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Factor Analysis of the Chemistry of Spanish Moss

By

Jon J. Connor and Hansford T. Shacklette<sup>1</sup>

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<sup>1</sup>Denver, Colorado

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## ABSTRACT

One hundred twenty-three samples of Spanish moss (Tillandsia usneoides L.) were collected from over its geographic range in the southeastern United States. The ash of these samples was analyzed for a variety of major and minor elements, and the resulting data were factor analyzed for pertinent geochemical associations. The first five eigenvalues of the correlation matrix account for 71 percent of the variation in these data, and a five-factor varimax model of element variation was constructed. Varimax factors 1 and 2 together describe most of the variation in the logarithmic concentrations of 13 elements: aluminum, barium, calcium, cobalt, gallium, iron, manganese, sodium, strontium, titanium, ytterbium, yttrium, and zirconium. The first 10 of these elements constitute a common pedologic association and, in fact, typical concentrations of these elements in the ash of Spanish moss are reasonably close (except for manganese) to the expected concentrations in soils of the eastern United States. Sodium in plant ash increases oceanward and reflects accumulation of sea salt. The source(s) of calcium and strontium is ambiguous, but a source of at least some part of these two elements appears to be airborne limestone dust. Thus, factors 1 and 2 are interpreted as reflecting essentially inert accumulation of airborne particulate material, most of it of natural origin. Varimax factors 3 and 4 together describe most of the variation in the logarithmic concentrations of boron, cadmium, chromium, copper, lead, lithium, nickel, vanadium, and zinc. Lead reflects automotive exhaust inasmuch as most samples in this study were collected along roads. The remaining elements in this association may also reflect automotive-related effects, at least in part, but more likely all nine elements constitute a suite of urban, industrial, or technologically induced metals. This association is stochastically independent, or nearly so, of factors 1 and 2 (airborne particulates) and is viewed as largely anthropogenic in origin. Varimax factor 5 accounts for most of the variation in the logarithmic concentrations of magnesium, phosphorus, and potassium. These three elements are major metabolic constituents of living plant tissue, and the association is nearly independent of the other four factors (the airborne particulates and the technological metals). This suggests that, regardless of source, the concentrations of magnesium, phosphorus, and potassium in plant ash are being controlled more by metabolic need than by environmental influence.

## INTRODUCTION

The effect of airborne materials on the quality of the human environment has prompted many investigators to search for means of measuring ambient atmospheric concentrations of these materials. Commonly, the methods consist of various procedures for collecting the materials by filtration processes followed by chemical analysis of the materials, or for continuous instrumental monitoring of gaseous or airborne compounds. Shacklette and Connor (1973) described the results of a study in which Spanish moss (Tillandsia usneoides L.) was used to assess the variability of airborne elements in the southeastern part of the United States. They concluded that elemental analysis of Spanish moss or its ash seems to be an economical and rapid method with which to examine the relative average concentrations of airborne elements.

Spanish moss is classed as an epiphyte (generally called "air plants") and most commonly grows on trees. It is not parasitic because it gets all essential elements and water from the air and produces its own food by photosynthesis. Like most other species of the pineapple family (Bromeliaceae), Spanish moss has highly specialized morphological adaptations that assist in obtaining water and other materials from the air. Thus, it appears to be an ideal natural "monitor" with which to investigate element burdens in the local atmosphere of its native habitat. Previous studies of elements in Spanish moss, in addition to Shacklette and Connor (1973), include MacIntire and others (1952), Martinez and others (1971), Benzing and Renfrow (1971), Robinson and others (1973), Caruccio and others (1975), and Schrimpff (1981).

The elements available to Spanish moss from the air have many natural sources. The most obvious sources are dust consisting of soil and rock particles and, near the sea, salt from ocean spray. The mineral content of air and rainwater, and its importance to plant growth were discussed by Ingham (1950), and the effects of solutes leached from tree foliage and deposited on Spanish moss were noted by Schlesinger and Marks (1977). Although Spanish moss may at places benefit from elements in these leachates, it is not dependent on them, as shown by its growth on wire fences and utility wires (Daubenmire, 1974, p. 308).

The air carries much particulate matter of plant origin, characterized by Benninghoff (1965, p. 142) as "...in enormous variety and large quantity," including spores, pollen, bacteria, single-celled algae, fungal mycelia, deciduous plant tissue parts, and fragments of vegetable humus. The exudates from forest trees and other plants contribute a share of the natural metal burdens of air. The volatile exudates from coniferous forests were analyzed by Curtin and others (1974) and were found to contain antimony, arsenic, barium, beryllium, bismuth, cadmium, chromium, cobalt, copper, gallium, iron, lanthanum, lead, lithium, magnesium, manganese, molybdenum, nickel, silver, sodium, strontium, tin, titanium, vanadium, yttrium, zinc, and zirconium. These volatile exudates consist largely of a variety of terpenes, and the world production of plant volatiles released into the atmosphere was estimated by Rasmussen and Went (1965, p. 220) to be  $438 \times 10^6$  tons per year. Went (1971) reported the polymerization of airborne terpenes into large (to 1 mm) clumps, which he called "air-soot," and that a certain amount of these clumps become attached to leaves and other plant parts.

Sub-micrometer-size particulate matter released by plants into the atmosphere was shown by Beauford and others (1977) to contain lead and zinc. Nyemyeryuk (1970) reported that the transpiration water given off by plants contained ammonium, calcium, chloride, magnesium, potassium, sodium, and sulphate ions. Fish (1972) found that strong electrical fields caused release from plants of airborne particles with diameters less than 0.6 micrometers.

In addition to these airborne particulates of plant origin, elements from inorganic sources form a background atmospheric burden of worldwide circulation. Zoller and others (1974), on the basis of air sampling at the South Pole, concluded that the elements were derived from crustal weathering or the ocean. These elements include aluminum, calcium, cerium, chromium, cobalt, europium, iron, lanthanum, manganese, potassium, samarium, scandium,

sodium, thulium, and vanadium. Brocas and Picciotto (1967) believed that most of the nickel in Antarctic snow was of extraterrestrial origin, and they calculated that the extraterrestrial matter deposited over the entire Earth's surface is 3-10 million tons per year. Although these elements are potentially available to Spanish moss, their absorption is probably overwhelmed by effects of dust deposition, salt spray, and airborne anthropogenic pollutants from local sources.

For selected metallic elements, higher than average concentrations in ash of moss may reasonably be inferred to reflect higher than average atmospheric concentrations, suggesting the utility of Spanish moss as a monitor of the local atmospheric element load. For example, ash of plants collected close to roadways contains 18 times as much lead as ash of plants collected far from roads (Connor and Shacklette, 1973); presumably this lead is derived from lead-bearing automotive exhaust. Also, plants collected close to the ocean contain elevated concentrations of sodium in ash, and four of six samples containing detectable tin in ash were collected within 100 km of the only tin smelter in the United States.

Difficulties in the use of Spanish moss as a natural atmospheric monitor, however, are both varied and serious. For example, Spanish moss is composed of living tissue which undoubtedly interacts chemically with the atmosphere and substances in it. The concentration in ash of any element whose airborne compounds are selectively absorbed or repelled by the living plant will not faithfully reflect its ambient atmospheric concentration. Moreover, periodic "cleansing" of the plant by rain or wind may remove loosely held substances. In addition, such washing effectively enlarges the volume of atmosphere available to the plant by virtue of the fact that rainfall may chemically scavenge a considerable volume of overlying atmosphere. Also, over the life of the plant, or the life of the collected part, the chemistry of the local atmosphere may drastically and erratically change. Thus, at best, the chemistry of the plant ash can only reflect a time-averaged atmospheric composition.

Nevertheless, the potential use of Spanish moss as an indicator of airborne metals seems obvious, and this report examines the limits of that potential. The examination was based on a study of the correlations among logarithmic concentrations of 25 elements in 123 samples of plant ash. Of the 25 elements used in this examination, aluminum, cobalt, gallium, ytterbium, yttrium, and zirconium occurred in concentrations too low to be detected in one or more samples, and one sample was not analyzed for lithium (Shacklette and Connor, 1973). In order to include these seven elements, arbitrary values were assigned as needed to produce a completely numeric data set. The substitute values are listed below.

Element	Substituted value	Number of samples (of 123) substituted
Aluminum, percent	15	3
Cobalt, ppm	5	21
Gallium, ppm	7	28
Lithium, ppm	22	1
Ytterbium, ppm	1.5	32
Yttrium, ppm	15	29
Zirconium, ppm	15	2

The single sample lacking a lithium analysis was assigned a value equal to the geometric mean of the 122 other lithium concentrations. The use of such values is admittedly arbitrary and is justified primarily by the belief that substitution of any reasonable value will not materially alter the conclusions derived from the factor analysis. Percent ash in each sample was added to the data set as a twenty-sixth variable.

Methods of sample collection and laboratory analysis as well as descriptions of sampling localities, element distribution maps, and element summaries may be found in Shacklette and Connor (1973). The factor analytical techniques were based on computer programs in Dixon (1975), and the U.S. Geological Survey's STATPAC system (VanTrump and Miesch, 1977).

## FACTOR ANALYSIS

Techniques of R-mode factor analysis were applied in an attempt to identify element associations in the ash of Spanish moss which may shed light on the probable sources of these metals in the atmosphere of the southeastern United States. R-mode factor analysis has been widely applied as a means of examining the covariation in a data set by describing such covariation in terms of some minimum number of new variables,  $k$  (called "factors"), always less than the number of original variables,  $m$ . Geometrically, the process involves defining each original variable as a unit vector in  $m$ -space, all originating from a common center, and with the angle between any two vectors inversely related to the covariation between the two variables. If examination of this vector complex indicates that the complex lies mostly in  $k$ -space ( $k$  less than  $m$ ), then the original data will likely be more easily interpreted in terms of  $k$  factors. Projections of the  $m$  vectors into the reduced space always results in shortening of the vectors, and their new lengths are taken as measures of the adequacy of the factor model. The square of the vector length is called the communality. The correlations of the vectors with the  $k$  factors are called the factor loadings. Numerous texts describe the mathematics of factor analysis. A widely used geologically oriented text is that of Davis (1973). Hopke (1980) described an application of factor analysis to aerosol composition of the Boston metropolitan area.

