

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

Element Baselines for Redwood National Park, California--

Composition of the Epiphytic Lichens

Hypogymnia enteromorpha and Usnea spp.

by

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This report is preliminary and has not been reviewed for conformity with the U.S. Geological Survey editorial standards and stratigraphic nomenclature. Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS.

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CONTENTS

	Page
Summary.....	1
Introduction.....	2
Use of lichens in biomonitoring.....	2
Location of the study area.....	2
Physiography of the study area.....	4
Vegetation of the study area.....	4
Sample collection, preparation, and analysis.....	6
Study design and statistical analysis of data.....	8
Results.....	10
Interpretations of the ANOV and summary statistics.....	10
Biogeochemical baselines.....	15
Element concentration comparisons.....	15
Chemistry of soil samples.....	17
Acknowledgments.....	18
References cited.....	19

APPENDICES

Appendix I.....	22
Appendix II.....	26

ILLUSTRATIONS

Figure 1. Location of the Little Bald Hills study area within Redwood National Park, northern California.....	3
Figure 2. Map showing the location of the study sites in the Little Bald Hills area.....	5
Figure 3. Simple linear regression plots of titanium concentrations in lichen tissue (dry weight base) versus percent ash yield	
Figure 3A. <u>Usnea</u> spp.....	7
Figure 3B. <u>Hypogymnia enteromorpha</u>	7
Figure 3C. <u>Parmelia chlorochroa</u>	7
Figure 4. Observed frequency distribution of the concentration of nickel in <u>Hypogymnia enteromorpha</u> tissue	
Figure 4A. Values plotted on a logarithmic scale.....	11
Figure 4B. Values plotted on an arithmetic scale.....	11

TABLES

Table 1. Analytical methodology and references for the analyses of sampled lichen material.....	9
Table 2. Variation in and summary statistics for the element concentrations in dry material of <u>Hypogymnia enteromorpha</u> , Little Bald Hills, Redwood National Park, California.....	13
Table 3. Variation in and summary statistics for the element concentrations in dry material of <u>Usnea</u> spp., Little Bald Hills, Redwood National Park, California.....	14
Table 4. Average concentrations of selected elements in lichens collected from areas defined as uncontaminated as reported in this study and from the literature.....	16

SUMMARY

In July, 1983 the U.S. Geological Survey (USGS) and the U.S. National Park Service (NPS) signed an interagency agreement to investigate suspected biogeochemical problems originating from airborne contaminants in and near selected national park units. Study designs and specific objectives differ from one park region to another and include: (1) the use of lichens (or other epiphytes) or vascular plant species as biomonitors of possible phytotoxic conditions; (2) the use of plant materials and soils to determine the region of measurable influence of a suspected point source of sulfur and/or metal contamination; and (3) the establishment of baseline biogeochemical and geochemical levels so that the magnitude of chemical changes with time can be monitored. Results of completed studies at Theodore Roosevelt and Everglades/Biscayne National Parks have now been published (Gough and others, 1985; Gough and others, 1986; and Jackson, Engleman, and Peard, 1985). Studies at Everglades/Biscayne National Parks and Santa Monica Mountains National Recreation Area are ongoing. Results and recommendations from these studies, as well as those in this report, are used in air-quality management decisions for the park units and for areas adjacent to them.

This report presents results of FY-84 studies at the Little Bald Hills region of Redwood National Park (RNP). These results are summarized as follows:

1. Samples of Hypogymnia enteromorpha and Usnea spp. (a mixture of species composed predominantly of U. lapponica and U. subfloridana) were collected to estimate baseline element levels in their tissue. These lichens are common epiphytes on Douglas-fir trees. The latter are found at scattered locations growing on the ultramafic-derived soils of Little Bald Hills. Baselines are given for barium, calcium, copper, manganese, nickel, phosphorus, strontium, vanadium, and zinc for both lichen species; for lithium, magnesium, and potassium for H. enteromorpha; and for aluminum, cerium, chromium, cobalt, iron, sodium, and titanium for Usnea.

Element concentrations of future collections of this same material can be compared to these baselines, and assessments can be made as to important changes in chemistry, if the same procedures of sample collection, preparation, and analysis are followed as are detailed in this study.

2. An unbalanced, nested, analysis-of-variance (ANOVA) design was used to partition the variability in the concentration of selected elements (in the tissue of both lichen species) between geographical distance increments and sample preparation and analysis procedures. The purpose of the design was to determine where the greatest proportion of the variability occurred so that possible geographical trends could be defined.

We found that there is very little natural variability in the concentrations of most elements in lichens. Because of this, the variability associated with sample processing (analytical error) becomes very important and is the dominant source of variability in the element-concentration data. Most commonly, for those elements with small proportions of analytical error, the greatest variability occurs between samples separated by small distances (200 to 700 m or <10 m) rather than between samples collected at larger distances (about 1 km). This means that, except for barium and cobalt, no large geographical trends were observed for element levels in lichen tissue along the Little Bald Hills ridge crest.

3. A very general comparison of element levels in H. enteromorpha from this study, compared to the chemistry of similar species reported in the literature, showed that magnesium and nickel levels are elevated, a reflection

of the ultramafic country rocks and the residual soils. Levels of cobalt could not be compared because of a lack of data in the literature for lichens; however, the concentrations of cobalt are elevated when compared to vascular plant species. It appears, therefore, that the biogeochemistry of both lichen species reflects the geochemistry of the ultramafic terrain over which they are growing.

4. These data provide a "snapshot" of the chemistry of corticolous (bark-inhabiting) epiphytic lichens against which possible future biogeochemical changes can be compared. The ability to make such comparisons is particularly important if an industrial facility begins operating near RNP. The construction of a laterite mining, milling, and refining facility at Gasquet Mountain northeast of Little Bald Hills, remains a possibility, particularly if development of national strategic and critical mineral reserves receives renewed emphasis and support.

5. We did not collect soil samples for chemical analysis in this study. Soil samples were provided by J. Popenoe of RNP-NPS, and semiquantitative analyses for this material are listed. All of the samples were geochemically similar to what would be expected in serpentine soils.

INTRODUCTION

Use of Lichens in Biomonitoring Studies

The use of lichens as indirect measures of air quality in urban areas has been extensively reviewed (Barkman, 1958; Ferry and others, 1973; Gilbert, 1973; Martin and Coughtrey, 1982). Martin and Coughtrey (1982, p. 131) list the following attributes of both lichens and mosses (non-vascular plants) that enhance their usefulness as accumulators of aerial fallout of metals compared to higher (vascular) plants: (1) "They are non-seasonal...in morphology and hence accumulation occurs throughout the year"; (2) "They possess a large surface area relative to dry weight and volume"; (3) "They lack a cuticular or similar wax covering on the thallus surface, thus allowing access of soluble metal ions to exchange sites"; (4) "They lack an absorptive system of comparable function to roots of higher plants; thus apart from old mine areas and other substrates rich in heavy metals, the major source of heavy metals is from the atmosphere"; (5) "They possess considerable ion-exchange properties by which heavy metals can be retained in the thallus"; and (6) "Their surface structure, roughness and topography is frequently such as to encourage the interception and retention of airborne particles."

Many epiphytic lichens, however, are very sensitive to the lower pH of percolating tree-canopy water that is common in urban or industrialized areas. As a consequence, they are often eliminated from the local flora. Where found in sufficient quantity, however, as they are at Little Bald Hills, they can be an ideal biological assay material for monitoring changes in plant tissue metal levels brought about by changing atmospheric chemistry.

Location of the Study Area

Little Bald Hills is located 16 km east of Crescent City, California, in northern Del Norte County (fig. 1). The area is an eastward projection of the northern tip of RNP and is located adjacent to Jedediah Smith Redwoods State Park and Six Rivers National Forest. Little Bald Hills, as distinguished from the more extensive Bald Hills prairie in the southern portion of RNP, is a crescent-shaped ridge about 610 m above the Smith River. The actual study

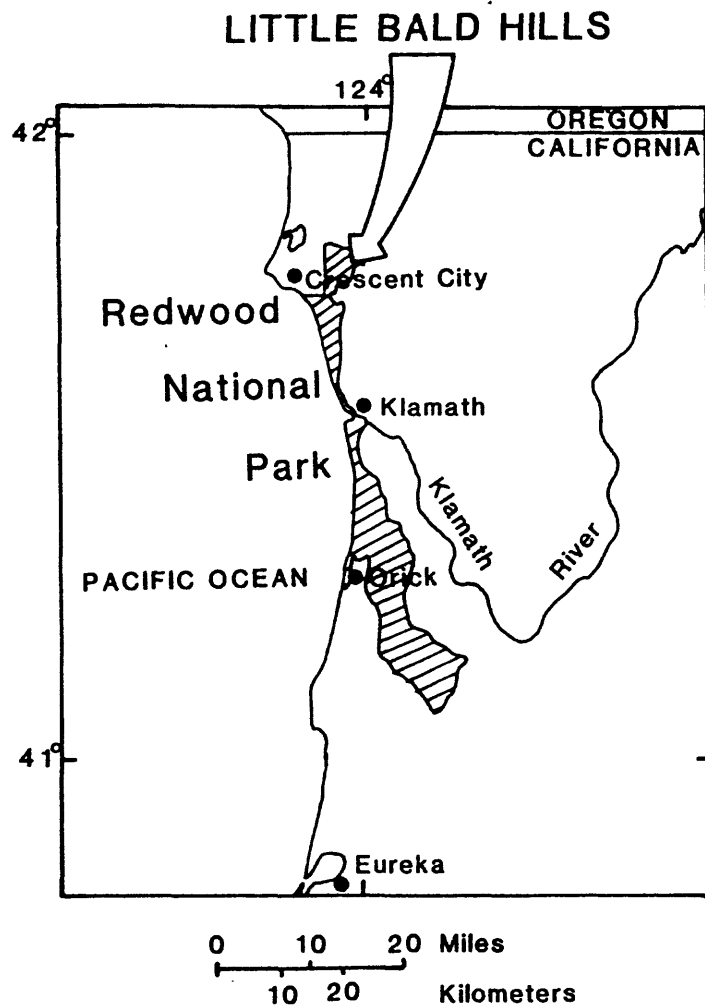


Figure 1. Location of the Little Bald Hills study area within Redwood National Park, northern California.

area is in the northeastern quarter of section 22 and the western one-half of section 23, T.16-N, R.1-E (fig. 2).

