Working

2000 ELEMENTAL ANALYSIS OF LICHENS IN SLEEPING BEAR DUNES NATIONAL LAKESHORE AND GEORGE WASHINGTON CARVER NATIONAL MONUMENT

Final Report

Clifford M. Wetmore
Plant Biology Department
University of Minnesota
St. Paul, Minn. 55108

James P. Bennett
Biological Resources Division
U. S. Geological Survey
University of Wisconsin
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ABSTRACT

In the final report of the first study of the lichens and air quality in the Sleeping Bear Dunes National Lakeshore (SLBE) (Wetmore 1988) and George Washington Carver National Monument (GWCA) (Wetmore 1992) it was recommended that a restudy of the elemental analysis of lichens be done every five years. This report is on the results of a restudy done in 2000.

In August; 2000, four species of lichens were collected at three of the same localities in SLBE as the previous studies. In GWCA only one species was resampled at one locality in May, 2000. The methods used were the same as in the previous studies.

Statistical analyses of data from SLBE indicated that of the 15 elements measured in both years, six were significantly different for *Cladina*: Cd, Cr, Mn, Na, Pb and S. Chromium, Mn and Na all increased, while the other three decreased. The analysis of the GWCA data showed that twelve elements out of 23 plus ash changed significantly between 1991 and 2000, although this is based on very small sample sizes.

The recommendation is made that the periodic restudy of elemental analyses of both areas be continued but on a more frequent interval in GWCA and with more samples to determine if the changes are consistent. The five-year periodic restudy in SLBE seems to be adequate.

ACKNOWLEDGMENTS

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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. Because 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 tissues 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, 1988).

During 1987 a complete study of lichens and air quality was done in the Sleeping Bear Dunes NL, including a species list and elemental analysis of two species at five 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.

In 1991 a similar complete study was done in GWCA with similar results and recommendations.

Methods

Methods used in the present study were the same as those of the previous studies (Wetmore, 1988, 1992), except that two more species were added at SLBE. The two species that were added are ones that are used by the authors in many other park studies, and will allow more comparisons with other parks. Global positioning system readings of latitude and longitude were taken at each site and are given in Appendix I. One bag of each species was collected at each site, cleaned, ground, and analyzed for chemical constituents. 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 by the Soil and Plant Analysis Lab, University of Wisconsin-Madison using the same methods used in the previous studies (Wetmore 1988, 1992).

SLEEPING BEAR DUNES NATIONAL LAKESHORE

Three of the previous localities on the mainland were again sampled in August, 2000. These localities were: NW of Little Platte Lake, NE of Glen Arbor, and Good Harbor Bay. In the 1987 study two species were analyzed (*Cladina rangiferina*, and *Hypogymnia physodes*). In this restudy two additional species (*Evernia mesomorpha* and Parmelia sulcata) were included where adequate material could be found to provide a better comparison with other regional studies at Isle Royale National Park (Wetmore, 1985), Voyageurs National Park (Wetmore, 1984), and Grand Portage National Monument (Wetmore, 1992). Standards were also included with the unknowns for quality assurance checks.

In 2000, 8 samples of *Cladina rangiferina, Evernia mesomorpha*, and *Parmelia sulcata*, and 6 samples of *Hypogymnia physodes* were collected and analyzed for 23 elements plus ash. None of the samples had detectable boron and this element was omitted from any statistical analyses. Ash was not measured on every sample because there wasn't enough material. There were a total of 678 data points available for analysis (Table 1).

Data for the elements which were measured in both 1987 and 2000 were merged and the means were tested statistically with t tests. Means are given for elements measured only in 2000. All statistics were performed using *Systat*.