Correlation coefficients among the logarithms of 25 element concentrations in ash and with log ash are given in table 1. The first 10 eigenvalues of this correlation matrix are listed in table 2. The first two eigenvalues are large compared to the remainder and indicate that the minimum number of factors in a geochemical model of these data should be at least two. Such a model would account for over half (52.7 percent) of the total variation in the original data. Only five eigenvalues exceed 1.0, and a five-factor model accounts for an acceptably high 71 percent of the variation in the data.

Variable communalities for models containing as many as eight factors are represented in figure 1. In a five-factor model, all communalities exceed 0.50, and a five-factor varimax model was used to summarize the chemical variation in ash of Spanish moss. Varimax loadings of each chemical variable on these five factors are listed in table 3.

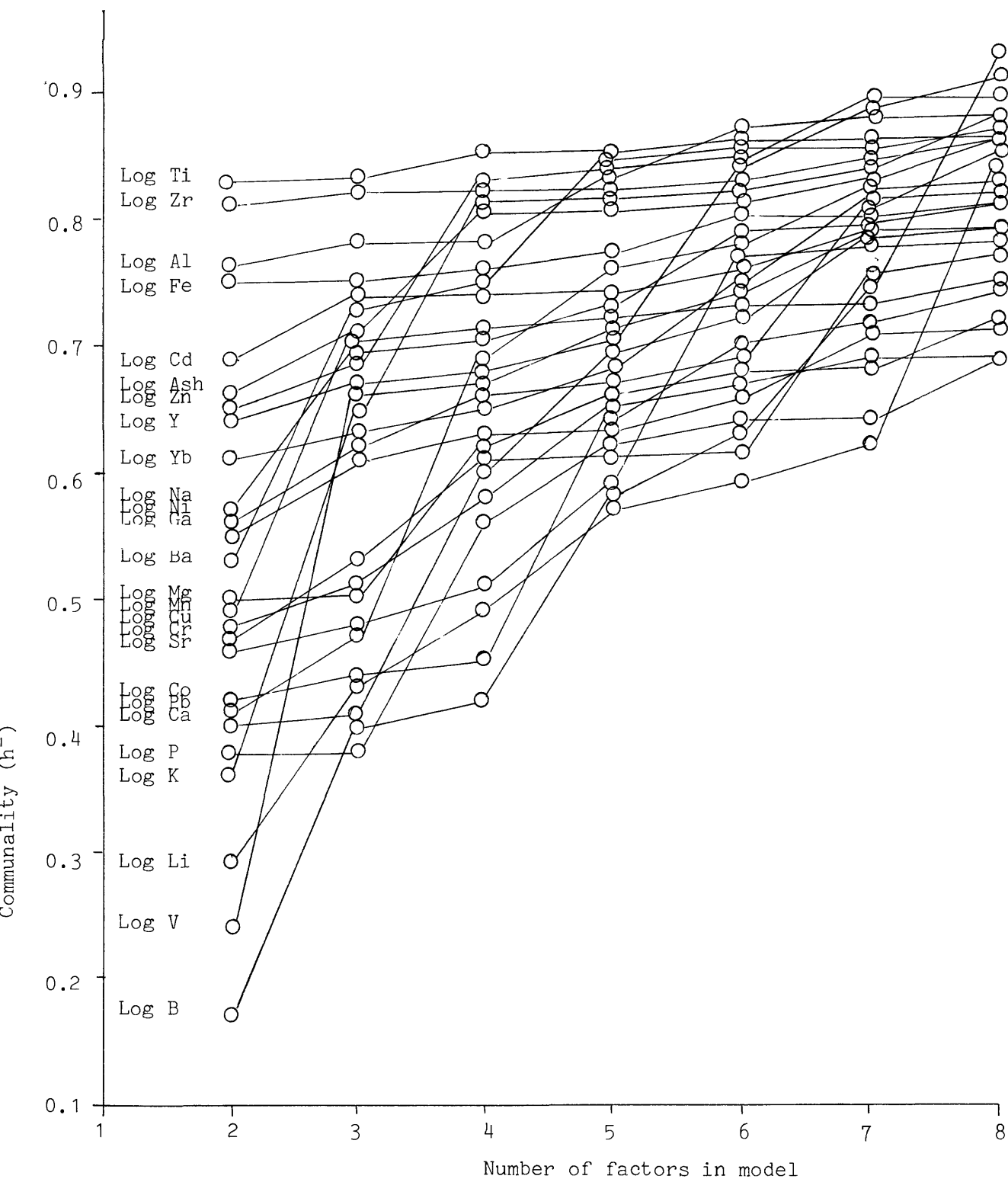


Figure 1.--Factor-variance diagram relating variable communalities ( $h^2$ ) to number of factors in the varimax model of ash geochemistry of Spanish moss.

Table 1.--Correlation coefficients among 26 variables measured in Spanish moss

[All chemical elements were measured in ash]

	Log Mg	Log Ti	Log Mn	Log B	Log Ba	Log Co	Log Cr	Log Cu	Log Ni	Log Pb	Log Sr	Log V	Log Y
Log Fe--	-0.19	0.76	0.61	0.07	0.63	0.53	0.57	0.22	0.51	0.22	-0.54	0.29	0.58
Log Mg--		-.26	-.02	.25	-.23	-.03	-.11	.25	.12	.12	.34	.19	-.27
Log Ti--			.55	-.03	.63	.48	.55	.16	.37	.07	-.63	.25	.70
Log Mn--				-.17	.68	.48	.33	.16	.35	.21	-.39	-.03	.48
Log B--					-.09	-.02	.02	.23	.28	.02	.11	.27	-.08
Log Ba--						.58	.39	.03	.30	.20	-.36	-.17	.40
Log Co--							.46	.13	.48	.15	-.23	.03	.44
Log Cr--								.36	.60	.25	-.27	.42	.42
Log Cu--									.57	.48	.03	.36	.20
Log Ni--										.35	-.12	.56	.30
Log Pb--											-.02	.17	.03
Log Sr--												-.04	-.46
Log V--													.26
Log Y--													
Log Zr--													
Log Al--													
Log Ga--													
Log Yb--													
Log Ash--													
Log Ca--													
Log Li--													
Log Na--													
Log K--													
Log P--													
Log Cd--													
Log Zn--													

Table 1.--Correlation coefficients among 26 variables measured in Spanish moss--Continued

	Log Zr	Log Al	Log Ga	Log Yb	Log Ash	Log Ca	Log Li	Log Na	Log K	Log P	Log Cd	Log Zn
Log Fe--	0.70	0.84	0.57	0.57	-0.10	-0.49	0.39	-0.51	0.14	-0.11	0.29	0.20
Log Mg--	-.34	-.22	-.21	-.27	-.62	.16	.21	.45	.41	.34	.37	.32
Log Ti--	.87	.83	.66	.68	-.03	-.63	.34	-.60	.18	-.12	.14	.09
Log Mn--	.62	.51	.35	.47	-.29	-.43	.12	-.59	.43	-.04	.21	.16
Log B---	-.11	.13	.04	-.07	-.34	.10	.32	.34	-.06	.24	.21	.17
Log Ba--	.67	.66	.41	.39	-.14	-.31	.14	-.62	.33	-.18	.26	.20
Log Co--	.42	.56	.53	.36	-.14	-.27	.27	-.38	.26	-.11	.24	.17
Log Cr--	.51	.53	.47	.39	-.09	-.30	.33	-.23	.09	-.03	.33	.31
Log Cu--	.15	.17	.19	.15	-.43	-.06	.28	.07	.18	.24	.48	.64
Log Ni--	.28	.43	.39	.25	-.40	-.20	.33	-.15	.21	.18	.48	.41
Log Pb--	.10	.16	.12	-.02	-.39	.09	.14	-.04	.33	.19	.57	.80
Log Sr--	-.66	-.55	-.35	-.49	-.14	.61	-.08	.39	-.08	.15	.03	.10
Log V---	.09	.25	.35	.21	-.25	-.19	.38	.10	.00	.25	.26	.22
Log Y---	.67	.61	.70	.85	.00	-.47	.24	-.57	.09	-.11	-.04	.00
Log Zr--		.77	.57	.66	.05	-.61	.26	-.64	.12	-.23	.07	.05
Log Al--			.67	.60	-.04	-.47	.45	-.49	.11	-.16	.21	.15
Log Ga--				.57	-.06	-.39	.38	-.47	.11	-.09	.09	.11
Log Yb--					.01	-.48	.26	-.56	.09	-.15	-.05	-.02
Log Ash-						.02	-.26	-.11	-.68	-.56	-.60	-.52
Log Ca--							-.26	.35	-.23	-.06	-.02	.08
Log Li--								.11	.22	.14	.27	.25
Log Na--									-.14	.27	.08	.03
Log K---										.41	.55	.44
Log P---											.44	.32
Log Cd--												.74
Log Zn--												

Table 2.--Eigenvalues ( $\lambda$ ) and cumulative variance associated with the first 10 principal components of the chemistry of Spanish moss ash

Principal component	Eigenvalue ( $\lambda$ )	Cumulative variance (in percent)
1-----	8.82	33.9
2-----	4.89	52.7
3-----	2.13	61.0
4-----	1.55	66.9
5-----	1.16	71.4
6-----	.99	75.2
7-----	.82	78.4
8-----	.76	81.3
9-----	.68	83.9
10-----	.54	86.0

The elements with the highest loadings on the first two factors are titanium, zirconium, yttrium, ytterbium, aluminum, iron, gallium, manganese, sodium, strontium, calcium, barium, and cobalt (table 3). As discussed in the following paragraphs, we believe most of these elements are present in Spanish moss principally as surface coatings of natural airborne particulates, mostly as windblown soil dust or sea spray. Thus, we have labeled these factors together as "natural particulates." The most important elements in the third and fourth factors are zinc, lead, copper, cadmium, nickel, chromium, boron, lithium, and vanadium (table 3). As these are believed to reflect largely urban or industrial sources of metals, we have labeled these factors together as "technological metals." The last factor appears to be biological in nature. It has a strong inverse correlation with ash content and positive correlations with magnesium, phosphorus, and potassium, which are major metabolic elements in plants. We have labeled this factor "metabolic constituents."

#### FACTORS 1 AND 2--NATURAL PARTICULATES

These factors are the most important descriptors of element variation in the varimax model of Spanish moss ash chemistry. Together, they account for over a third (37.4 percent) of the total observed variation in the ash data, and they describe more than half of the variation in the logs of titanium, zirconium, yttrium, ytterbium, aluminum, iron, gallium, manganese, sodium, strontium, calcium, barium, and cobalt.