Physiography of the Study Area

The study area is composed of mostly Mesozoic ultramafic intrusives (Cater and Wells, 1953; Strand, 1964). An endemic mix of Coastal and Klamath province vegetation in the Little Bald Hills is the result of the physical and chemical nature of the country rocks and recurrent fires. The mixture of communities reflects a major regional fault, the Coast Range Thrust Fault, in the Little Bald Hills which separates the Coast Range (and its Franciscan assemblage sedimentary rocks) from the ultramafic rocks of the Klamath Mountain province (Madej and others, 1986). The steep sideslopes, especially to the south in the headwaters of drainages, reflect a coherent sandstone unit common in the Mill Creek basin.

The area is known for its wet winters and dry summers. Despite approximately 250 cm of annual rainfall, the shallow soils retain little moisture. During the summer the Little Bald Hills is on the edge of the coastal fog belt and is often above and east of the fog strata. The average daily maximum temperature is about 30°C in summer and the daily minimum is about 0°C in winter.

Vegetation of the Study Area

The following have been identified as the four predominant vegetation communities (stands) in the Little Bald Hills region: (1) Pinus jeffreyi Grev. & Balf. (Jeffrey pine) stands are primarily found on the ridgetops, growing on the ultramafic terrain. Jeffrey pine is the most distinctive tree of the area, generally forming open savanna-like stands with Festuca idahoensis Elmer and Rhamnus californica Esch. common in the understory. (2) Adjacent to the Jeffrey pine stands, on soils of the Franciscan assemblage, are Pseudotsuga menziesii (Mirb.) Franco (Douglas-fir) forests with an understory of Vaccinium ovatum Pursh., Polystichum munitum (Kaulf.) Presl., Festuca californica Vasey, and R. californica. Chamaecyparis lawsoniana (A. Murr.) Parl. is an associate of Douglas-fir and Alnus oregona Nutt. which is common in riparian areas. (3) Nearly pure stands of Pinus attenuata Lemmon (knobcone pine) are indicative of wildfires which last occurred in this area about forty years ago. (4) Growing as a fringe below the ridge top, generally on poorly drained Miocene sediments of the Wimer formation, are thickets of Arctostaphylos spp. (manzanita), primarily A. columbiana Piper.

Of the 186 species representing 134 genera of vascular plants that have been identified in the Little Bald Hills area, seven are endemic to ultramafic substrates in northwest California and southwest Oregon. Most of the plants identified are native, despite a history of grazing between the 1860's and park creation in 1968 (Hektner, 1986). The lichen flora of the area is less well known, with 43 species identified (Van Hook, 1984). No lichen studies have been conducted elsewhere in the park, and the non-vascular flora is poorly known. Of the 18 species on Redwood National Park's list of rare, threatened, and endangered vascular plants, nine have been collected on serpentine soils in or near the Little Bald Hills area. None are federally listed as endangered, but six are candidates for listing (U.S. Department of the Interior, 1986).

LITTLE BALD HILLS, REDWOOD PARK CALIFORNIA

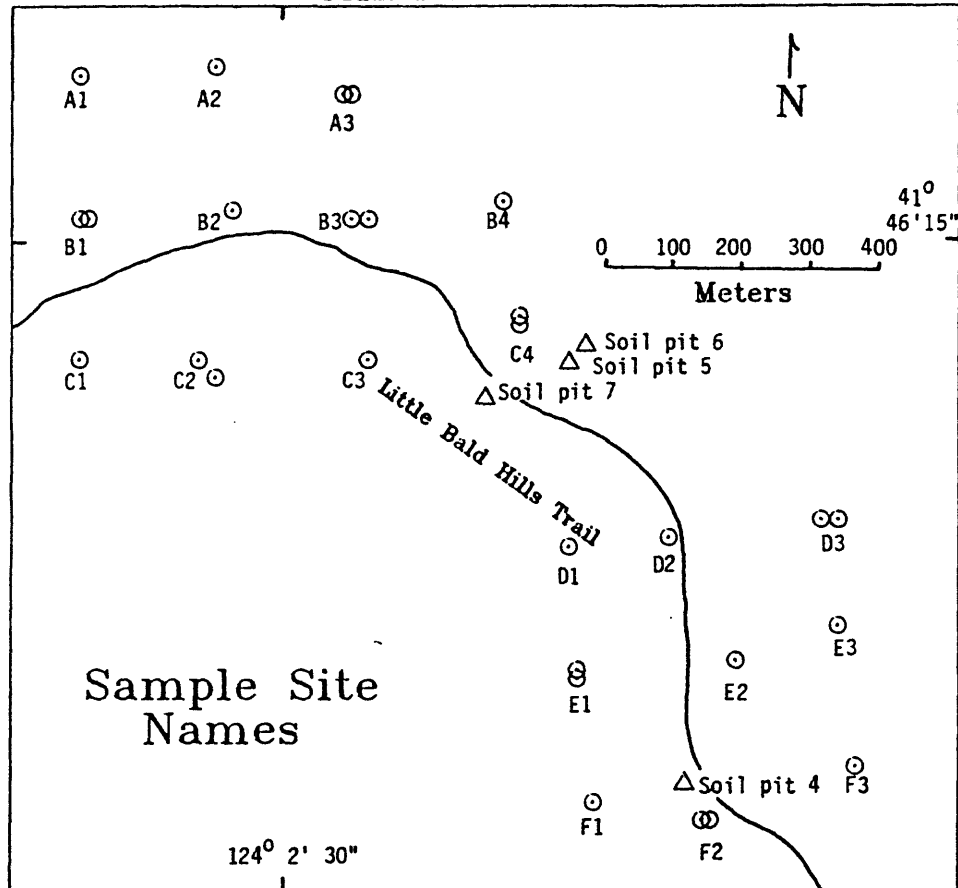


Figure 2. Map showing the location of the study sites in the Little Bald Hills area.

SAMPLE COLLECTION, PREPARATION, AND ANALYSIS

All field work was performed on June 27-30, 1984. Because the composition of both the vascular and non-vascular vegetation changes rapidly with changing elevation, slope angle, and aspect, we confined all of our work to the Little Bald Hills ridge crest.

Two study areas, whose centers were separated by 1 km (fig. 2), were established within the ultramafic terrain. Within the two areas, sample sites were located 200 m apart on a square grid. The northwestern area contained eleven sites (labeled with prefixes A, B, and C), whereas the southeastern area had nine sites (labeled with prefixes D, E, and F).

A site was defined as a single mature Douglas-fir (diameter at breast height, dbh, of 19 to 58 cm) with abundant lichen growth on the lower branches. The twenty-nine trees sampled for lichens had a mean dbh of 35 cm (standard deviation of 10.4). Once a site was carefully defined by compass and tape measure, the nearest Douglas-fir meeting the size and lichen cover criteria was selected for sampling. Usually more than one tree occupied a sampling site and these tree groups did not appear to be randomly distributed but instead occupied a specific ecological niche within the ultramafic terrain. All sampled trees were marked with plastic flagging and with an aluminum tag nailed to the trunk at about 2 m above the ground.

The number of lichen samples collected at each site was determined randomly (see Study Design section). At all sites samples of Hypogymnia enteromorpha (Ach.) Nyl. and Usnea spp. (mostly U. lapponica Vain. and U. subfloridana Stirt.) were collected. Samples consisted of clumps of numerous lichen thalli that were combined after their removal from the top side of each of the easily accessible lower branches of a single Douglas-fir. Each sample consisted of approximately 10-20 g and 20-30 g of H. enteromorpha and Usnea, respectively. The samples were stored in paper bags of known element content and allowed to dry at room temperature.

Microscopic examination of the lichen thalli collected in this mesic environment did not show gross surficial particulate contamination. This is in contrast to our experience in the use of soil lichens as metal accumulators in semi-arid environments (Gough and Erdman, 1977; Jackson and others, 1985). Studies have shown that lichen tissue often have fallout-derived particles that are deeply imbedded in intertwined tissue (Garty and others, 1979). These particles can not be removed by standard cleaning procedures.

One method of judging the degree of contamination originating from soil is to examine the relative abundance of titanium in the plant tissue and the relation between titanium levels and ash yield (Martin and Coughtrey, 1982). Figure 3 shows plots of titanium in three different lichen collections, Usnea spp. and Hypogymnia enteromorpha (figs. 3A and 3B, this study), and Parmelia chlorochroa (fig. 3C, Gough and Erdman, 1977). Not only does the total amount of titanium in lichen tissue increase from 3A to 3C but the relation of titanium to ash yield becomes more pronounced (correlation coefficients of 0.03, 0.27, and 0.93, for 3A, 3B, and 3C, respectively). In the 1977 study, samples of P. chlorochroa possessed entrapped soil particles. H. enteromorpha and Usnea were visually judged to be fairly free of surficial contamination. This conclusion is supported by the titanium vs. ash yield plots.

In the laboratory the contents of each bag was emptied into a porcelain pan. Tap water was added and miscellaneous organic material was removed with forceps. The thalli were therefore not washed except for submergence in tap water.