Results and Discussion

Of the 15 elements measured in both years (Table 2), six were significantly different for *Cladina*: Cd, Cr, Mn, Na, Pb and S. Chromium, Mn and Na all increased, while the other three decreased. For *Hypogymnia*, 10 of the fifteen elements changed significantly between years: Al, Cd, Cr, Cu, Fe, Mg, Na, Ni, S and Zn. Of these, Al, Cr, Cu, Fe, Mg, Na, Ni and S all increased, and Cd and Zn decreased. Given that Cr and Na increased significantly in both species, and Cd decreased, these may be real changes through time. There are no obvious explanations for explaining these changes, given what is known about sources near the park. Some of the elements in *Hypogymnia* that have increased, i.e. Al, Cr and Fe, are associated with soils, so perhaps the 2000 samples had a higher degree of soil contamination. Sulfur increased significantly in *Hypogymnia*, but decreased in *Cladina*, so it is not clear if any reductions in sulfur emissions has had an impact. Lead did decrease in both species, although not significantly in *Hypogymnia*, which may be due to too small a sample size.

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 changes in certain elements are due to random changes or part of a trend with some significance.

GEORGE WASHINGTON CARVER NATIONAL MONUMENT

The same species was studied in GWCA as the in original study. The collection was made near the original locality along the creek south of the pond in May, 2000.

Results and Discussion

Table 3 gives the results of the elemental analyses for 2000. The means for both years are compared in Table 4. When more than one was below the detection limits none of the values were used in the calculations.

Twelve elements out of 23 plus ash changed significantly between 1991 and 2000, although this is based on very small sample sizes (Table 4). Of the twelve elements that changed, seven increased, including Al, Fe, Mg, Mn, Na, Ni and S. All of these except for S probably increased due to soil contamination, as suggested by the one very high ash percentage. Sulfur may have increased due to atmospheric deposition or soil contamination. Five elements decreased, including Ca, Cd, Cu, P and Pb. Lead probably decreased due to the lead reduction in gasoline. Of the remaining four, two are nutritional elements (Ca and P), and the other two are heavy metals (Cd and Cu), so no logical explanation exists for these results. Potassium and zinc, both nutritional elements, did not change significantly between the two years, suggesting that the lichens are under no physiological stress.

Recommendations

Sampling of this lichen should continue, and it should be sampled more frequently to determine if the changes are consistent. Sample sizes should be increased to three if possible, and efforts to clean the lichens more should be emphasized.

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Table 1. Element concentration values (ppm) of Sleeping Bear Dunes NL lichens in 2000.