A graphic evaluation of ash composition in terms of these two factors is shown in figure 2. The two factors define a cross section of the five-factor varimax model, and all chemical variables are represented as vectors projected onto this cross section. The distal end of each vector is defined by the loadings of the respective variable on the two factors (table 3). The strength of association of any variable to another, or to any factor axis, is inversely proportional to the angle between the two vectors or between the vector and the axis. A small angle reflects a strong positive association. A 90-degree angle reflects no association, and a highly obtuse angle reflects a strong negative association. Short vectors (those with distal ends near the origin of the plot) are inadequately represented by these two factors, and their relations should be ignored.

The diagram in figure 2 is dominated by a fan of vectors that subtend an angle of some 60 degrees between the log barium vector and the log ytterbium vector. The 10 elements represented in this fan are common constituents of soils or near-surface sediments in the southeastern part of the United States. A comparison of the typical amounts of these elements in plant ash to typical amounts in soil (table 4) is close enough (with the exception of manganese) to suggest that the average plant ash is composed largely of soil material. Thus, the first two factors in the model reflect, to a large extent, simple accumulation of windblown soil or other near-surface material.

Log sodium, log strontium, and log calcium are negatively correlated with log aluminum and other variables of the soil component. Evidently, plant ash contains either relatively large amounts of the soil-related metals or relatively large amounts of sodium, strontium, and calcium. The most likely explanation for this inverse relation is that the ash consists of two dominant

Table 3.--Loadings of chemical variables on the factors of the five-factor varimax model

[\*, loading is significantly different from zero at the 0.05 probability level; number in parentheses is percent of variation described by factor]

Variable	Loadings					Sum of percentages
	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	
	Natural particulates	Technological metals	Metabolic constituents			
Log titanium---	0.87(76)*	0.26(7)*	0.10(1)	0.12(1)	-0.01(<1)	85
Log zirconium---	.84(71)*	.31(9)*	.09(1)	-.04(<1)	-.08(1)	82
Log yttrium---	.83(69)*	.05(<1)	.08(1)	.08(1)	-.08(1)	72
Log ytterbium---	.82(68)*	.04(<1)	.02(<1)	.05(<1)	-.07(<1)	68
Log aluminum---	.72(52)*	.43(18)*	.16(2)	.31(10)*	-.09(1)	83
Log iron-----	.71(50)*	.39(15)*	.25(6)*	.23(5)*	-.03(1)	77
Log gallium---	.67(45)*	.20(4)	.17(3)	.30(9)*	-.11(1)	62
Log manganese---	.57(33)*	.49(24)*	.13(2)	-.18(3)	.31(10)*	70
Log sodium-----	-.64(40)*	-.39(16)*	-.03(<1)	.38(15)*	.12(2)	73
Log strontium---	-.74(55)*	-.02(<1)	.07(1)	.14(2)	.02(<1)	58
Log calcium---	-.78(60)*	.09(1)	.14(2)	-.01(<1)	-.24(6)*	69
Log zinc-----	-.06(<1)	.12(1)	.85(73)*	.03(<1)	.31(10)*	84
Log lead-----	-.02(<1)	.12(1)	.84(70)*	-.14(2)	.16(3)	76
Log copper-----	.12(2)	-.15(2)	.74(55)*	.22(5)*	.14(2)	66
Log cadmium---	-.02(<1)	.19(4)	.66(44)*	.16(2)	.49(24)*	74
Log nickel-----	.31(9)*	.14(2)	.59(34)*	.45(20)*	.08(1)	66
Log chromium---	.48(23)*	.17(3)	.49(24)*	.30(9)*	-.16(3)	62
Log boron-----	-.16(3)	-.01(<1)	.04(<1)	.73(53)*	.12(1)	57
Log lithium---	.27(7)*	.09(1)	.11(1)	.66(44)*	.20(4)	57
Log vanadium---	.30(9)*	-.43(19)*	.37(14)*	.55(30)*	.03(<1)	72
Log ash-----	.04(<1)	-.09(1)	-.34(12)*	-.24(6)*	-.80(64)*	83
Log magnesium---	-.36(13)*	-.04(<1)	.09(1)	.33(11)*	.64(41)*	66
Log phosphorus---	-.07(1)	-.35(13)*	.20(4)	.13(2)	.66(44)*	64
Log potassium---	.15(2)	.24(6)*	.19(4)	-.12(1)	.83(69)*	82
Log barium-----	.47(22)*	.77(60)*	.14(2)	-.10(1)	.08(1)	86
Log cobalt-----	.37(14)*	.65(43)*	.16(3)	.23(5)*	.03(<1)	65

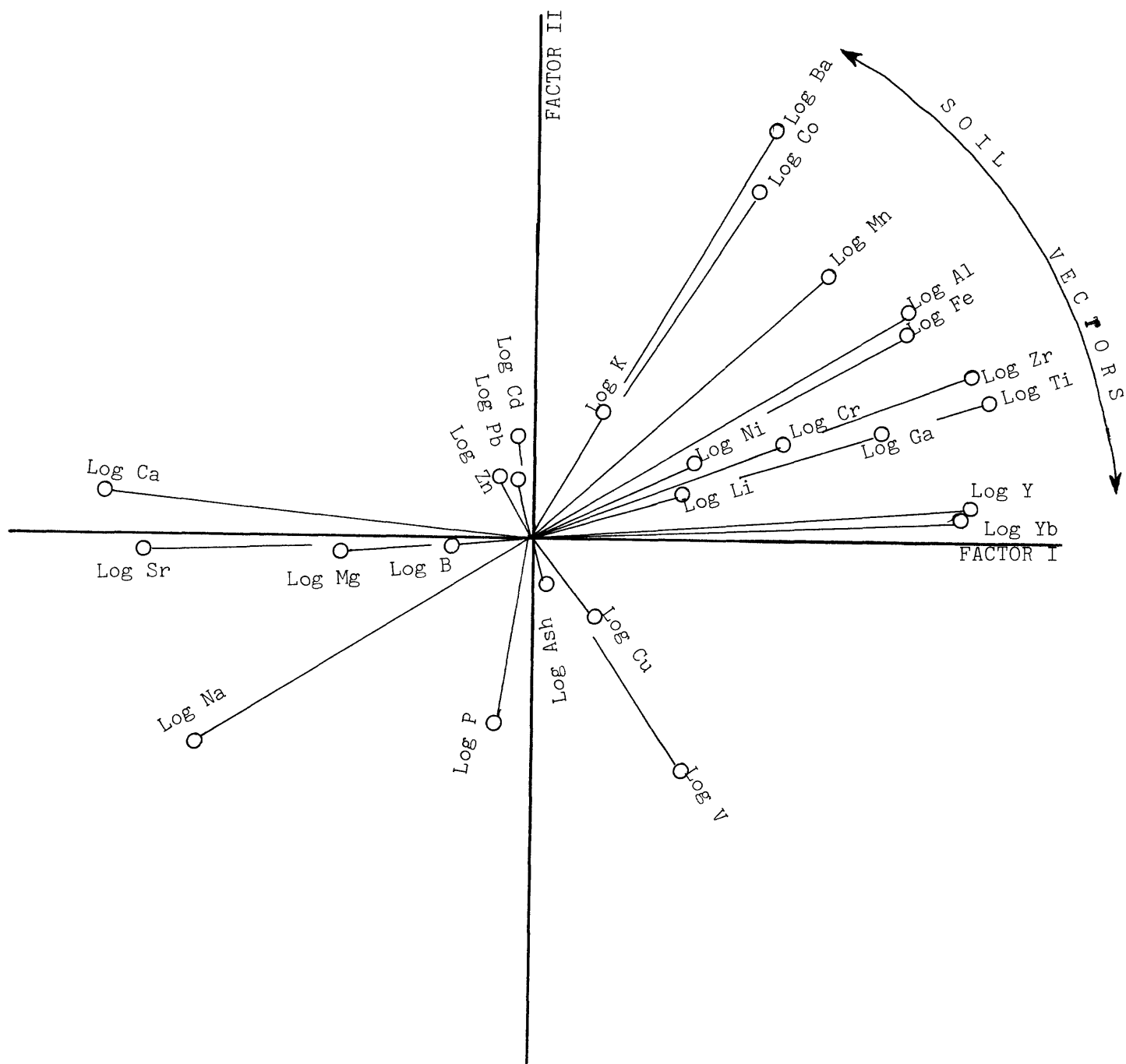


Figure 2.--Relations of chemical variables (vectors) to each other and to factors 1 and 2 in the 5-factor varimax model of variation.

Table 4.--Typical concentrations (in parts per million) of selected elements in ash of Spanish moss and soils of the eastern United States

Element	Spanish moss ash (geometric mean, Shacklette and Connor, 1973)	Eastern U.S. soils (geometric mean, Shacklette and others, 1973)
Titanium---	2,300	3,000
Zirconium--	110	250
Yttrium----	30	23
Ytterbium--	2.4	3
Aluminum---	40,800	33,000
Iron-----	15,800	15,000
Gallium----	9.8	10
Manganese--	2,300	285
Barium-----	564	300
Cobalt-----	9.8	7

constituents (or their ashed equivalents), one of which was derived from soil and the other derived from materials high in sodium, strontium, and calcium. The amount of ash bears no apparent relation to the relative amounts of either of these two constituents, inasmuch as log ash has loadings near zero on both factors (table 3), and the inverse relation of the two element suites likely reflects local differences in the average long-term atmospheric particulate load.

Sodium in ash is clearly related to nearness to the ocean (fig. 3) and, hence, reflects accumulation of salt from that source. The inverse relation of log aluminum to log sodium (fig. 2) is noted in figure 3 by the contour line representing a ratio of aluminum to sodium of 1.0. This contour closely follows the Atlantic and Gulf coasts.

Calcium is an essential constituent of living plant tissue, but its lack of correlation with the other metabolic constituents, magnesium, phosphorus, and potassium (table 1), is puzzling. Calcium in ash apparently occurs as calcite (fig. 4). The ash represented in figure 4 contains 16 percent calcium, equivalent to 40 percent calcite. Other constituents include dolomite, langbeinite (a potassium magnesium sulfate), and minor clay and quartz. The clay and quartz content undoubtedly reflect airborne clay and quartz, but the calcium and potassium compounds probably reflect oxidative changes upon ashing of the dried organic-rich material. In most higher plants, of which Spanish moss is one, calcium occurs between the cell walls as a salt of pectic acid. Pectic acid is a long chain polysaccharide that would oxidize completely during the ashing process, leaving, perhaps, calcite (L. P. Gough, written communication, 1982).