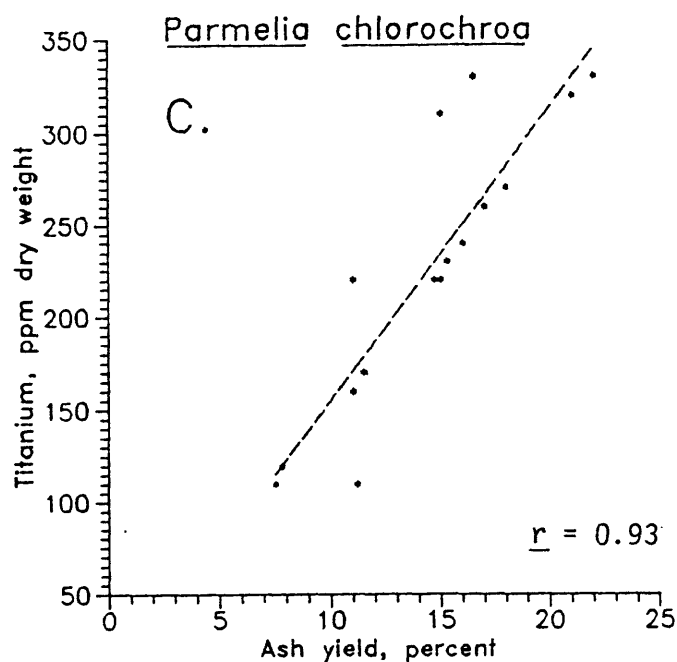
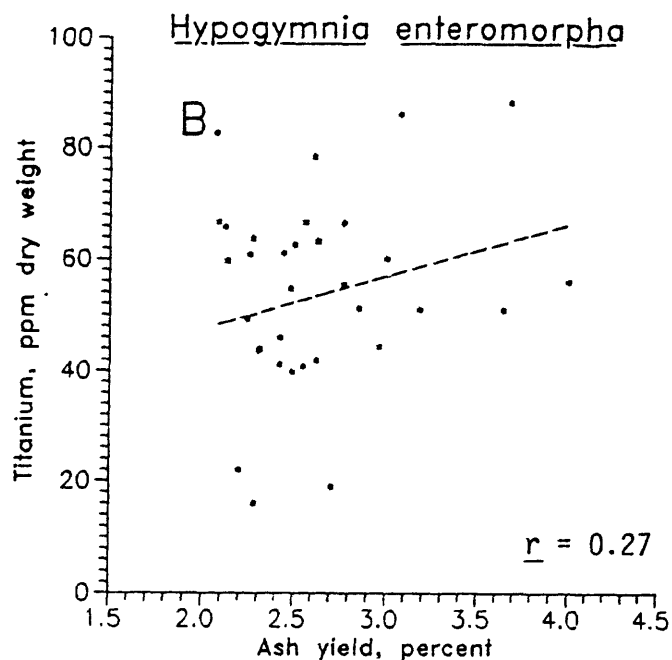
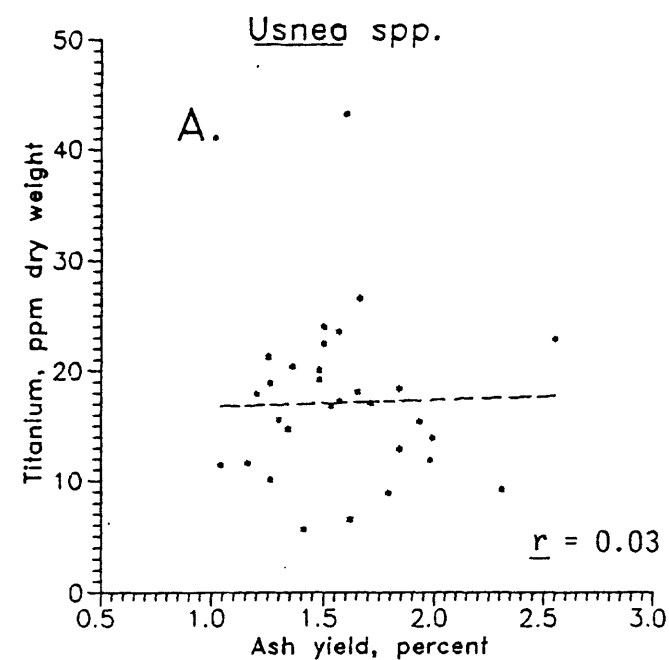


Figure 3. Simple linear regression plots of titanium concentrations in lichen tissue (dry weight base) versus percent ash yield.

- 3A. Usnea spp., this study
- 3B. Hypogymnia enteromorpha, this study.
- 3C. Parmelia chlorochroa, Gough and Erdman (1977)

The samples were dried at about 38°C for 48 hours in a forced-air oven and then ground in a glass blender with a stainless steel blade. The Hypogymnia material pulverized uniformly. The Usnea medulla (inner-most tissue), however, proved to be resistant to pulverization by dry blending, by blending with liquid nitrogen, or by grinding with a mortar and pestle. Usnea medulla was finally prepared by repeated snipping using stainless steel shears. The less dense medulla fragments intermixed with the more dense cortex (outer-most tissue) and created a non-uniform mass. The problems associated with an inhomogeneous sample are discussed in the Results section. Table 1 lists the analytical methods used in this study.

Prior to the tap water rinse, the contents of each bag of dried material were taxonomically determined and herbarium voucher specimens were made. The Hypogymnia samples were found to be uniform; however, as anticipated, the Usnea samples were mixtures of several species. Based on standard lichenological chemical tests, the material from the bags was found to vary from pure U. lapponica specimens to pure U. subfloridana specimens. In the field these two species are similar in appearance as both are isidiate-sorediate, light-yellowish green, tufted, papillate, and often with blackened bases. U. comosa (Ach.) Ach. and U. dasypoga (Ach.) Nyl. have been tentatively identified as intermixed, to varying degrees, with the two dominant species. We have no measure of the variability in the biogeochemical data that might be introduced by this mixture of species. Usnea species identification is very difficult and nearly impossible in the field; future sampling efforts will encounter this same problem. If the proportion of Usnea species in future collections remains nearly the same as those in this study, then any error associated with admixed species may be fairly constant.

STUDY DESIGN AND STATISTICAL ANALYSIS OF DATA

Detailed discussions of the use of the unbalanced, nested, analysis-of-variance (ANOVA) design in geochemical studies are given by Tourtelot and Miesch (1975), Tidball (1976), Tidball and Ebens (1976), and Severson and Tidball (1979) and for biogeochemical studies by Erdman and others (1976) and Erdman and Gough (1977). These discussions will not be repeated here. The unbalanced design allows for economy of field time and laboratory expense without sacrificing important statistical information (Miesch, 1976).

The sampling design allowed us to estimate how the element content of the lichens varies with distance and with sample preparation and analytical procedures. The following statistical model was used to partition the variance:

$$s^2_{\log x} = s^2_{\alpha} + s^2_{\beta} + s^2_{\gamma} + s^2_{\delta},$$

where the total observed logarithmic variance in the study area, for a given element concentration in either Hypogymnia or Usnea, is represented by the term $s^2_{\log x}$ and is the sum of the estimates of four sources of variation. The factor s^2_{α} represents variability due to differences between the two areas separated by about one kilometer (fig. 2); s^2_{β} represents differences between sample sites or distances of from 200 to 700 m; s^2_{γ} represents differences between lichen samples collected from adjacent trees at a given site or distances of <10 m; and the last term, s^2_{δ} , defines variation from sample collection, preparation, and analysis.

Table 1.--Analytical methodology and references for the analyses of
sampled lichen material and soils.

Variable	Method	Reference
Concentrations of total S	Combustion infrared photometry on dry lichen material	Jackson and others, 1985
Concentrations of Al, Ba, Ca, Cd, Ce, Co, Cr, Cu, Fe, Ga, K, La, Li, Mg, Mn, Mo, Na, Nd, Ni, P, Pb, Sc, Sn, Sr, Ti, V, Y, and Zn	Inductively coupled argon-plasma-optical emission spectrometry on acid-digested ash of lichen material	Crock and others, 1983
Ash yield	Gravimetric on lichen dry material	Aliquots of sample weighed, burned to ash at 500°C, and the ash weighed and calculated as percentage of dry weight
Concentrations of B, Ba, Ca, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sc, Ti, V, Zn, and Zr	6-step semiquantitative emission spectrography on ground soil material	Grimes and Marranzino, 1968; Motooka and Grimes, 1976

In this study, a balanced design would have resulted in 40 samples for each of two lichen species (without the addition of analytical splits). By unbalancing at the <10 m level, however, only about two-thirds of this number was actually collected (see Appendix I).

Data reported by the analyst on an ash-weight basis were converted to the more conventional dry-weight basis prior to statistical analysis. Frequency distributions for the element content of the plants studied were found to be positively skewed, particularly for the minor-essential and non-essential trace elements. A logarithmic transformation of such data adjusts the distribution curves so that they are more nearly normal. Figures 4A and 4B show the frequency distribution of nickel concentrations in H. enteromorpha plotted on logarithmic and arithmetic scales, respectively. The importance of the change in the shape of the distribution can be seen in these two plots.

Statistical tests that require a normal frequency distribution of the data are better satisfied by a logarithmic transformation of the data (fig. 4A). Our summary statistics are reported as the geometric mean (GM) and geometric deviation (GD). For those elements that had censored values (values below the lower limit of analytical determination, LLD), the GM and GD were estimated using the technique of Cohen (1959). For those elements without censoring, the GM was calculated as the antilogarithm of the mean of the logarithmic values and the GD was calculated from the total variation as estimated by the ANOV. The latter calculation accounts for the effects of the nested ANOV design. Total variation, as estimated by the square of the logarithmic standard deviation, is always smaller than total variation as estimated by the nested ANOV design. For this study, we have chosen the most conservative reporting procedure and present the larger estimate of the GD.

Because of sample-specific ash yield values, the conversion from an ash weight base to a dry weight base produces variable LLD values for elements with censoring. The mean and deviation estimation technique of Cohen (1959), however, cannot handle variable LLD values. A single LLD was created using a technique devised by A. T. Miesch (personal communication, 1986) which selects a common value based on a procedure that produces the fewest number of changes in the data.

The ANOV requires completely numeric data sets; therefore, all censored data were substituted with a real value equal to 0.7 times the LLD in ash. This multiplier is an acceptable fraction of the LLD as used in these types of studies (see, for example, Miesch, 1976). We assumed that this substitution would result in valid ANOV results as long as censoring did not exceed about one-third of the total number of values. If an element was more than one-third censored, it was dropped from the study. The analysis of the data was performed using the U.S. Geological Survey's STATPAC library (VanTrump and Miesch, 1977).

RESULTS

Interpretations of the ANOV and Summary Statistics

Hypogymnia enteromorpha and Usnea were sampled using a gridded sampling design detailed above. The purpose of the study was to estimate at what intervals the areal variability in lichen chemical element composition occurred. This information was used to assess whether or not regional element patterns in lichens were present, and to determine the appropriate way to calculate biogeochemical baselines.

