Fe, Cr, S}, and perhaps Cu and K, between 1986 and 1992. This increase may not be important because these increases may be due to random changes. Some of these five elements are not important components of air pollution but may be due to airborne dust.

The reason for the higher levels of element groups at Lac La Croix and the lower levels at Trap Lake probably is not due to a regional west-east gradient because the intermediate localities are not regularly arranged.

It does not appear that there has been significant change in the air quality of the BWCA since 1986.

RECOMMENDATIONS

The original recommendation that elemental analyses be restudied every five years is again made here. Continued periodic study will help to determine whether the increase in certain elements is due to random changes or part of a trend with some significance.

A study of methods of lichen sampling is recommended to find a way to reduce the

variability due to differences in individual thalli. The BWCA is well suited for this study because of the abundance of suitable lichens for easy cleaning.

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