Alternatively, at least some of the calcite in the plant ashes of this study almost certainly reflects accumulation of airborne limestone particulates. Gatz (1977, table 6), in a St. Louis-based study, found that as much as 18 percent of the particulate load in air was limestone dust. Probable sources for such particulates could include clouds of limestone dust from carbonate aggregate road surfaces, limestone quarries, cement factories, or agricultural liming. Conceivably, any covariation of tissue calcium with tissue magnesium, phosphorus, and potassium is being overwhelmed by the surface accumulation of limestone dust, accounting for the failure to find a positive logarithmic correlation of calcium with magnesium, phosphorus, and potassium. Clearly, the role of calcium in this study is complex.

Factors 1 and 2, as indicated in figure 2, appear to reflect two chemically distinct soil types: The first (factor 1) is high in yttrium and ytterbium; the second is high in barium and cobalt. As noted previously, both types are inversely related to sea salt, but the yttrium-ytterbium-rich soil has a stronger inverse relation to calcite (log calcium) than does the barium-cobalt-rich soil.

A measure of the importance or intensity of each factor in each sample of this study may be seen in the factor score for each sample. These scores are computed from Dixon (1975, p. 179) as:

$$F = ZR^{-1}A, \quad (1)$$

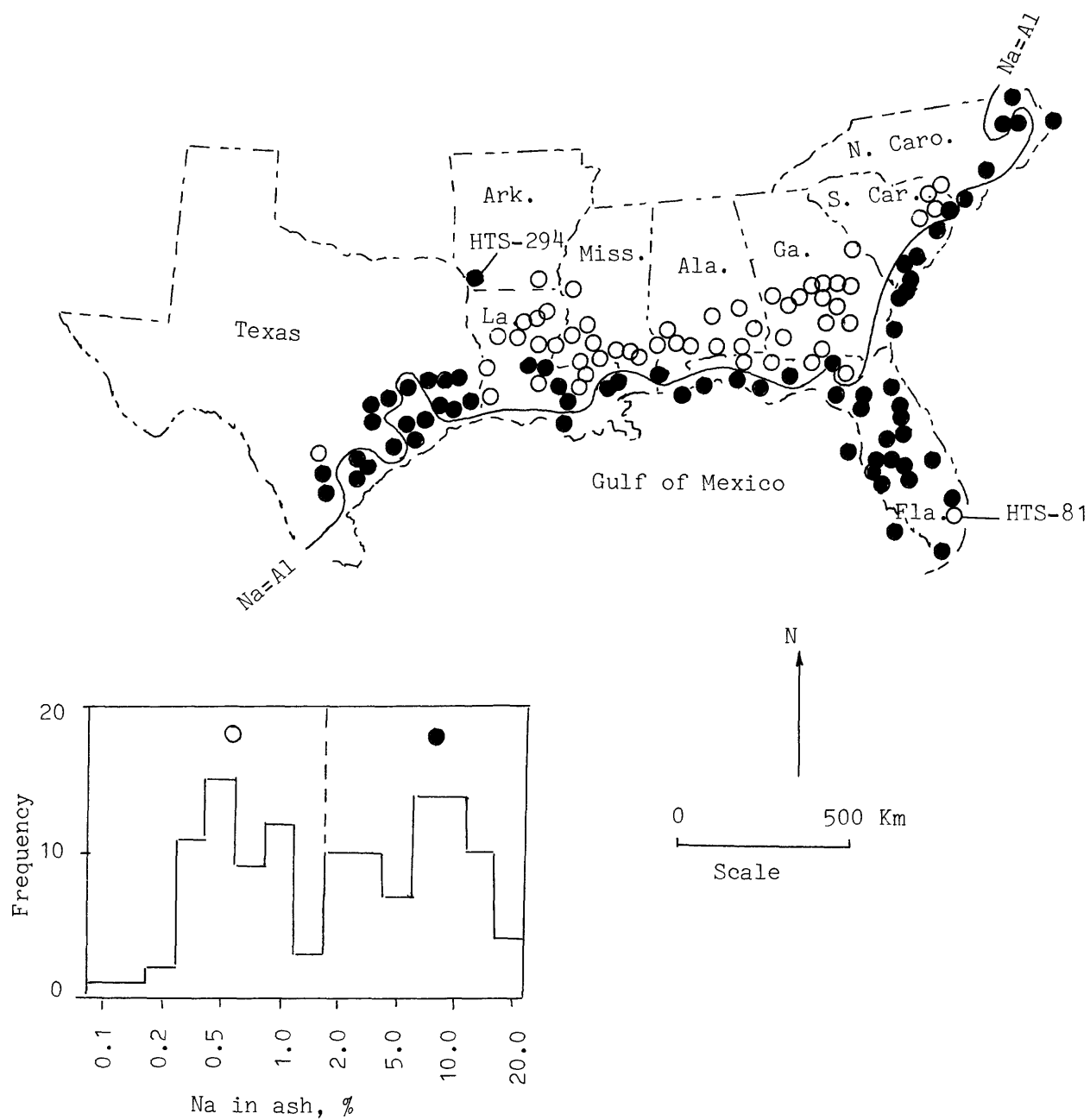


Figure 3.--Sodium in ash of Spanish moss (adapted from Shacklette and Connor, 1973, p. F34). Points interior to the contour line, except for HTS-294, have  $Al > Na$ ; points seaward of the line, except for HTS-81, have  $Na > Al$ .

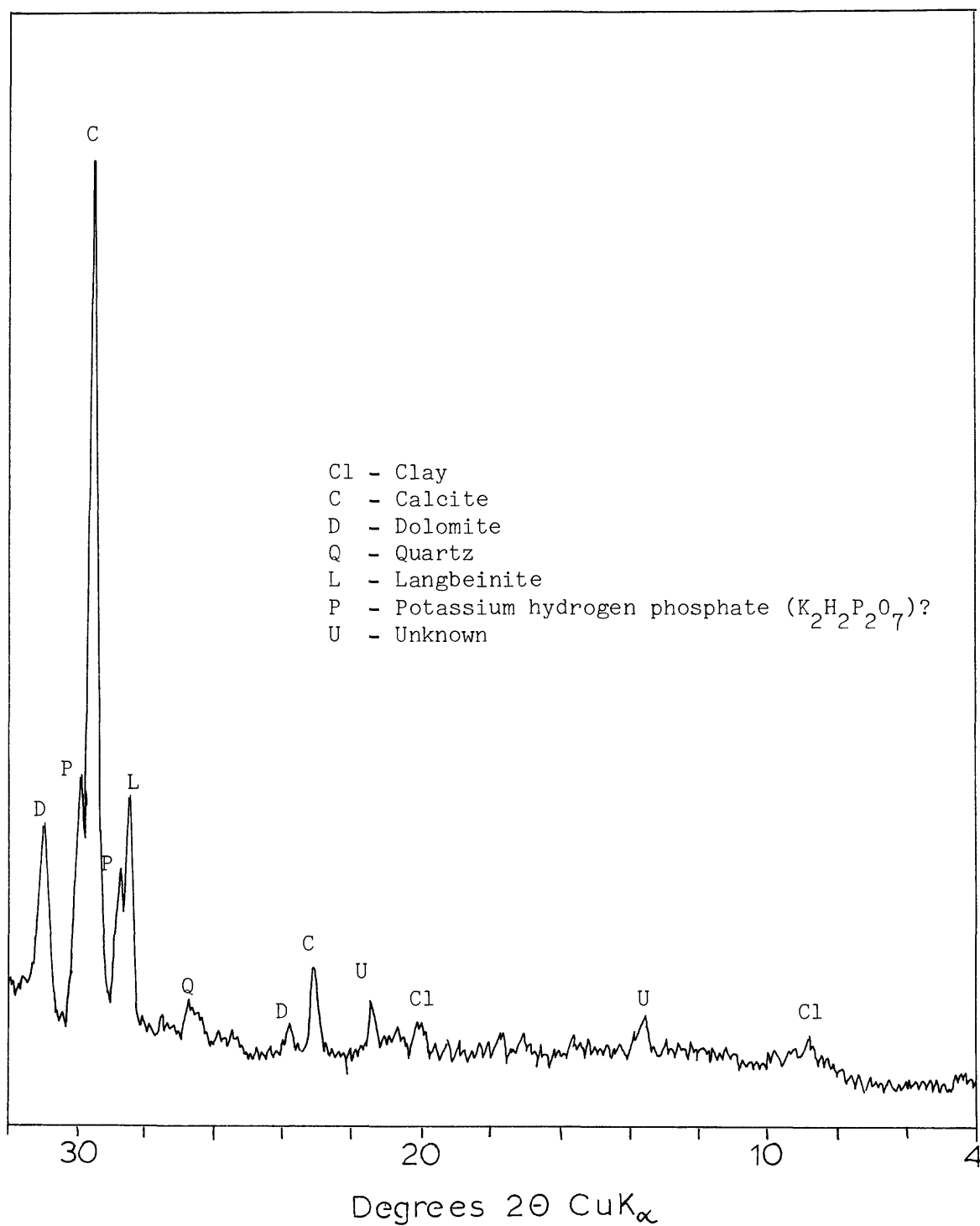


Figure 4.--X-ray diffraction pattern of ash of Spanish moss.

where F is a matrix of factor scores (of 123 rows and 5 columns), Z is the data matrix transformed to standard measure (123 rows and 26 columns),  $R^{-1}$  is the inverse of the logarithmic correlation matrix (table 1, 26 rows and 26 columns), and A is the matrix of factor loadings (table 3, 26 rows and 5 columns).

If the matrix Z is recast into logarithmic form ("unstandardized"), the factor scores can then be computed using the original logarithmic data. This change can be accomplished by:

$$X_{ij} = s_i z_{ij} + m_i, \quad (2)$$

where  $X_{ij}$  is the logarithmic concentration of variable i in sample j,  $s_i$  is the log standard deviation of variable i,  $z_{ij}$  is the standardized value of the logarithmic concentration of variable i in sample j, and  $m_i$  is the log mean of variable i.