Hypogymnia enteromorpha

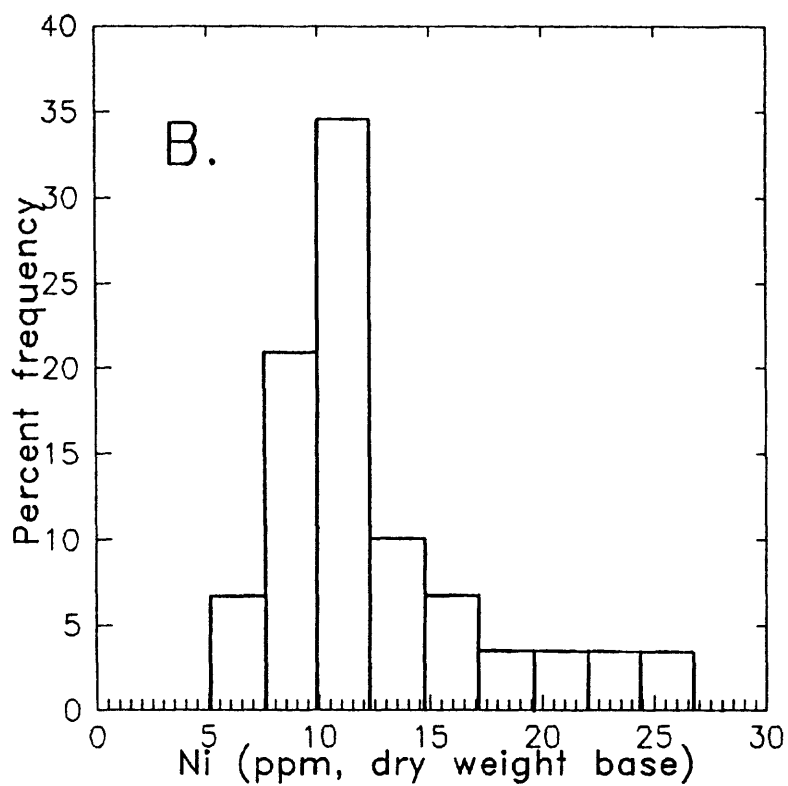
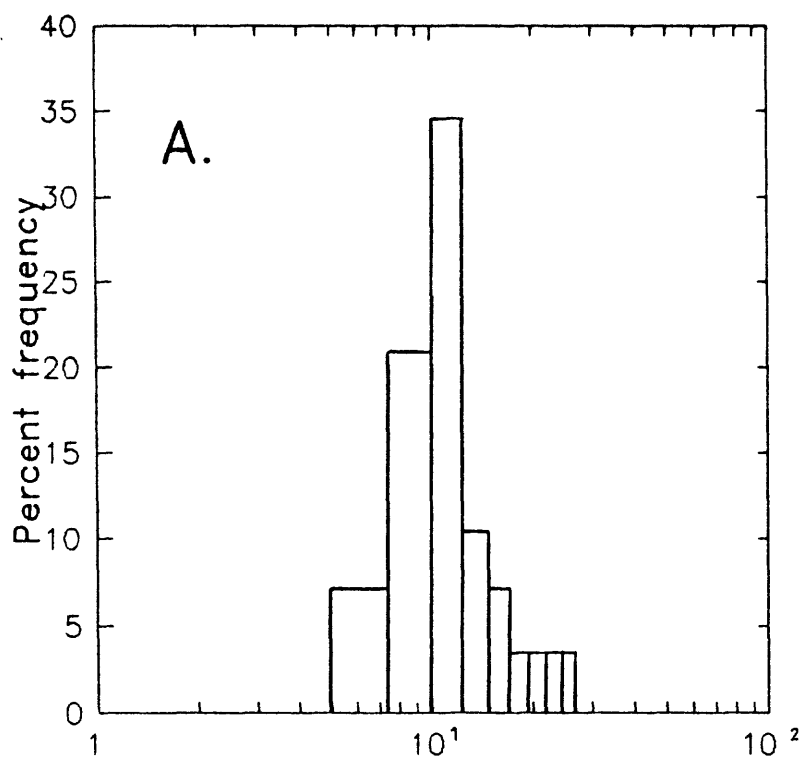


Figure 4. Observed frequency distribution of the concentration of nickel in Hypogymnia enteromorpha tissue (n=28).

4A. Values plotted on a logarithmic scale.

4B. Values plotted on an arithmetic scale.

The ANOV design partitions the total measured element-concentration variation into two fundamental parts: a natural-variation component (using distance-related increments) and an analytical-error component. If the analytical error is large for an element, relative to the natural variation, then it may not be feasible to characterize the natural variation in the data. Many more samples would need to be collected or a more precise analytical method would have to be utilized in order to reduce this analytical variation to an acceptable level. However, if analytical variation is significantly small relative to natural variation, then it may be possible to calculate baseline element concentrations.

Analytical results are given in Appendix I. Tables 2 and 3 give the results of the ANOV for element concentrations in H. enteromorpha and Usnea, respectively, and also include the summary statistics (GM, GD, observed range, and the expected 95 percent range) for each element.

Ash yield and total sulfur for H. enteromorpha are based on 35 samples. Because of insufficient lichen material in samples HYA111 and HYC222 (Appendix I), however, the other variables listed in table 1 are defined by 33 samples. For Usnea a similar situation exists except that three samples (USA111, USB111, and USC411) yielded insufficient material, resulting in a total of 32 samples for all variables except ash yield and percent total sulfur.

The "total \log_{10} variance" is the sum of the four variance components; the antilogarithm of the square root of this value is the GD for that group of samples (Appendix I). The rest of the columns under "analysis of variance" contain the variance components as percentages of the total variance.

As mentioned in the Study Design and Statistical Analysis of Data section above, the GM and GD of a lognormal distribution are better measures of central tendency and scatter than are the arithmetic mean and standard deviation. The geometric means and observed ranges are based on $n=28$ (table 2) and $n=26$ (table 3); this is because several samples had insufficient material and also because of the averaging of analytical split values prior to calculating the summary statistics (Appendix I). The expected 95 percent range is the "baseline", as first proposed by Tidball and Ebens (1976), and is calculated as a concentration range bracketed by the GM/GD^2 to the $GM \times GD^2$.

The proportion of the total \log_{10} variance that is associated with each of the three distance increments, plus the proportion of the variability caused by analytical imprecision, are given for 25 elements plus ash yield in H. enteromorpha and for 21 elements plus ash yield for Usnea materials. ANOV was not performed for elements with greater than one-third of their concentration values reported as below the LLD (see data analysis section above).

The data in tables 2 and 3 show that, except for barium and cobalt, a very small proportion (commonly <1 percent) of the total variability for concentrations of elements in both lichen species occurred at the one-kilometer level. This means that the element concentrations of the lichens varied little over the greatest distance measured when compared to changes over smaller distances (200 to 700 m or <10 m). Over half of the elements in H. enteromorpha varied by 30 percent or more at the smallest distance (samples collected from trees no more than 10 m apart). This was not quite the same for the Usnea samples which had as much or more variability between sample sites as well as between samples from trees at a site. In general, therefore, lichens sampled very close together vary more in their chemistry than do samples collected up to 1 km apart. None of this has much practical importance, however, because, without major exception, the total variability in the data was very small (total \log_{10} variance, tables 2 and 3). This means

TABLE 2. VARIATION IN AND SUMMARY STATISTICS FOR THE ELEMENT CONCENTRATIONS IN DRY MATERIAL OF *HYPOGYMNA ENTEROMORPHA*, LITTLE BALD HILLS, REDWOOD NATIONAL PARK, CALIFORNIA

[VARIANCE ANALYSIS BASED ON 33 SAMPLES, SUMMARY STATISTICS BASED ON 28 SAMPLES (33 MINUS FIVE ANALYTICAL SPLITS); *, COMPONENT OF VARIANCE WAS TESTED SIGNIFICANT AT THE 0.05 PROBABILITY LEVEL; RATIO, PROPORTION OF THE NUMBER OF ANALYSES HAVING VALUES ABOVE THE LOWER LIMIT OF DETERMINATION TO THE TOTAL NUMBER OF ANALYSES; LEADERS (---), NO DATA AVAILABLE]]

ANALYSIS OF VARIANCE										SUMMARY STATISTICS (N = 28)			
ELEMENT OR ASH YIELD	TOTAL LOG ₁₀ VARIANCE	PERCENTAGE OF TOTAL VARIANCE BETWEEN:					GEOMETRIC MEAN (PPM)	GEOMETRIC DEVIATION ¹	OBSERVED RANGE (PPM)	EXPECTED 95 PERCENT RANGE ² (BASELINE, PPM)			
		1.0 KM DISTANCE	200-700 M DISTANCE	<10 M DISTANCE	ANALYSES								
ASH, % ⁴	0.0051	1.8	34	7.2	57	2.6	1.18	1.4 - 4.0	--	--			
ALUMINUM	33:33 .0242	<1*	8.0	21	71	1100	1.43	300 - 1800	--	--			
BARIUM	33:33 .0498	34	25	14	27	24	1.67	10 - 110	8.6	67			
CADMIUM	--	--	--	--	--	--	--	<.08 - .33	--	--			
CALCIUM	33:33 .0470	<1	41	37	21	3800	1.65	1200 - 13000	1400	-10000			
CERIUM	32:33 .0228	<1	9.6	<1	90	.55 ³	1.42 ³	<.18 - .89	--	--			
CHROMIUM	33:33 .0312	<1	19	17	63	4.9	1.50	2.4 - 13	--	--			
COBALT	33:33 .0274	11	<1	31	58	.32	1.46	.15 - .72	--	--			
COPPER	33:33 .0404	3.7	<1	62	34	3.7	1.59 ³	1.3 - 9.9	1.5	9.4			
GALLIUM	30:33 .0257	<1	21	<1	79	.31 ³	1.45 ³	<.18 - .49	--	--			
IRON	33:33 .0231	<1	<1	25	75	850	1.42	360 - 1900	--	--			
LANTHANUM	33:33 .0311	5.2	4.1	37	54	.37	1.50	.09 - .68	--	--			
LEAD	33:33 .0238	<1	<1	48	52	12	1.43 ³	3.6 - 20	--	--			
LITHIUM	32:33 .0299	<1	<1	49	50	.33 ³	1.49 ³	<.09 - .55	.15	.73			
MAGNESIUM	33:33 .0253	1.4	<1	50	49	1300	1.44	340 - 1800	630	2700			
MANGANESE	33:33 .0450	5.7	41	28	26	89	1.63	40 - 250	33	240			
MOLYBDENUM	15:33 --	--	--	--	--	--	--	<.09 - .18	--	--			
NEODYMIUM	25:33 --	--	--	--	--	.30 ³	1.34 ³	<.18 - .50	--	--			
NICKEL	33:33 .0319	<1	<1	55	44	11	1.51	5.0 - 26	4.8	25			
PHOSPHORUS	33:33 .0240	<1	13	42	45	670	1.43	230 - 1200	330	1400			
POTASSIUM	33:33 .0208	<1	<1	50	50	1800	1.39 ³	620 - 2300	930	3500			
SCANDIUM	32:33 .0185	<1	14	<1	86	.26 ³	1.37 ³	<.09 - .46	--	--			
SODIUM	33:33 .0213	<1	<1	35	65	320	1.40	120 - 490	--	--			
STRONTIUM	33:33 .0338	<1	26	45	28	18	1.53	5.5 - 40	7.7	42			
SULFUR ¹	35:35 .0972	<1	<1	<1	99	470	2.05	60 - 640	--	--			
TIN	13:33 --	--	--	--	--	--	--	<.9 - 4.4	--	--			
TITANIUM	33:33 .0283	<1	7.6	21	72	51	1.47	16 - 88	--	--			
VANADIUM	33:33 .0259	8.0	10	46	36	2.5	1.45 ³	.73 - 6.3	1.9	5.2			
YTRIUM	32:33 .0190	<1	14	<1	86	.22 ³	1.37 ³	<.09 - .37	--	--			
ZINC	35:35 .0237	<1	<1	61	39	25	1.43	9.1 - 40	12	51			

¹THE GEOMETRIC DEVIATION IS EQUAL TO THE ANTILOGARITHM OF THE SQUARE ROOT OF THE TOTAL LOG₁₀ VARIANCE WHERE N = 33.