Al	As	Ca	Cd	Co	Cr	Cu	Fe	Hg	K	Mg	Mn	Mo	Na	Ni	P	Pb	S	Se	Ti	V	Zn	Ash	Locality
Cladina rangiferina																							
213.7	0.173	770.2	0.061	0.065	0.424	1.583	207.8	0.045	1512.6	383.5	37.810	0.094	35.186	0.369	380.4	1.222	497.1	0.570	6.106	0.527	18.381		Little Platte Lake
233.0	0.213	799.5	0.069	0.069	0.478	1.708	230.1	0.028	1550.2	411.9	41.454	0.099	57.686	0.337	377.4	1.278	519.8	0.377	7.244	0.555	20.179		Little Platte Lake
173.9	0.139	1250.1	0.087	0.053	0.351	1.315	141.6	0.019	1831.1	398.2	21.280	0.091	21.554	0.240	652.2	1.018	458.1	0.229	5.430	0.375	15.237	2.010	Glen Arbor
177.3	0.175	1251.4	0.110	0.058	0.414	1.454	156.3	0.014	2156.0	445.4	23.659	0.101	23.020	0.298	784.4	1.520	572.9	0.401	5.681	0.415	17.975		Glen Arbor
247.1	0.221	2775.7	0.082	0.095	0.538	1.976	266.2	0.023	1427.0	764.1	25.881	0.078	27.228	0.524	321.8	0.977	643.5	0.305	9.509	0.685	18.905	1.490	Good Harbor Bay W
278.9	0.241	2865.2	0.083	0.109	0.624	2.033	300.6	0.021	1368.3	752.1	22.635	0.071	36.607	0.620	319.1	1.611	633.7	0.368	9.957	0.754	18.443		Good Harbor Bay W
200.7	0.156	823.2	0.083	0.069	0.441	1.534	175.1	0.013	1021.4	349.7	36.817	0.068	28.947	0.322	235.3	1.185	433.4	0.147	6.381	0.506	16.749	2.800	Good Harbor Bay E
213.0	0.194	786.1	0.078	0.071	0.440	1.520	195.4	0.012	982.7	352.8	35.902	0.067	31.036	0.359	224.7	1.532	478.6	0.428	7.504	0.525	16.884		Good Harbor Bay E
Evernia mesomorpha																							
778.4	0.658	11141.3	0.305	0.300	2.013	4.682	1022.6	0.288	1940.1	499.3	16.452	0.272	47.302	2.360	480.9	9.299	1606.9	0.802	29.702	2.653	36.361		Good Harbor Bay W
850.5	0.907	21356.0	0.416	0.373	2.033	4.846	1105.2	0.371	1848.5	570.8	17.960	0.262	57.279	2.780	523.5	14.014	1678.9	0.906	33.722	2.884	37.223		Good Harbor Bay W
380.4	0.544	12845.7	0.189	0.247	1.384	3.605	406.9	0.152	3190.6	680.8	17.299	0.135	32.620	1.744	939.6	2.539	1416.5	0.491	17.353	1.069	24.585		Glen Arbor
401.4	0.501	13324.6	0.190	0.248	1.126	3.562	417.1	0.154	3467.7	688.1	17.246	0.140	39.728	1.715	1093.7	2.480	1527.7	0.537	16.994	1.039	23.411		Glen Arbor
733.3	0.735	1608.2	1.224	0.200	1.546	5.227	833.8	0.385	2914.0	490.2	27.519	0.266	31.971	1.303	765.8	5.515	1894.0	0.857	24.109	2.062	44.208	3.240	Good Harbor Bay E
756.5	0.798	2672.3	0.317	0.234	1.546	5.863	875.7	0.452	3155.3	555.5	30.556	0.273	31.289	1.381	883.6	6.336	2010.4	0.682	26.212	2.364	48.845	4.390	Good Harbor Bay E
712.1	0.704	1013.1	0.206	0.186	1.627	4.230	836.8	0.323	2319.8	417.5	19.677	0.244	32.384	1.125	595.6	6.017	1665.3	0.665	26.971	2.067	39.769		Little Platte Lake
839.6	0.750	1079.3	0.291	0.241	1.969	5.371	982.3	0.472	2625.5	482.3	24.603	0.312	31.791	1.546	630.1	7.174	1908.6	0.828	35.377	2.643	45.709	1.580	Little Platte Lake
Hypogymnia physodes																							
715.9	0.598	14326.0	0.916	0.320	1.679	5.939	814.3	0.207	2509.4	706.2	46.747	0.268	27.976	2.153	662.2	43.078	1802.8	0.969	25.342	2.307	81.085	5.370	Little Platte Lake
690.8	0.645	12741.0	0.845	0.328	1.709	6.341	836.7	0.254	2726.6	741.3	58.461	0.289	31.520	2.235	692.4	13.026	1936.4	1.055	24.815	2.404	91.094	3.980	Little Platte Lake
623.9	0.719	19404.3	0.775	0.366	1.457	6.825	700.7	0.216	3436.9	792.1	74.050	0.262	29.768	2.867	932.2	12.881	1918.8	0.796	22.876	2.200	78.198	4.620	Good Harbor Bay E
694.3	0.704	17847.7	0.762	0.370	1.629	6.631	766.2	0.271	3335.4	767.6	65.991	0.277	28.760	2.815	915.3	13.128	1854.5	1.048	23.793	2.271	77.388	7.120	Good Harbor Bay E
912.3	0.766	45459.5	0.733	0.576	2.133	6.169	1163.6	0.263	2071.7	748.6	25.358	0.398	46.226	4.791	548.2	23.668	1722.3	1.185	39.645	3.416	69.859	4.380	Good Harbor Bay W
868.0	0.716	49759.6	0.845	0.604	2.162	6.126	1094.4	0.248	1989.2	711.2	25.716	0.337	33.303	5.434	556.5	21.813	1724.6	1.127	38.330	3.388	67.227		Good Harbor Bay W
Parmelia sulcata																							
615.2	0.755	2728.4	0.524	0.213	0.926	6.954	593.9	0.135	3435.2	611.3	66.829	0.230	37.014	1.323	1086.2	11.754	1738.0	1.245	13.982	2.015	94.998		Good Harbor Bay E
626.7	0.798	2891.8	0.494	0.227	0.972	7.178	612.3	0.137	3348.4	594.2	60.558	0.226	34.300	1.421	1124.3	14.032	1707.1	1.281	14.139	2.202	101.380	36.700	Good Harbor Bay E
971.7	0.961	5749.1	0.821	0.383	1.892	8.848	982.1	0.183	2996.0	705.3	79.782	0.309	26.757	2.353	1022.4	12.247	1931.8	1.186	26.404	3.072	104.814	4.950	Little Platte Lake
824.1	0.804	7277.3	1.019	0.337	1.558	7.826	802.2	0.152	3087.0	649.3	69.030	0.267	32.243	2.018	963.9	9.668	1749.1	1.075	22.794	2.604	99.521	7.980	Little Platte Lake
826.5	0.761	11474.9	0.814	0.398	1.766	8.294	899.5	0.112	3956.5	1212.0	40.979	0.207	27.594	2.384	1878.1	9.583	1397.6	0.959	30.327	2.712	91.399	5.250	Glen Arbor
717.4	0.720	9071.9	0.502	0.340	1.452	8.340	769.5	0.077	4149.3	1308.1	34.865	0.180	15.587	1.881	1840.9	7.338	1261.3	0.521	26.750	2.310	41.099	5.580	Glen Arbor
1224.6	0.971	8725.9	0.524	0.548	2.270	8.614	1446.0	0.153	2566.8	848.9	42.537	0.294	28.793	2.750	979.8	25.045	1829.4	1.067	36.743	4.352	90.777	4.710	Good Harbor Bay W
1060.1	0.931	10641.6	0.473	0.491	2.076	7.986	1276.8	0.144	2344.7	758.9	33.101	0.310	69.329	2.669	909.3	23.434	1727.6	1.044	35.369	4.068	89.162		Good Harbor Bay W