The score for factor 1 in an individual ash sample is computed from:

$$F_{1j} = b_0 + b_1(\text{Log Ash})_j + b_2(\text{Log Al})_j + \dots + b_{26}(\text{Log Zr})_j, \quad (3)$$

where  $F_{1j}$  represents the score for factor 1 in the jth ash, the b's represent the constant ( $b_0$ ) and the coefficients listed in the first column of table 5, and the variables are logs of element concentrations (expressed in the units listed in table 5) in the jth ash. Scores for factor 2 used the coefficients in the second column of table 5.

Maps of the scores for factors 1 and 2 are shown in figures 5 and 6. High scores indicate relatively large amounts of soil-derived metals in ash; low (negative) scores indicate relatively large amounts of sodium (from sea salt) or calcite in ash. The sample ash exhibiting the highest score for factor 1 (that is, the ash with the largest ratio of yttrium-ytterbium-rich soil to calcite and sodium) comes from a sample collected in southwest Georgia. The ash with the lowest score (the ash with the smallest ratio) comes from a sample collected near Fort Lauderdale, Fla. The sample ash with the highest score for factor 2 (large amounts of barium-cobalt-rich soil) comes from a sample collected near Baton Rouge, La., and the ash with the lowest score comes from a plant collected near Lakeland, in central Florida.

Both factors have strong regional trends (figs. 5 and 6). These trends were estimated using stepwise trend analysis as described by Miesch and Connor (1968). Fifteen potential regressors were defined:  $X$ ,  $Y$ ,  $X^2$ ,  $XY$ ,  $Y^2$ ,  $X^3$ ,  $X^2Y$ ,  $XY^2$ ,  $Y^3$ ,  $\text{Log } X$ ,  $\text{Log } Y$ ,  $(\text{Log } X)(\text{Log } Y)$ ,  $e^X$ ,  $e^Y$ , and  $e^Xe^Y$ , where  $X$  is north latitude divided by 100 and  $Y$  is west longitude divided by 100. A statistically significant trend in the first factor was found to be:

$$T_1 = -97.77 - 0.000253(\text{LAT})^3 + 70.76(\text{Log LAT}), \quad (4)$$

where  $T_1$  estimates a score for factor 1 and LAT stands for north latitude. The trend equation in (4) accounts for 41.6 percent of the total variation in figure 5; that is, over 40 percent of the variation seen in the scores of factor 1 is regional. The strong northward increase in the yttrium-ytterbium-rich soil component (factor 1) presumably reflects a northward

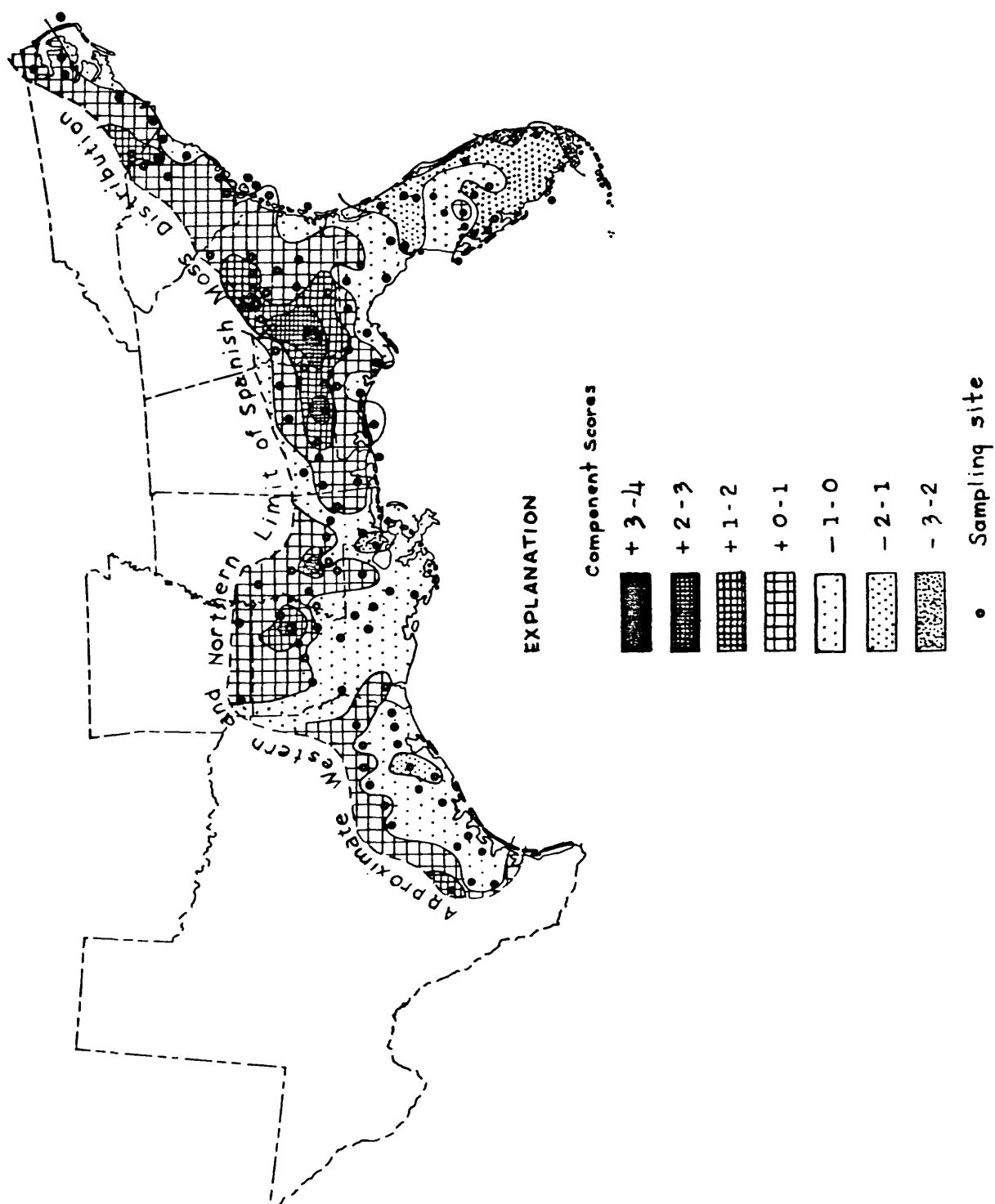


Figure 5a.--Contour map of scores for factor 1.

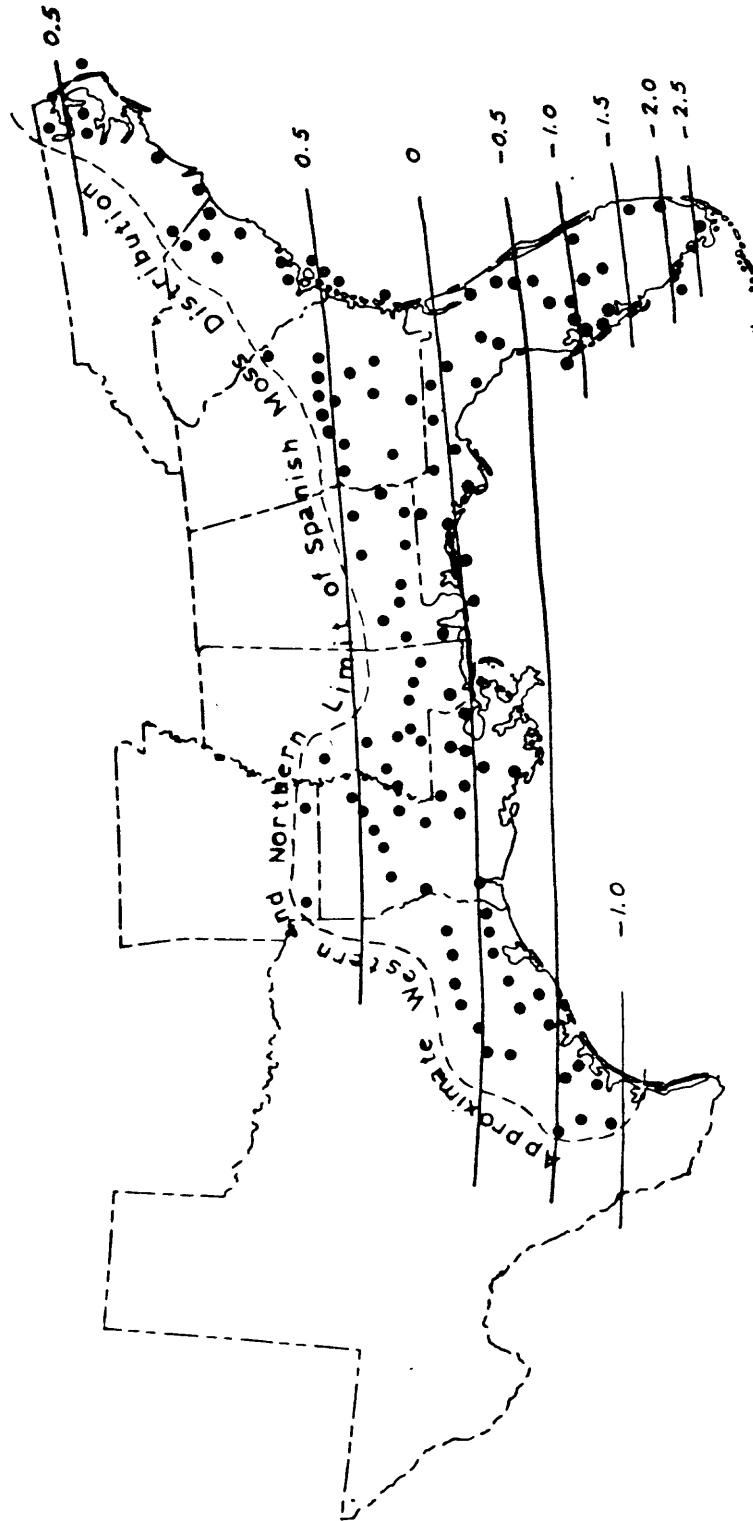


Figure 5b.--Regional trend in scores of factor 1.