²BECAUSE OF EXCESSIVE ANALYTICAL ERROR (>50 PERCENT), BASELINES FOR ASH YIELD, AL, CE, CO, CR, FE, GA, LA, NA, PB, S, SC, TI, AND Y WERE NOT CALCULATED.

³GEOMETRIC MEAN AND DEVIATION CALCULATED USING THE TECHNIQUE OF COHEN (MIESCH, 1976).

⁴FOR ASH YIELD AND SULFUR N = 35 (VARIANCE ANALYSES) AND N = 30 (SUMMARY STATISTICS).

TABLE 3. VARIATION IN AND SUMMARY STATISTICS FOR THE ELEMENT CONCENTRATIONS IN DRY MATERIAL OF USNEA SPP., LITTLE BALD HILLS, REDWOOD NATIONAL PARK, CALIFORNIA

[VARIANCE ANALYSIS BASED ON 32 SAMPLES, SUMMARY STATISTICS BASED ON 26 SAMPLES (32 MINUS SIX ANALYTICAL SPLITS)]; *, COMPONENT OF VARIANCE WAS TESTED SIGNIFICANT AT THE 0.05 PROBABILITY LEVEL; RATIO, PROPORTION OF THE NUMBER OF ANALYSES HAVING VALUES ABOVE THE LOWER LIMIT OF DETERMINATION TO THE TOTAL NUMBER OF ANALYSES; LEADERS (---), NO DATA AVAILABLE]

ANALYSIS OF VARIANCE										SUMMARY STATISTICS (N = 26)			
ELEMENT OR ASH YIELD	PERCENTAGE OF TOTAL VARIANCE BETWEEN:					ANALYSES	GEOMETRIC MEAN (PPM)	GEOMETRIC DEVIATION ¹	OBSERVED RANGE (PPM)	EXPECTED 95 PERCENT RANGE (BASELINE, PPM) ²			
	1-0 KM DISTANCE	200-700 M DISTANCE	<10 M DISTANCE	TOTAL LOG ₁₀ VARIANCE	RATIO								
ASH, % ⁴	<1	29*	<1*	71	1.6	1.33	0.9	2.6	--	--			
ALUMINUM	<1*	46*	42	12	260	1.49	100	700	120	580			
BARITUM	29*	42	18	10	16	1.61	10	44	6.2	41			
CADMIUM	--	--	--	--	--	--	<.05	.20	--	--			
CALCIUM	<1	27	55*	18	3300	1.38	1900	8700	1700	6300			
CERIUM	<1	44	29	27	.223	1.433	<.13	.59	.11	.45			
CHROMIUM	10*	24*	48	18	1.0	1.72	.34	2.7	.34	3.0			
COBALT	26	50	6.0	18	.19	1.38	.12	.35	.01	.36			
COPPER	<1	<1	92	7.7	2.6	1.75	1.3	10	.85	8.0			
GALLIUM	--	--	--	--	--	--	.09	.19	--	--			
IRON	6.0	48	34*	11	170	1.523	60	400	74	390			
LANTHANUM	--	--	--	--	.113	1.783	<.05	.40	--	--			
LEAD	<1	31	16	53	7.5	1.25	5.5	15	--	--			
LITHIUM	--	--	--	--	.0973	1.513	<.36	.26	--	--			
MAGNESIUM	<1	<1	42	58	1600	1.21	1200	2600	--	--			
MANGANESE	<1	79*	14	7.2	97	1.72	40	330	33	290			
MOLYBDENUM	--	--	--	--	--	--	<.05	.11	--	--			
NEODYMIUM	--	--	--	--	--	--	<.09	.26	--	--			
NICKEL	<1	63*	<1	37	6.0	1.40	3.4	15	3.1	12			
PHOSPHOROUS	<1	67	21	13	420	1.44	270	860	200	870			
POTASSIUM	<1	<1	24	76	1800	1.273	1200	2700	--	--			
SCANDIUM	--	--	--	--	.083	1.363	<.06	.18	--	--			
SODIUM	1.0	53	11	34	300	1.29	190	560	180	500			
STRONTIUM	<1	42	26	32	18	1.29	12	30	11	30			
SULFUR ⁴	<1	15	<1	85	380	1.29	220	580	--	--			
TIN	--	--	--	--	--	--	<.5	3.4	--	--			
TITANIUM	<1	50	37*	12	16	1.55	5.6	43	6.6	38			
VANADIUM	<1	57	27	17	.53	1.523	.21	1.4	.23	1.2			
YTRIUM	<1	45	<1	55	.103	1.513	<.06	.24	--	--			
ZINC	<1	<1	60	40	21	1.26	14	38	13	33			

¹THE GEOMETRIC DEVIATION IS EQUAL TO THE ANTILOGARITHM OF THE SQUARE ROOT OF THE TOTAL LOG₁₀ VARIANCE WHERE N = 32.

²BECAUSE OF EXCESSIVE ANALYTICAL ERROR (>50 PERCENT), BASELINES FOR ASH YIELD, K, Mg, Pb, S, AND Y WERE NOT CALCULATED.

³GEOMETRIC MEAN AND DEVIATION CALCULATED USING THE TECHNIQUE OF COHEN (MIESCH, 1976).

⁴FOR ASH YIELD AND SULFUR N = 35 (VARIANCE ANALYSES) AND N = 29 (SUMMARY STATISTICS).

that the variability associated with sample preparation and analysis becomes very important because the statistics calculated from such data reflect predominantly analytical imprecision and not the natural variability.

Biogeochemical Baselines

Tables 2 and 3 give baseline values for element concentrations (parts per million, dry weight base) in H. enteromorpha and Usnea. Baselines were not calculated if the analytical variance exceeded 50 percent of the total variability for an element. Because of Usnea-sample inhomogeneity (see sample preparation section above) we expected the analytical error terms in table 3 to exceed those for H. enteromorpha in table 2. This was not the case, as results for H. enteromorpha showed 13 elements with large error terms (>50 percent) whereas results for Usnea showed only five. We feel large error terms preclude the meaningful interpretation of baseline values. It would appear, therefore, that snipping Usnea samples did produce a homogeneous sample.

One conclusion from this study is that the little natural variability that occurs, in the chemistry of these two lichen species at Little Bald Hills, is found between nearby samples rather than between samples collected at greater distances (up to 1.5 km) (fig. 2). If a re-sampling of this material is needed for comparative purposes in the future then it does not matter where the samples are collected as long as they are from the ridge-crest area. Had we found a large proportion of the variability at the top level (between gridded areas) then a regional trend in the data would have been apparent and the location of a re-sample would be important. Also, defining of a baseline for a given element having a regional trend across the ridge would not have been appropriate.

These biogeochemical data should be useful in future studies when the chemistry of new samples, collected, prepared and analyzed in the same manner as in this study, are compared to the baselines reported here. The laterite mining and milling operation proposed for Gasquet Mountain, 15 km east of Little Bald Hills, (U.S. Department of Agriculture, Forest Service, 1983) could be expected to release metals that are enriched in the ultramafic rocks being mined (chromium, cobalt, magnesium, manganese, and nickel) and considerable amounts of sulfur into the atmosphere. Using H. enteromorpha and Usnea as biomonitors, it should be possible to document biogeochemical changes in this section of the park. Chemical analysis could then be used to assess the potential of harmful phytotoxic effects of the metals and sulfur.

Element Concentration Comparisons

A very general comparison of the element levels in H. enteromorpha (column 1) collected in this study with similar (but not identical) material as reported in the literature is given in table 4. The Usnea data are not compared because we found only a few references in the literature for similar material from studies conducted in uncontaminated areas. What we present in table 4 is studies that deal with foliose ("leafy") lichens growing as epiphytes (corticolous), or on soil or organic matter over soil (terricolous). Studies of lichens growing over rock are not included. Such comparison involving different species, habitats, growth forms, or methods of a sample preparation and analysis is useful; however, it is also very limited.

Table 4.--Average concentrations of selected elements in foliose lichens collected from areas defined as uncontaminated as reported in this study and from the literature

Element	Corticolous (epiphytic)						Terricolous		
	<u>Hypogymnia</u> <u>enteromorpha</u>	<u>Parmelia</u> <u>sulcata</u>	<u>Hypogymnia physodes</u>			<u>Peltigera</u> <u>canina</u>	<u>Parmelia chlorochroa</u>		
	GM ¹	GM ²	AM ³	AM ⁴	AM ⁵	AM ⁶	AM ⁷	GM ²	GM ⁸
Aluminum	1100	2000	--	--	--	--	--	600	5300
Barium	24	79	--	--	--	--	--	32	52
Calcium, %	.38	.44	--	--	--	--	--	1.4	--
Chromium	4.9	7.3	--	--	--	--	3.1	4.2	4.6
Copper	3.7	24	--	--	22	--	10.3	10	9.8
Iron	850	2700	1500	--	1100	1400	192	1200	2000
Lead	12	26	--	--	15	--	8.6	--	15
Magnesium, %	.13	.073	--	--	--	--	--	.036	.090
Manganese	89	72	--	--	--	100	48	34	38
Nickel	11	6.6	--	--	--	--	3.2	--	1.4
Phosphorus	670	790	--	--	--	--	--	640	--
Strontium	18	28	--	--	--	--	--	16	49
Sulfur	470	1200	--	--	--	--	--	1000	670
Titanium	51	16	--	--	--	--	--	12	240
Vanadium	2.5	4.4	--	1.6	--	--	--	1.8	8.1
Yttrium	.22	2.5	--	--	--	--	--	.96	4.5
Zinc	25	95	98	--	21	140	71	44	--

¹This study; ²Gough and others (1985); ³Lodenius and Kumpulainen (1983); ⁴Nygard and Harju (1983);

⁵Seaward (1974); ⁶Lounamaa (1965); ⁷Seaward and others (1978); ⁸Erdman and Gough (1977).