Table 2. Comparison and summary of elemental analysis of lichens in Sleeping Bear Dunes NL. Numbers in **bold** are statistically significant at the 0.07 probability level.

Element	1987	2000	T	T probability	1987	2000	T	T probability	2000	
	Cladina rangiferina				Hypogymnia physodes				Evernia	Parmelia
Al	228.32	217.2	0.475	0.643	452.75	750.86	6.026	0.001	681.533	858.289
As		0.189				0.691			0.700	0.837
Ca	898.76	1415.185	1.49	0.167	12738.33	26589.69	2.051	0.095	8130.068	7320.119
Cd	0.204	0.082	6.157	0	1.137	0.813	10.691	0	0.392	0.646
Co		0.074				0.427			0.254	0.367
Cr	0.273	0.464	5.217	0	0.713	1.795	8.995	0	1.655	1.614
Cu	1.876	1.64	1.751	0.1	4.813	6.338	7.127	0	4.674	8.005
Fe	214.38	209.14	0.197	0.847	506.21	896.01	4.907	0.003	810.048	922.801
Hg		0.022				0.243			0.325	0.137
K	1555.378	1481.16	0.528	0.613	2841.47	2678.2	0.642	0.547	2682.687	3235.481
Mg	373.49	482.2	1.606	0.139	653.76	744.53	4.5	0.003	548.056	835.979
Mn	18.04	30.68	4.14	0.003	51.45	49.39	0.241	0.818	21.414	53.460
Mo		0.084				0.305			0.238	0.253
Na	21.186	32.658	2.371	0.035	15.22	32.93	6.318	0.001	38.045	33.952
Ni	0.66	0.384	2.526	0.176	1.043	3.382	2.823	0.026	1.744	2.100
P	372.23	411.91	0.555	0.596	666.45	717.79	0.506	0.629	739.102	1225.615
Pb	2.896	1.293	4.651	0.002	23.01	21.266	0.364	0.73	6.672	14.137
S	695.56	529.63	3.62	0.003	1686.667	1826.58	2.359	0.05	1713.520	1667.721
Se		0.353				1.03			0.721	1.047
Ti		7.23				29.13			26.305	25.814
V		0.543				2.664			2.098	2.917
Zn	17.09	17.84	1.164	0.263	90.35	77.48	2.521	0.04	37.514	89.144
Ash		2.1				5.09			3.070	10.862
# of samples	9	8			3	6			8	8