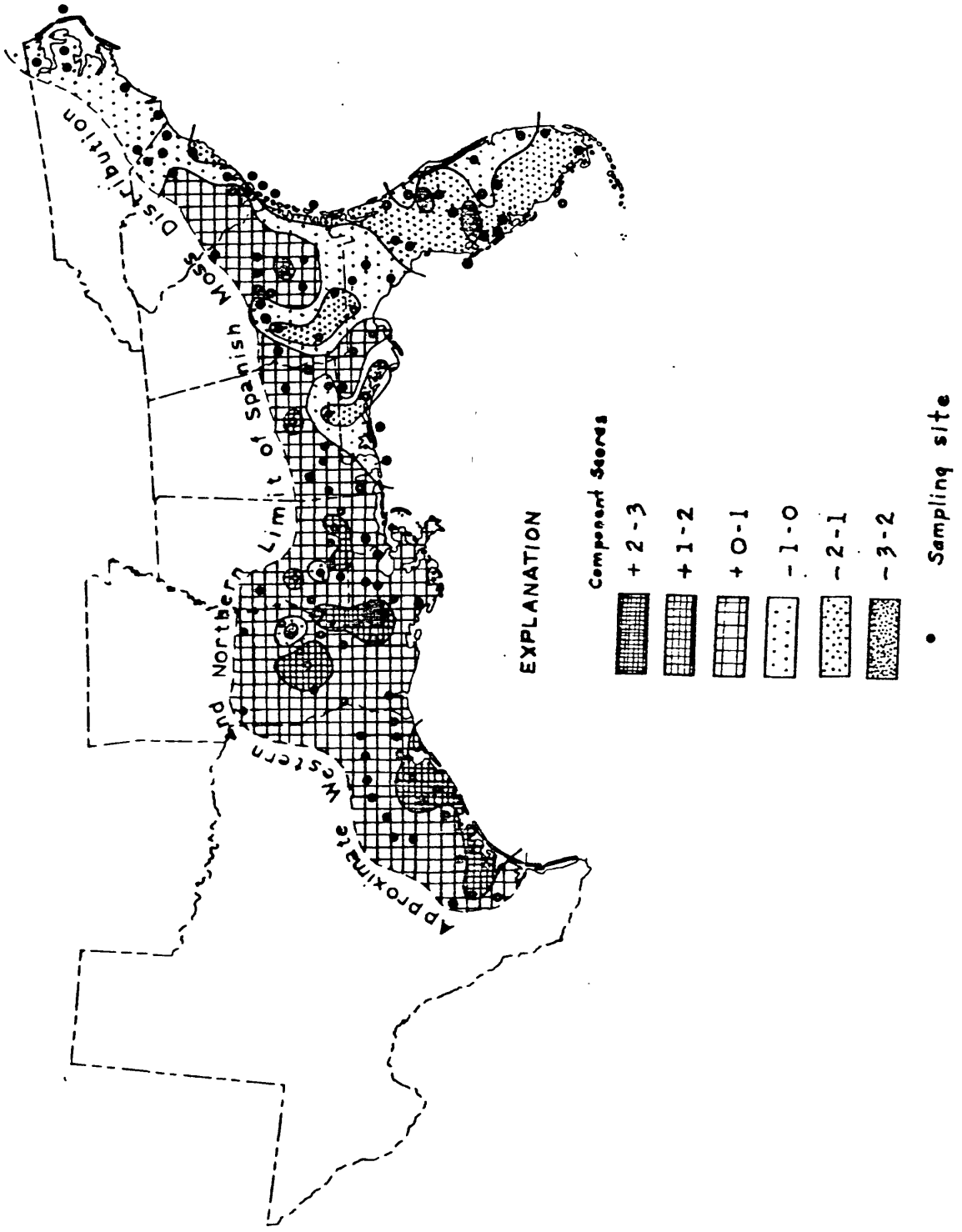


Figure 6a.--Contour map of scores for factor 2.

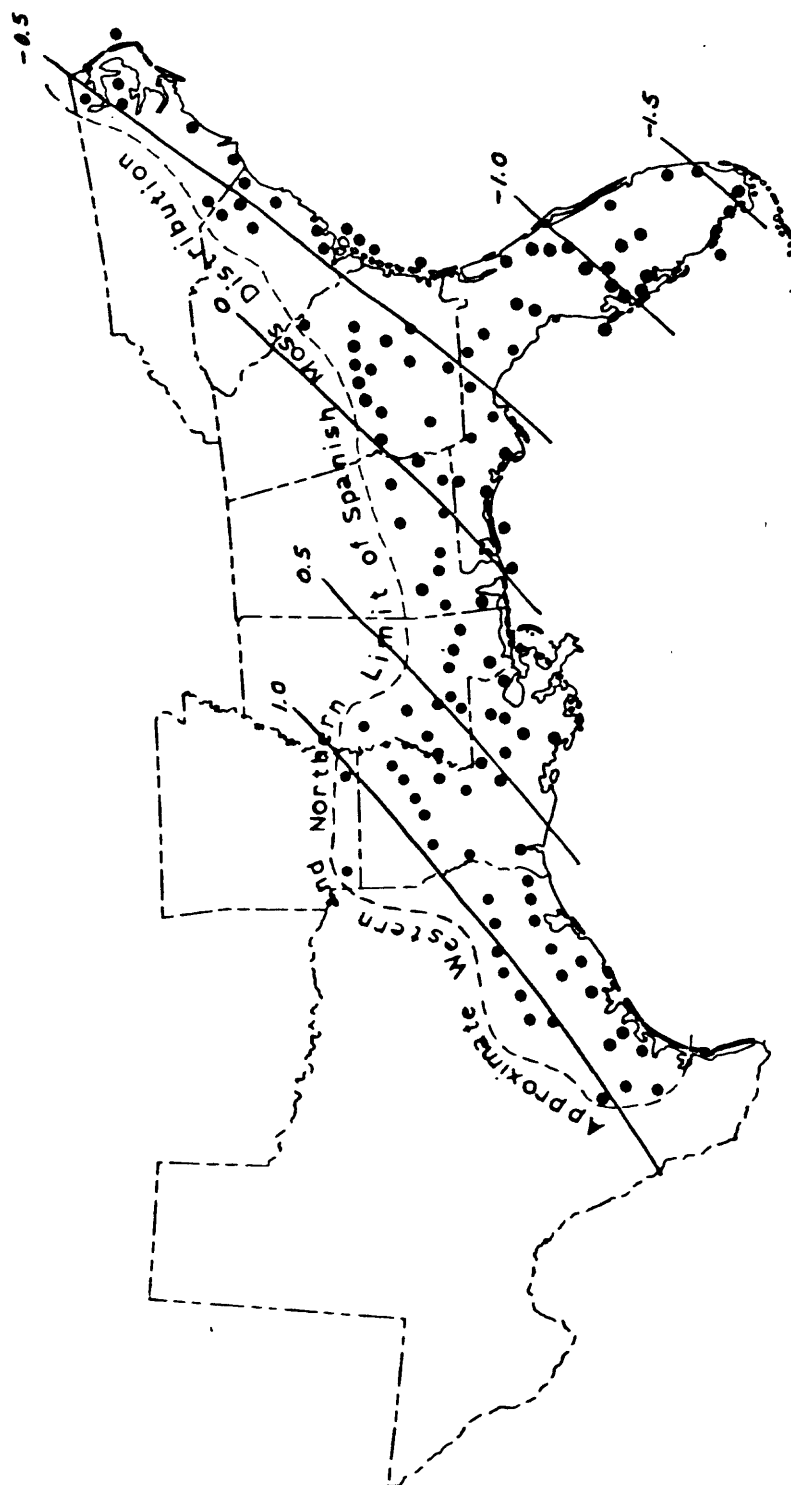


Figure 6b.---Regional trend in scores of factor 2.

Table 5.--Parameters for use in computing component scores

Variable	Components				
	1	2	3	4	5
	Natural particulates		Technological metals		Metabolic
	Constants ( $b_o$ )				
	0.2348	-1.7691	-8.3097	-9.4415	-3.1189
Coefficients					
Ash, percent-----	0.0274	-0.1916	0.2354	-0.2762	-1.7385
Aluminum, percent-	.1071	.4403	-.0857	.4418	-.1676
Barium, ppm-----	-.1372	.9967	-.0650	-.0484	.0421
Boron, ppm-----	-.6375	.8973	-.9124	3.1006	.0016
Cadmium, ppm-----	-.1992	.2850	.6698	-.0875	.3746
Calcium, percent--	-1.1044	1.1298	.6320	.2749	-.9718
Chromium, ppm-----	.0981	.0328	.6740	.3246	-.6319
Cobalt, ppm-----	-.3247	1.5217	-.2012	.6632	-.1265
Copper, ppm-----	.0975	-.5647	.8986	-.1195	-.2140
Gallium, ppm-----	.4080	.0755	.0194	.6455	-.3319
Iron, percent-----	.1863	.3863	.0722	.3049	-.1514
Lead, ppm-----	-.0735	-.0451	.6966	-.3998	-.1523
Lithium, ppm-----	.0230	.3478	-.5993	1.7382	.2788
Magnesium, percent	-.2377	.2469	-.4700	.6307	.9953
Manganese, ppm----	.1255	.3519	-.0819	-.2686	.3486
Nickel, ppm-----	-.0303	.1083	.5996	.5772	-.3116
Phosphorus, ppm---	.4589	-1.2703	-.0900	-.1944	1.4286
Potassium, percent	.1663	.2230	-.3029	-.4916	1.4581
Sodium, percent---	-.1273	-.1166	-.1641	.3270	.0270
Strontium, ppm----	-.6506	.5876	.1124	.4326	-.2161
Titanium, percent-	.4369	-.0487	-.0871	.0652	.0590
Vanadium, ppm-----	.4619	-1.2981	.4261	.6560	-.1920
Ytterbium, ppm----	.7497	-.6367	-.0794	.1197	.0668
Yttrium, ppm-----	.7312	-.6160	.0205	-.0829	-.0164
Zinc, ppm-----	-.1815	-.0061	1.1476	-.4402	-.0722
Zirconium, ppm----	.3696	.0188	.0093	-.1618	-.0198

increase in such soil in the atmosphere. The highest atmospheric concentrations, then, would appear to lie along a rough east-west line, from northern Louisiana through southern Mississippi and Alabama into southwestern Georgia.

Scores for the second factor were also examined by trend analysis, and the best predictor equation was found to be:

$$T_2 = -5.261 + 0.00002261(\text{LAT})(\text{LONG})^2, \quad (5)$$

where  $T_2$  stands for an estimated score on factor 2. The equation in (5) accounts for 50.5 percent of the total variation in the scores for factor 2. The westward increase in the barium-cobalt-rich soil component (factor 2) presumably reflects high atmospheric concentrations of such soil in central and southeastern Texas.