Soils from ultramafic parent material are usually very high in chromium, cobalt, magnesium, manganese, and nickel (Kabata-Pendias and Pendias, 1984). It would not be surprising to find elevated levels of these metals in collected lichens because the metals are available and could be assimilated, either through direct deposition of dust on the thallus or through absorption from metal-laden leach-water percolating down through the tree canopy. Table 4 shows that magnesium and nickel levels in H. enteromorpha are larger than most values reported in the literature. Levels of cobalt could not be compared because of a lack of data in the literature for lichens; however, the concentrations of cobalt appear elevated when compared to vascular plant species (see, Kabata-Pendias and Pendias, 1984; Ebens and Shacklette, 1982). It is interesting that chromium concentrations in H. enteromorpha are not very different from levels reported in the literature for non-ultramafic areas. Chromium levels in Usnea are even lower (table 3). Nevertheless, it appears the biogeochemistry of both lichen species reflect to some degree the geochemistry of the ultramafic terrain over which they are growing.

These data provide a "snapshot" of the chemistry of epiphytic lichens against which future biogeochemical conditions can be compared. This ability is important if industrial facilities begin operating near RNP. The construction of a laterite mining, milling, and refining facility at Gasquet Mountain northeast of Little Bald Hills remains a possibility, particularly if development of natural strategic and critical mineral reserves receives renewed emphasis and support.

Chemistry of Soil Samples

A systematic collection of soil samples from the lichen study area was not conducted as part of this study; however, Appendix II lists the chemical composition of soil samples collected at varying depths by J. Popenoe in May, 1984. These analyses are semiquantitative and were performed to obtain an idea of general element concentrations. No element concentration trends with depth were observed. These data appear typical of the chemistry of serpentine soils (Kabata-Pendias and Pendias, 1984).

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REFERENCES

- Barkman, J. J., 1958, Phytosociology and ecology of cryptogamic epiphytes: Assen, The Netherlands, Van Gorcum and Company, 628 p.
- Cater, F. W., and Wells, F. G., 1953, Geology and mineral resources of the Gasquet quadrangle, California-Oregon: U.S. Geological Survey Bulletin 995-C, pp. 79-133.
- Cohen, A. C., Jr., 1959, Simplified estimators for the normal distribution when samples are singly censored or truncated: *Technometrics*, v. 1, p. 217-237.
- Crock, J. G., Lichte, F. E., and Briggs, P. H., 1983, Determination of elements in National Bureau of Standards' Geological Reference Materials SRM 278 Obsidian and SRM 688 Basalt by inductively coupled argon plasma-atomic emission spectrometry: *Geostandards Newsletter*, v. 7, no. 2, p. 335-340.
- Ebens, R. J., and Shacklette, H. T., 1982, Geochemistry of some rocks, mine spoils, stream sediments, soils, plants, and waters in the western energy region of the conterminous United States: U.S. Geological Survey Professional Paper 1237, 173 p.
- Erdman, J. A., and Gough, L. P., 1977, Variation in the element content of Parmelia chlorochroa from the Powder River Basin of Wyoming and Montana: *The Bryologist*, v. 80, p. 292-303.
- Erdman, J. A., Shacklette, H. T., and Keith, J. R., 1976, Elemental composition of selected native plants and associated soils from major vegetation-type areas in Missouri: U.S. Geological Survey Professional Paper 954-C, 87 p.
- Ferry, B. W., Baddeley, M. S., and Hawksworth, D. L., 1973, Air pollution and lichens: Toronto, University of Toronto Press, 389 p.
- Garty, J., Galun, M., and Kessel, M., 1979, Localisation of heavy metals and other elements accumulated in lichen thallus: *New Phytologist*, v. 82, p. 159-168.
- Gilbert, O. L., 1973, Lichens and air pollution, in Ahmadjian, V. and Hale, M. E. (eds.), *The lichens*: New York, Academic Press, pp. 443-472.
- Gough, L. P., and Erdman, J. A., 1977, Influence of a coal-fired power plant on the element content of Parmelia chlorochroa: *The Bryologist*, v. 80, p. 492-501.
- Gough, L. P., Peard, J. L., Severson, R. C., Jackson, L. L., Arbogast, B. F., Motooka, J. M., Snow, S. W., Engleman, E. E., and Bennett, J. P., 1985, Baseline elemental-composition of selected plants and soils, and assessment of airborne element contamination, Theodore Roosevelt National Park, North Dakota, 47 p.

- Gough, L. P., Jackson, L. L., Bennett, J. P., Severson, R. C., Engleman, E. E., Briggs, P. H., and Wilcox, J. R., 1986, The regional influence of an oil-fired power plant on the concentration of elements in native materials in and near south Florida national parks: U.S. Geological Survey Open-file Report 86-395, 63 p.
- Grimes, D. J., and Marranzino, A. P., 1968, Direct-current arc and alternating-current spark emission spectrographic field methods for the semiquantitative analysis of geologic materials: U.S. Geological Survey Circular 591, 6 p.
- Hektner, M. M., 1986, Plants of the Little Bald Hills: Unpublished manuscript, on file, Redwood National Park, Arcata, California.
- Jackson, L. L., Engleman, E. E., and Peard, J. L., 1985, Determination of total sulfur in lichens and plants by combustion-infrared analysis: Environmental Science and Technology, v. 19, p. 437-441.
- Kabata-Pendias, A., and Pendias, H., 1984, Trace elements in soils and plants: Boca Raton, Florida, CRC Press, 315.
- Lodenius, M., and Kumpulainen, J., 1983, Cd, Fe, and Zn content of the epiphytic lichen Hypogymnia physodes in a Finnish suburb: The Science of the Total Environment, v. 32, p. 81-85.
- Lounamaa, K. J., 1965, Studies on the content of iron, manganese and zinc in macrolichens: Annales Botanici Fennici, v. 2, p. 127-137.
- Madej, M. A., O'Sullivan, C., and Varnum, N., 1986, An evaluation of land use, hydrology, and sediment yield in the Mill Creek watershed, northern California: Redwood National Park Technical Report Number 17, National Park Service, Redwood National Park, Arcata, California, 66 p.
- Martin, M. H., and Coughtrey, P. J., 1982, Biological monitoring of heavy metal pollution--land and air: New York, Applied Science Publishers, 475 p.
- Miesch, A. T., 1976, Geochemical survey of Missouri--methods of sampling, laboratory analysis, and statistical reduction of data in a geochemical survey of Missouri, with sections on laboratory methods: U.S. Geological Survey Professional Paper 954-A, 39 p.
- Motooka, J. M., and Grimes, D. J., 1976, Analytical precision of one-sixth order semiquantitative spectrographic analyses: U.S. Geological Survey Circular 738, 25 p.
- Nygard, S., and Harju, L., 1983, A study of the short range pollution around a power plant using heavy fuel oil by analysing vanadium in lichens: Lichenologist, v. 15, p. 89-93.
- Seaward, M. R. D., 1974, Some observations on heavy metal toxicity and tolerance in lichens: Lichenologist, v. 6, p. 158-164.

- Seaward, M. R. D., Goyal, R., and Bylinska, E. A., 1978, Heavy metal content of some terricolous lichens from mineral-enriched sites in northern England: *Naturalist*, v. 103, p. 135-141.
- Severson, R. C., and Tidball, R. R., 1979, Spatial variation in total element concentration in soil within the Northern Great Plains coal region: U.S. Geological Survey Professional Paper 1134-A, 18 p.
- Strand, R. G., 1964, Geologic map of California, Weed Sheet: California Division of Mines and Geology, 1 map, scale 1:250,000.
- Tidball, R. R., 1976, Chemical variation of soils in Missouri associated with selected levels of the soil classification system: U.S. Geological Survey Professional Paper 954-B, 16 p.
- Tidball, R. R., and Ebens, R. J., 1976, Regional geochemical baselines in soils of the Powder River Basin, Montana-Wyoming, in Laudon, R. B., ed., *Geology and energy resources of the Powder River Basin: Wyoming Geology Association, 28th Annual Field Conference, Casper, Wyo. Guidebook*, p. 299-310.
- Tourtelot, H. T., and Miesch, A. T., 1975, Sampling designs in environmental geochemistry: Geological Society of America Special Paper 155, p. 107-118.
- U.S. Department of Agriculture, Forest Service, 1983, Draft environmental impact statement/environmental impact report--Gasquet Mtn. mining project: Washington, U.S. Forest Service and California, County of Del Norte SCH#80092401, pages not numbered consecutively.
- U.S. Department of the Interior, National Park Service, 1986, Revised resources management plan, Redwood National Park: National Park Service, Redwood National Park, Crescent City, California, 275 p.
- Van Hook, S., 1984, Species lists for lichen surveys in the Little Bald Hills area: Unpublished manuscript, on file, Redwood National Park, Arcata, California.
- VanTrump, George, Jr., and Miesch, A. T., 1977, The U.S. Geological Survey RASS-STATPAC system for management and statistical reduction of geochemical data: *Computers and Geoscience*, v. 3, p. 475-488.

EXPLANATION OF APPENDIXES

APPENDIX I

Tables giving the sample identification, location, and chemical composition of lichen samples, Little Bald Hills, Redwood National Park, northern Del Norte County, California. The sample identifications are keyed as follows: First and second positions--HY (hypogymnia enteromorpha), IS (Usnea spp); third and fourth positions--site location (see fig. 2); fifth position (1 or 2)--site replicated sample; sixth position (1 or 2)--analytical duplicated sample.

APPENDIX II

Tables giving the sample identification, location, and chemical composition of serpentine soils collected by J. Popenoe, Little Bald Hills, Redwood National Park, northern Del Norte County, California. The sample identifications are keyed as follows: First and second positions--year of collection; third, fourth, and fifth positions--Redwood National Park; sixth position (4, 5, 6, or 7)--soil pit from which samples were collected (see fig. 2); seventh position--depth of sample (1 = A horizon; 2 = B horizon; 3 and 4 = C horizon); eighth position--analytical duplicated sample.