Table 3. Elemental concentrations in two samples of *Parmelia rudecta* from George Washington Carver NM, 2000.

Element	Sample 1	Sample 2
Al	865	1036
As	0.57	0.60
Ca	76084	56455
Cd	0.31	0.27
Co	0.62	0.57
Cr	1.46	1.77
Cu	4.72	5.07
Fe	669	831
Hg	0.090	0.084
K	2764	2891
Mg	692	697
Mn	32	41
Mo	0.25	0.23
Na	69	132
Ni	5.27	4.77
P	820	819
Pb	4.57	4.76
S	1405	1338
Se	0.45	0.59
Ti	27.1	27.4
V	2.34	2.55
Zn	30	30
Ash	16.28	

Table 4. Comparison and summary of elemental analysis of lichens in George Washington Carver NM. Numbers in **bold** are statistically significant at the 0.07 probability level.

Element	1991	2000	T	T probability	Comments
Al	506.33	950.62	6.51	0.007	
As		0.58			
B	1.78				Both 2000 samples BDL
Ca	96443.00	66269.39	3.60	0.037	
Cd	0.72	0.29	8.53	0.003	
Co		0.60			
Cr	1.27	1.61	1.86	0.160	
Cu	9.71	4.90	15.32	0.001	
Fe	323.33	749.72	6.84	0.006	
Hg		0.09			
K	2976.33	2827.62	1.35	0.269	
Mg	583.00	694.21	6.58	0.007	
Mn	14.07	36.48	6.13	0.009	
Mo		0.24			
Na	33.41	100.58	2.85	0.065	
Ni	1.75	5.02	15.86	0.001	
P	1149.67	819.37	21.51	0.000	
Pb	19.30	4.67	10.71	0.002	
S	1146.67	1371.76	3.12	0.052	
Se		0.52			
Ti		27.22			
V		2.44			
Zn	30.24	30.15	0.11	0.919	
Ash		16.28			One sample only
# of samples	3	2			

APPENDIX I

Latitude and Longitude of Elemental Analysis Localities - 2000

The following latitudes and longitudes were obtained during the 2000 survey by a Garmin GPS unit. The words in **bold** are those used in the tables.

Sleeping Bear NL

NW of **Little Platte L**ake at end of Peterson Road. On dunes back from shore with jack pines, white pines and juniper. Sec. 22, T27N, R15W. 44°43'44"N 86°06'10"W.

4 miles northeast of **Glen Arbor** at boundary of park west of Bass Lake. In apple orchard and abandoned fields. Sec. 7, T29N, R13W. 44°55'22"N 85°54'52"W.

Good Harbor Bay W southeast of Shalda Creek. Near shore in open jack pines and juniper between road and lake. Sec. 4, T29N, R13W. 44°56'25"N 85°52'38"W.

Good Harbor Bay E north of Little Traverse Lake. Back from shore in woods with oaks, pines, and openings and some quaking aspen. Sec. 3 & 10, T29N, R13W. 44°56'11"N, 85°51'12"W.

G. W. Carver NM

36°39'06"N, 94°55'53"W
59'15" 21°19"