Additional variables involved in a statistically significant way with these natural particulates are the logarithms of nickel, chromium, lithium, vanadium, magnesium, phosphorus, and potassium (table 3). Nickel, chromium, lithium, and vanadium are common constituents of soil, and they are probably being accumulated to some degree as part of the soil components. Potassium, and perhaps magnesium, are also probably being so accumulated, but as primary constituents of living plant tissue, they are being controlled more by the physiological demands of the plant than by simple surface capacity for accumulation. In addition, log magnesium is positively related in a weak way to log calcium and reflects the association of minor dolomite with calcite in the ash (fig. 4). Also, log phosphorus is negatively related in a weak way to the barium-cobalt-rich soil component. Conceivably, this reflects a phosphorus-enriched atmosphere along the Atlantic coastal plain of North Carolina and Florida, where over four-fifths of the nation's phosphate is mined (National Research Council, 1979, p. 52).

In summary, the two most important factors appear to reflect simple accumulation of natural atmospheric particulates. These particulates apparently include two types of soil dust, ocean salt, and limestone dust. Where the soil fractions in plant ash are enhanced, the salt and limestone fractions are diminished, and this relation probably reflects a similar relation in the local atmosphere: the landward atmosphere is enhanced in soil dust, and the seaward atmosphere is enhanced in salt and limestone dust. Variation in total ash content is unrelated to variation in these fractions, suggesting that the surface of the living plant tends to be continually "saturated" with whatever fraction is dominant in the local atmosphere.

#### FACTORS 3 AND 4--TECHNOLOGICAL METALS

Factors 3 and 4 account for 23.0 percent of the total variation in the original data and describe over half of the variation in the logs of zinc, lead, copper, nickel, and boron (table 3). A vector diagram illustrating the relations among these variables is shown in figure 7. Like the soil metals (fig. 2), the technological metals also form a vector fan. The vectors in this fan represent cadmium, chromium, vanadium, and lithium, as well as the metals listed above. Most of the short vectors represent elements in the natural particulates (fig. 2), which vary in a manner nearly independent of

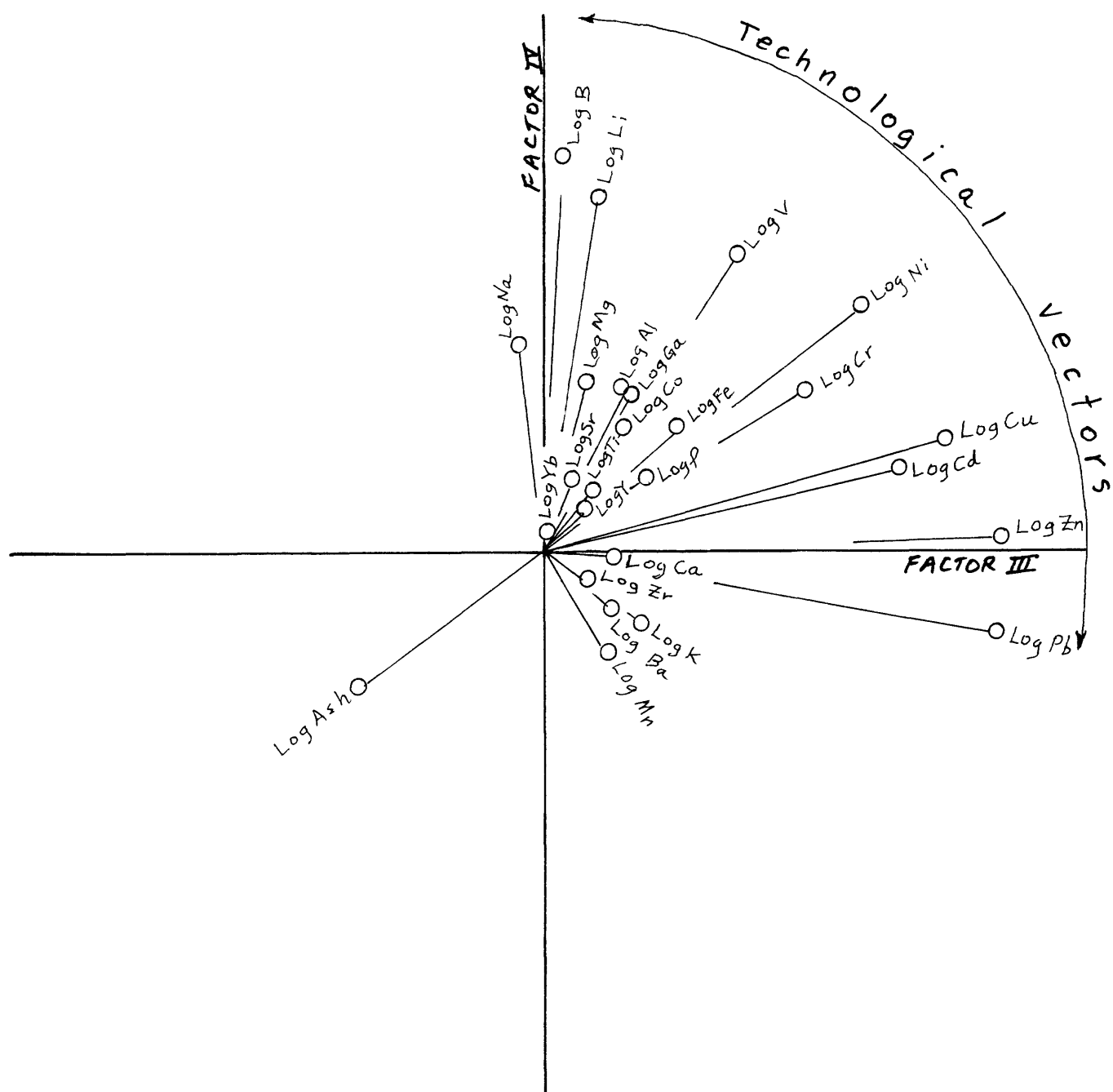


Figure 7.--Relations of chemical variables (vectors) to each other and to factors 3 and 4 in the 5-factor varimax model of variation.

the technological metals. Thus, accumulation of the technological metals in Spanish moss appears to occur almost independently of the accumulation of the natural particulates. Also, as ash content increases, the accumulation of the technological metals tends to decrease slightly.

Although all of the nine technological metals occur in trace amounts in soil, the generally low logarithmic correlations of these metals with log aluminum indicates that sources other than soil control their occurrence in Spanish moss ash. The source of lead (factor 3) is unquestionably vehicular exhaust emissions, which have been estimated to account for as much as 98 percent of the atmospheric lead in the country (Cannon, 1976, table 35). Over three-fourths of the Spanish moss samples in this study were collected along roads; the ash of one sample collected along Interstate Highway 75 in northern Florida contained 5 percent lead. The close relations of zinc, copper, and cadmium to lead in the vector fan indicate that these metals are also related to vehicular traffic, if not in exhaust fumes then perhaps to road materials (asphalt, for example) or the vehicles themselves (tires, grease and oil, and metal body parts, for example). Cannon and Anderson (1971) noted elevated levels of chromium, zinc, nickel, and copper in vegetation adjacent to highways.

Boron, lithium, and vanadium lie at the other end (factor 4) of the technological-metals vector fan. Zoller and others (1973), in a study of atmospheric vanadium, concluded that a major source in the northeastern cities of the United States is the combustion of vanadium-rich residual oil for heat and electric-power generation. Schroeder (1970, p. 802) noted, "The mean concentrations of vanadium in the air of Atlantic cities was twice as high during the first and fourth quarters of the year as in the second and third. These variations suggest that fuel oil used for heating contributes half the vanadium in air." Even in Alaska, Rahn and others (1981) attributed high vanadium-aluminum ratios in the atmosphere (with respect to such ratios in the Earth's crust) to air pollution.

Even if the vanadium in Spanish moss ash is derived from the combustion of fuel oil, it is unlikely that either boron or lithium is reflecting the same source. Cadmium, chromium, nickel, and vanadium are important in steel manufacturing; cadmium, chromium, copper, lithium, nickel, and zinc are commonly alloyed with other metals; copper and zinc are in brass; and boron and lithium are in glass products. Caruccio and others (1975) found elevated nickel in Spanish moss near a battery-fabrication plant in South Carolina.

Coal combustion is an additional obvious source of these (and other) metals to the atmosphere. Stolzenburg and others (1982, p. 82), in a study of suspended particulates in an unidentified industrial site, estimated that 34 percent of the particulates came from coal and fuel oil fly ash, automotive emissions, and iron and steel manufacture. In a nearby rural site, these same sources still accounted for 13 percent of the atmospheric load. A similar study in St. Louis (Gatz, 1977, p. 22) attributed 10-20 percent of the total urban aerosol load to these same sources. The technological metals in Spanish moss obviously reflect accumulation of artificial aerosols, in contrast to accumulation of natural particulates represented by factors 1 and 2.

Aluminum, cobalt, gallium, iron, magnesium, and sodium are positively associated in a minor way with the boron-rich end of the technological-metals fan. Although all six elements are involved in industrial processes of one kind or another, the element association as a whole is a geologic one. All are common constituents of sedimentary rock or soil, as are boron, lithium, and vanadium. Thus, the boron-rich end of the technological spectrum (factor 4) probably reflects, to some small extent, accumulation of natural particulates as well as accumulation of anthropogenic aerosols.

Scores for factors 3 and 4 (the lead-rich and boron-rich ends of the technological-metals spectrum) are shown in figures 8 and 9. The score for an individual ash is computed from:

$$F_{3j} = b_0 + b_1(\text{Log Ash})_j + b_2(\text{Log Al})_j + \dots + b_{26}(\text{Log Zr})_j, \quad (6)$$

where  $F_{3j}$  represents the score for factor 3 in the  $j$ th ash, the  $b$ 's represent the constant ( $b_0$ ) and the coefficients listed in the third column of table 5, and the variables are logs of element concentrations (expressed in the units listed in table 5) in the  $j$ th ash. Scores for factor 4 used the coefficients in column 4 of table 5.

Plants whose ash exhibits the highest and lowest scores on factor 3 (the lead-rich end) were both collected in Florida. The highest score was for a plant collected in central Florida, and the lowest was for a plant collected from the southern tip of Florida, on Paradise Key, Everglades National Park. The fact that the lowest score occurs in an area where man's impact on the local environment has been minimal further reflects the fact that this component is an anthropogenic one. Other areas represented by high scores for factor 3 are the Galveston-Houston area in Texas (where tin was also detected) and much of Louisiana, the Florida panhandle, and the northern fringe of the plant's range through Mississippi, Alabama, and Georgia. The sample with the highest score on factor 4 (the boron-rich end) is one collected near Montgomery, Ala., and the sample with the lowest was collected in northeastern Louisiana. Scores for ash from samples along the eastern seaboard tend to be high (where Schroeder, in 1970, noted elevated levels of atmospheric vanadium), but scores for ash from local areas in Alabama and Texas are also high.