CHEMICAL COMPOSITION (DRY WEIGHT BASIS) OF EPHEMERAL LICHENS.

[--, no data available; <, less than the analytical lower limit of determination (adjusted for solution and sample composition matrix effects); conversion from ash weight to dry weight base produces variable lower limits]

Sample	Ash, %	Al, %	Ba, ppm	Ca, %	Cd, ppm	Ce, ppm	Co, ppm	Cr, ppm	Cu, ppm	Fe, ppm	Ga, ppm	K, %	La, ppm	Li, ppm	Mg, %
<u>HYPOGYMNIUM ENTEROMORPHIA</u>															
HVA111	1.4	--	--	--	--	--	--	--	--	--	--	--	--	--	--
HVA211	3.7	.18	110	.81	.15	.70	.52	8.8	4.4	1,300	.44	.20	.48	.55	.18
HVA311	3.6	.18	40	.62	<.15	.55	.51	9.1	5.5	1,500	.36	.23	.51	.51	.18
HVA321	3.2	.13	40	.54	.13	.54	.32	5.1	3.5	900	.29	.24	.35	.38	.14
HVA322	2.8	.13	40	.50	.11	.50	.30	6.1	3.0	900	.28	.19	.33	.39	.14
HYB111	2.3	.09	30	.25	.18	.39	.51	8.7	4.1	1,100	.28	.20	.32	.28	.11
HYB121	2.3	.03	10	.12	<.09	<.18	.18	2.7	1.3	400	<.18	.06	.09	<.09	.03
HYB211	2.2	.09	20	.43	.11	.52	.54	8.3	3.4	1,000	.25	.17	.36	.29	.12
HYB212	3.1	.17	30	.34	.12	.98	.89	16.9	4.9	1,900	.49	.20	.68	.52	.18
HYB311	2.2	.05	20	.15	<.09	.26	.15	2.4	1.7	400	<.18	.10	.20	.15	.05
HYB321	3.0	.12	30	.36	<.12	.57	.39	4.8	3.6	900	.30	.18	.42	.36	.15
HYB411	2.3	.08	50	.49	<.09	.42	.25	3.9	3.2	600	.21	.19	.21	.28	.14
HYC111	4.0	.12	40	1.32	.16	.48	.36	3.3	3.4	800	.32	.19	.28	.32	.09
HYC211	3.0	.09	40	.47	.33	.38	.36	3.3	4.7	700	.30	.11	.33	.33	.15
HYC221	2.1	.13	20	.23	<.08	.66	.32	4.7	3.8	900	.34	.18	.53	.38	.11
HYC222	2.3	--	--	--	--	--	--	--	--	--	--	--	--	--	--
HYC311	2.1	.12	20	.25	<.08	.54	.31	4.2	3.3	900	.35	.17	.46	.35	.11
HYC411	2.4	.12	20	.37	<.10	.59	.32	5.9	3.7	900	.34	.19	.39	.37	.17
HYC421	2.4	.11	30	.36	<.10	.56	.27	4.1	3.4	700	.31	.21	.36	.31	.14
HYD111	2.6	.13	20	.41	<.10	.69	.33	4.6	3.1	900	.36	.19	.43	.36	.15
HYD211	2.6	.13	20	.39	<.10	.65	.34	5.2	6.8	900	.31	.20	.42	.37	.15
HYD212	2.7	.06	10	.21	<.11	.30	.16	2.6	3.3	500	<.22	.10	.22	.19	.08
HYD311	2.9	.11	20	.68	<.11	.57	.26	4.8	3.1	700	.26	.17	.29	.31	.15
HYD321	2.2	.11	20	.38	<.09	.52	.22	4.0	3.1	800	.29	.16	.38	.31	.13
HYD322	2.5	.13	20	.38	<.10	.63	.25	4.5	3.5	900	.38	.18	.45	.38	.15
HYE111	2.3	.12	20	.32	<.09	.57	.27	5.4	4.1	800	.32	.19	.41	.34	.14
HYE121	2.5	.13	20	.40	<.10	.55	.37	4.7	3.2	900	.37	.20	.45	.35	.15
HYE211	2.1	.11	20	.34	<.09	.58	.26	5.3	3.2	800	.26	.17	.38	.34	.13
HYE212	2.5	.12	20	.35	<.10	.62	.30	5.7	3.5	900	.27	.20	.45	.37	.14
HYE221	2.3	.11	20	.40	<.09	.56	.31	6.1	9.9	900	.25	.18	.43	.34	.13
HYE311	2.6	.16	20	.31	<.10	.87	.33	5.9	4.1	1,100	.38	.20	.64	.46	.15
HYF111	2.4	.10	20	.46	<.10	.48	.22	3.1	3.9	700	.24	.20	.34	.29	.14
HYF211	2.6	.17	20	.34	<.11	.71	.34	5.8	4.2	1,100	.34	.21	.66	.50	.13
HYF221	2.6	.17	20	.26	<.10	.89	.31	5.2	4.4	1,100	.39	.20	.68	.52	.15
HYF311	2.8	.11	20	.50	<.11	.39	.33	3.3	3.6	800	.39	.22	.30	.30	.14
<u>USNEA SPP. (MOSTLY U. LAPPONICA AND U. SUBFLORIDANA)</u>															
USA111	.9	--	--	--	--	--	--	--	--	--	--	--	--	--	--
USA211	2.0	.02	40	.44	.14	.18	.20	1.2	2.2	100	<.16	.17	<.08	<.08	.18
USA311	2.0	.03	20	.40	<.08	.16	.18	1.2	2.0	200	<.16	.24	<.68	.10	.18
USA312	1.7	.03	20	.41	<.07	.17	.17	1.1	2.1	200	<.14	.24	<.07	.10	.17
USA321	1.5	.03	20	.23	<.06	.15	.15	1.2	3.1	200	<.12	.19	.12	.13	.15

Sample	Mn, ppm	Mo, ppm	Na, ppm	Nd, ppm	Ni, ppm	P, ppm	Pb, ppm	S, ppm	Sc, ppm	Sn, ppm	Str, ppm	Ti, ppm	V, ppm	Y, ppm	Zn, ppm
HYPOGYMNIA ENTEROMORPHA--Continued															
HYA111	--	--	--	--	--	--	--	290	--	--	--	--	--	--	--
HYA211	210	.15	480	.40	23	800	19	640	.37	4.4	40	88	3.7	.29	31
HYA311	80	<.15	470	.36	25	1,100	20	620	.40	3.6	31	51	3.6	.29	26
HYA321	70	<.13	410	<.25	12	1,200	17	60	.29	<1.3	31	51	3.1	.19	27
HYA322	60	<.11	360	.25	12	1,100	15	560	.28	1.7	30	66	2.7	.19	25
HYB111	120	.12	410	.32	12	700	11	450	.25	2.1	13	44	2.2	.18	30
HYB121	60	<.09	120	<.18	5	200	4	460	<.09	1.1	5	16	1.7	<.09	9
HYB211	80	.11	310	.25	14	700	13	490	.25	<.9	17	49	2.2	.22	25
HYB212	110	<.12	490	.46	23	800	18	500	.46	<1.2	20	86	4.0	.37	30
HYB311	40	<.09	180	<.18	6	300	5	510	.13	<.9	6	22	1.1	.11	12
HYB321	110	<.12	330	.39	21	700	15	450	.27	1.5	21	60	2.7	.24	29
HYB411	60	.14	250	<.18	10	900	12	370	.18	1.6	35	44	2.3	.14	23
HYC111	210	<.16	320	<.32	10	1,000	14	350	.24	<1.6	27	56	2.2	.24	40
HYC211	190	<.12	360	.27	11	700	15	470	.18	2.4	23	44	2.3	.18	36
HYC221	100	.13	320	.34	9	500	15	580	.28	1.3	15	66	2.8	.25	25
HYC222	--	--	--	--	--	--	--	540	--	--	--	--	--	--	--
HYC311	130	.12	310	.25	10	500	10	470	.27	.8	14	67	2.5	.23	23
HYC411	90	.12	370	.29	10	700	14	410	.27	1.0	19	61	2.7	.24	24
HYC421	110	<.10	310	.19	9	800	13	520	.22	<1.0	21	46	2.2	.19	27
HYD111	140	.10	330	.31	11	800	14	450	.25	<1.0	17	41	2.6	.23	26
HYD211	70	.10	370	.42	12	800	15	550	.26	<1.0	17	42	6.3	.24	26
HYD212	40	<.11	190	.24	6	400	8	480	.14	<1.1	9	19	4.3	.11	14
HYD311	70	<.11	290	<.23	9	600	12	540	.23	<1.1	19	51	2.3	.20	26
HYD321	90	<.09	290	.25	9	600	14	430	.25	<.9	16	49	2.5	.22	22
HYD322	100	.10	330	.35	11	600	15	380	.27	<1.0	18	63	2.8	.25	25
HYE111	70	.09	340	.30	12	700	11	520	.27	<.9	15	64	2.5	.23	30
HYE121	120	<.10	320	.40	15	800	12	410	.27	<1.0	20	40	2.5	.22	24
HYE211	50	.09	280	.30	10	600	12	440	.23	<.9	18	60	2.6	.21	26
HYE212	50	<.10	350	.32	11	600	13	310	.25	<1.0	19	55	2.7	.22	27
HYE221	60	<.09	290	.27	13	600	13	480	.25	<.9	17	61	2.5	.23	29
HYE311	50	.13	410	.44	11	600	14	500	.33	<1.0	18	67	3.1	.31	28
HYF111	60	<.10	310	.27	8	800	12	430	.22	<1.0	19	41	2.2	.17	24
HYF211	60	.16	420	.50	15	600	16	560	.34	<1.1	18	63	3.4	.32	21
HYF221	70	.18	470	.44	13	600	16	640	.34	1.0	20	70	3.7	.34	23
HYF311	250	<.11	280	.22	12	1,100	12	370	.22	1.1	19	55	2.3	.17	30
USNEA SPP. (MOSTLY U. LAPPONICA AND U. SUBTILORIDANA--Continued)															
USA111	--	--	--	--	--	--	--	220	--	--	--	--	--	--	--
USA211	100	<.08	320	<.16	9	400	8	260	<.08	<.8	24	12	.4	.08	24
USA311	70	<.06	380	<.16	7	900	10	450	<.08	<.8	22	14	.6	<.08	24
USA312	70	<.07	360	<.14	6	900	10	340	.09	<.7	22	17	.6	.09	22
USA321	50	<.06	350	<.12	5	700	9	300	.09	<.6	23	23	.7	.09	17

Sample	Ash, %	Al, %	Ba, ppm	Ca, %	Cd, ppm	Ce, ppm	Co, ppm	Cr, ppm	Cu, ppm	Fe, ppm	Ga, ppm	K, %	La, ppm	Li, ppm	Mg, %
USNEA SPP. (MOSTLY U. LAPPONICA AND U. SUBFLORIDANA--Continued)															
USB111	1.4	--	--	--	--	--	--	--	--	--	--	--	--	--	--
USB121	1.7	.04	20	.30	.12	.25	.35	2.2	2.2	300	.13	.17	.18	.17	.15
USB211	1.2	.03	10	.19	.12	.20	.35	2.3	1.6	300	<.10	.16	.14	.13	.14
USB212	1.6	.03	10	.20	.09	.16	.35	2.4	1.6	300	<.13	.10	.13	.11	.14
USB311	1.3	.02	20	.31	<.05	.23	.23	.6	2.5	200	<.10	.17	.12	.08	.16
USB321	1.6	.04	20	.31	.06	.31	.25	2.7	10.5	200	<.13	.17	.20	.14	.17
USB411	1.3	.02	20	.25	<.05	.14	.13	.6	1.4	100	<.10	.18	<.05	.05	.13
USC111	2.6	.04	30	.87	.20	.33	.31	1.3	4.6	200	<.20	.21	.10	.15	.17
USC211	1.0	.02	10	.21	.06	.21	.18	.7	1.4	200	<.08	.15	.11	.06	.14
USC221	1.3	.03	20	.26	.06	.24	.19	1.0	1.6	200	<.10	.14	.16	.11	.13
USC311	1.5	.04	10	.27	<.06	.21	.23	1.4	3.8	200	.17	.17	.17	.12	.15
USC312	1.5	.04	10	.28	<.06	.24	.22	1.2	3.7	200	.13	.16	.15	.12	.15
USC411	1.8	--	--	--	--	--	--	--	--	--	--	--	--	--	--
USC421	1.4	.02	10	.28	<.06	.16	.17	.7	1.7	100	<.11	.18	.07	.07	.16
USD111	1.8	.02	10	.45	.07	.18	.18	.5	3.4	100	<.14	.20	<.07	<.07	.18
USD211	1.2	.02	10	.28	<.05	.14	.14	.7	3.2	100	<.09	.13	.07	.06	.12
USD212	1.8	.03	10	.40	<.07	.20	.22	1.5	5.3	200	<.15	.17	.09	.09	.18
USD311	1.8	.02	10	.48	<.07	.17	.15	.6	2.4	100	<.15	.22	.07	.07	.18
USD321	2.3	.01	10	.25	<.09	<.18	.12	.5	6.9	100	<.18	.09	<.09	<.09	.12
USD322	1.3	.02	10	.33	<.05	.15	.13	.5	8.4	100	<.10	.15	<.05	.06	.14
USE111	1.3	.03	10	.25	<.05	.27	.16	.8	2.4	200	<.11	.17	.11	.08	.17
USE121	1.5	.03	20	.34	<.06	.26	.23	.9	1.8	200	<.12	.20	.11	.11	.18
USE211	1.5	.03	10	.36	<.06	.18	.18	1.3	3.1	200	<.12	.16	.09	.10	.14
USE212	1.6	.03	10	.33	<.07	.15	.17	1.4	3.1	200	<.13	.17	.10	.12	.14
USE221	1.5	.03	10	.35	<.06	.29	.18	1.2	1.6	200	<.12	.15	.17	.12	.15
USE311	1.3	.03	10	.24	<.05	.30	.14	1.3	2.0	200	<.10	.16	.21	.09	.15
USF111	1.6	.01	10	.44	<.06	<.13	.13	.3	1.3	100	<.13	.19	<.06	<.06	.19
USF211	1.4	.03	10	.27	.05	.29	.16	1.2	4.5	200	<.11	.16	.20	.12	.15
USF221	1.6	.07	20	.43	.10	.59	.24	2.6	3.4	400	.16	.27	.40	.26	.26
USF311	1.9	.02	30	.50	<.08	<.15	.21	.7	1.9	100	.19	.25	<.08	<.08	.18

APPENDIX I (cont.)

CHEMICAL COMPOSITION (DRY WEIGHT BASE) OF EPIPHYTIC LICHENS.--Continued

Sample	Mn, ppm	Mo, ppm	Na, ppm	Nd, ppm	Ni, ppm	P, ppm	Pb, ppm	S, ppm	Sc, ppm	Sn, ppm	Sr, ppm	Ti, ppm	V, ppm	Y, ppm	Zn, ppm
USNEA SPP. (MOSTLY U. LAPPONICA AND U. SUBFLORIDANA--Continued)															
USB111	--	--	--	--	--	--	--	450	--	--	--	--	--	--	--
USB121	230	<.07	460	<.13	8	400	7	440	.13	<.7	18	27	.9	.12	30
USB211	80	<.05	360	<.10	6	300	7	380	.10	<.5	12	18	.6	.10	22
USB212	80	<.06	360	<.13	7	300	7	380	.09	<.6	12	17	.6	.09	20
USB311	110	.09	270	<.10	10	300	7	390	.06	2.1	16	16	.5	.12	20
USB321	140	.11	300	<.13	15	300	7	410	.09	<.6	19	24	.7	.14	30
USB411	50	<.05	230	<.10	4	500	6	370	.05	<.5	21	10	.3	.06	14
USC111	330	<.10	410	<.20	6	800	8	290	.10	<.10	28	23	.7	.18	38
USC211	90	<.04	260	<.08	4	300	8	290	.05	<.4	14	11	.4	.09	19
USC221	120	<.05	260	<.10	5	300	8	440	.09	<.5	16	21	.7	.11	16
USC311	170	<.06	300	<.12	6	300	7	360	.09	<.6	15	24	.7	.11	20
USC312	160	<.06	300	.12	5	300	7	440	.09	<.6	14	21	.7	.10	19
USC411	--	--	--	--	--	--	--	270	--	--	--	--	--	--	--
USC421	70	<.06	240	<.11	4	500	7	370	<.06	<.6	17	6	.3	.08	20
USD111	200	<.07	210	<.14	5	500	6	320	<.07	<.7	16	9	.3	.07	20
USD211	60	<.05	220	<.09	4	300	5	500	.06	<.5	11	12	.3	.07	14
USD212	90	<.07	350	<.15	7	400	9	380	.07	<.7	17	18	.5	.11	22
USD311	100	<.07	260	<.15	5	500	7	440	<.07	.7	16	13	.4	.09	26
USD321	80	<.09	170	<.18	5	300	6	400	<.09	<.9	11	9	.3	<.09	15
USD322	100	<.05	210	<.10	7	400	7	350	.05	.6	14	10	.4	.06	19
USE111	70	<.05	310	<.11	6	400	7	420	.08	<.5	13	15	.5	.12	21
USE121	120	<.06	290	<.12	7	500	6	390	.08	<.6	18	17	.5	.11	20
USE211	50	<.06	340	<.12	5	300	6	180	.07	<.6	18	19	.6	.09	18
USE212	40	<.07	350	<.13	5	300	6	350	.08	<.7	17	18	.6	.07	18
USE221	60	<.06	270	<.12	5	300	9	360	.09	<.6	15	23	.7	.12	26
USE311	50	.05	320	<.10	6	300	10	430	.09	3.4	15	19	.6	.13	21
USEF11	80	<.06	230	<.13	3	500	6	400	<.06	<.6	19	6	.2	<.06	18
USEF21	60	.08	350	<.11	7	300	9	460	.08	<.5	18	20	.7	.14	20
USEF221	110	.10	560	.26	9	600	15	450	.18	.6	30	43	1.4	.24	27
USEF311	310	<.06	230	<.15	7	800	7	580	<.08	<.8	19	15	.9	.08	27

APPENDIX I (cont.)

CHEMICAL COMPOSITION OF SOIL SAMPLES COLLECTED BY J. POPENOE

[N, not detected; <, detected but below the limit of determination shown; >, determined to be greater than the value shown.]

Sample	B, ppm	Ba, ppm	Ca, %	Co, ppm	Cr, ppm	Cu, ppm	Fe, %	Hg, %	Mn, ppm
84RNP411	10	<15	.50	150	5,000	20	10	7	1,000
84RNP421	10	<15	.50	200	5,000	30	10	7	1,000
84RNP511	N	20	.50	300	>5,000	50	20	5	1,500
84RNP521	N	<15	.30	300	>5,000	50	20	5	1,500
84RNP611	N	50	.30	300	>5,000	50	15	3	2,000
84RNP621	N	50	.50	500	>5,000	70	20	5	2,000
84RNP622	N	30	.50	300	>5,000	50	20	3	2,000
84RNP631	N	20	.30	500	>5,000	50	20	3	1,500
84RNP641	N	20	.20	300	>5,000	70	20	3	1,500
84RNP642	N	20	.30	300	>5,000	70	20	3	1,500
84RNP711	N	20	.70	300	>5,000	50	20	3	1,500
84RNP721	N	30	.50	300	>5,000	50	20	3	1,500
84RNP731	N	<15	.50	300	>5,000	50	15	3	1,500
84RNP732	N	30	.70	300	>5,000	50	20	5	1,500

Sample	Ni, ppm	Pb, ppm	Sc, ppm	Ti, %	V, ppm	Zn, ppm	Zr, ppm
84RNP411	5,000	10	10	.05	70	N	20
84RNP421	5,000	10	10	.07	70	N	<10
84RNP511	5,000	15	20	.10	150	<200	20
84RNP521	5,000	10	30	.15	150	<200	30
84RNP611	5,000	15	30	.15	100	200	30
84RNP621	5,000	15	30	.20	150	<200	30
84RNP622	5,000	15	30	.20	150	200	30
84RNP631	5,000	15	30	.20	150	<200	20
84RNP641	5,000	<10	30	.15	150	<200	10
84RNP642	5,000	10	30	.10	150	<200	20
84RNP711	3,000	15	30	.20	150	<200	30
84RNP721	5,000	15	30	.15	150	<200	50
84RNP731	5,000	15	20	.10	100	<200	30
84RNP732	5,000	10	30	.15	100	200	30

APPENDIX II.