The scores for factors 3 and 4 were examined by stepwise trend surface analysis, using the same 15 potential regressors used in the analysis of factors 1 and 2. No significant regional trends were found, and we conclude that these factors, unlike factors 1 and 2 (natural particulates), display only local variation. Thus, the source or sources of the elements important to these factors are widely distributed and presumably diverse in character, as are industrial and urban activities.

#### FACTOR 5--METABOLIC CONSTITUENTS

Factor 5 accounts for 11.0 percent of the total chemical variation in the data, and it accounts for more of the variation in the logs of ash content, magnesium, phosphorus, and potassium than any other factor (table 3). Because magnesium, phosphorus, and potassium constitute major metals active in plant metabolism, their concentration in living tissue should be controlled largely, if not exclusively, by physiological demand. Simple (inert) accumulation,

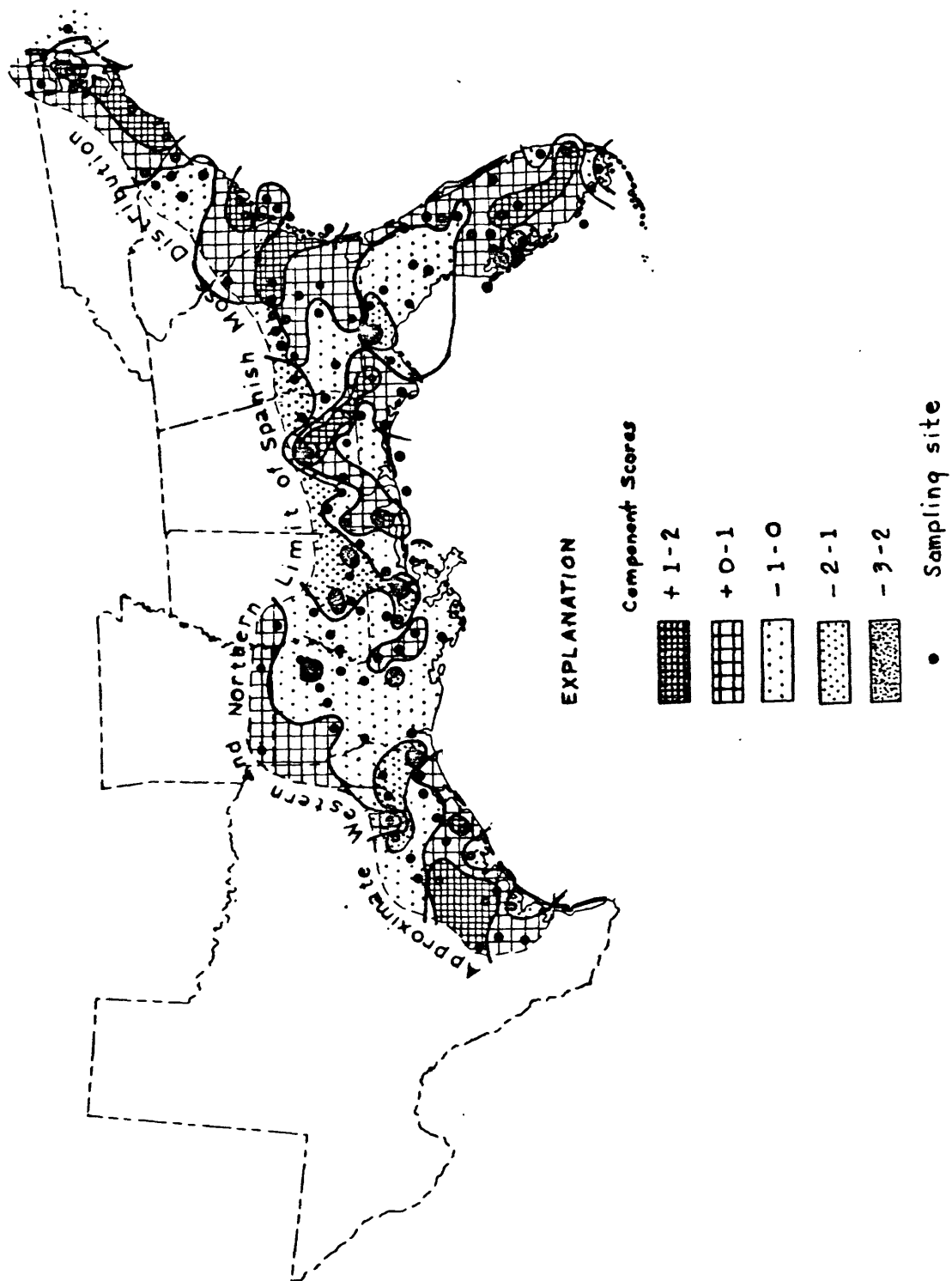
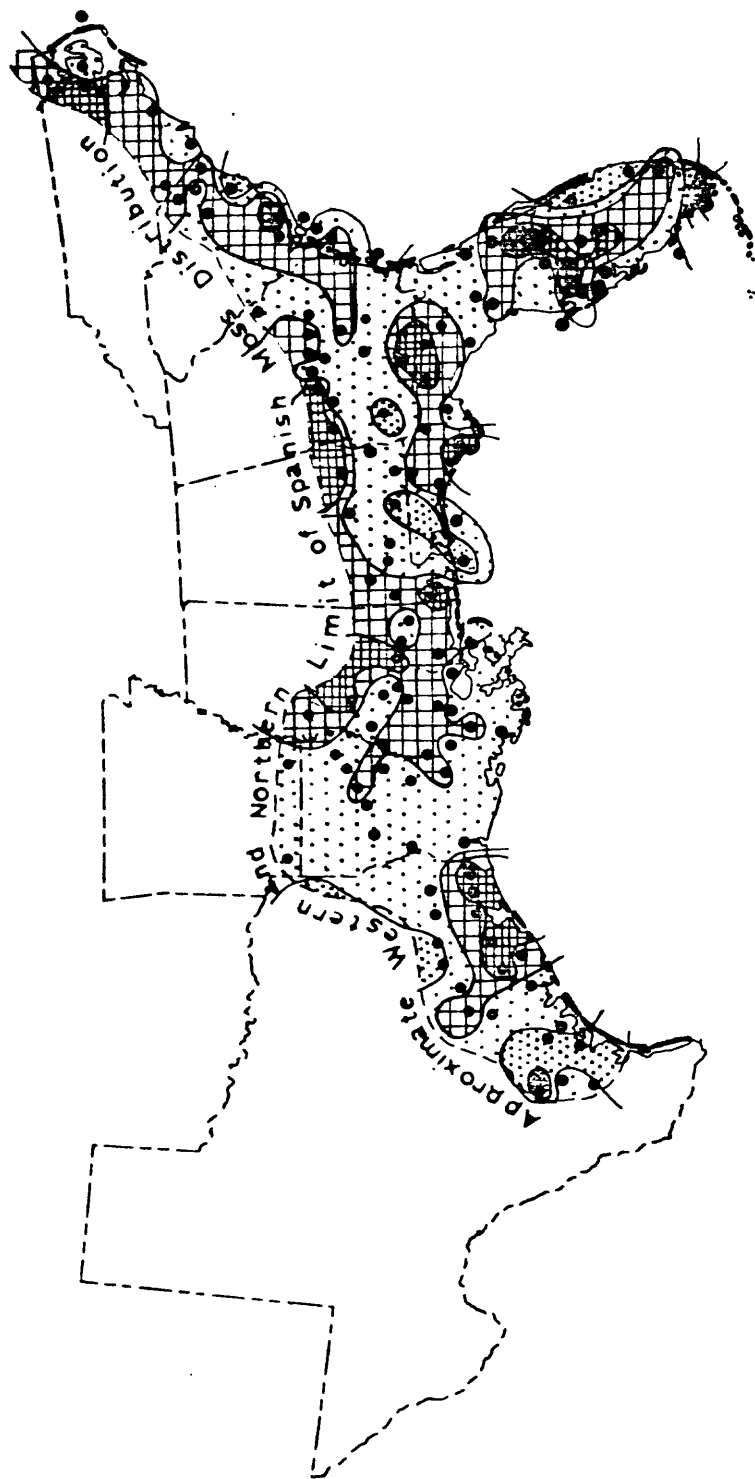


Figure 8.--Contour map of scores for factor 3.



# EXPLANATION

## Component Scores

+ 2 - 3

+ 1 - 2

+ 0 - 1

- 1 - 0

- 2 - 1

- 3 - 2

• Sampling site

Figure 9.--Contour map of scores for factor 4.

which has been invoked to explain the presence of other metals in Spanish moss ash, seems untenable here.

The strong inverse relation of magnesium, phosphorus, and potassium to ash content (table 1) most likely reflects the increase in total sample mass by accumulated aerosols. As integral components of living tissue, magnesium, phosphorus, and potassium might be expected to occur in fixed proportions both to themselves and to the living mass of the plant as a whole. Thus, a plant with a large ash content reflects a large dilution of metabolically controlled elements by airborne materials; and a plant with a low ash content, because of a smaller accumulation of airborne materials, exhibits a greater proportion of the major metabolic elements in its ash.

The specific atmospheric source(s) of the magnesium, phosphorus, and potassium that was found in the ash is unknown. Although ordinary soil dust probably contains a supply sufficient to account for the amounts found, the independence of the metabolic and natural-particulates components suggests specific biological interactions of plant tissue with these elements in ordinary atmospheric sources. Schlesinger and Marks (1977) found that trees with a high rate of foliar leaching (for example, cypress and oaks) provided an abundant supply of calcium, magnesium, phosphorus, and potassium for the growth of Spanish moss. They also found that this plant, if growing on trees having a low rate of foliar leaching (for example, pines), contained low concentrations of these elements. The metabolically essential elements, as well as others, may conceivably be supplied to Spanish moss by leachates and exudates from the host trees. However, at sites such as dead trees, telephone wires, and, possibly, pine trees, other sources must provide these elements.

Aerosol accumulation by Spanish moss is undoubtedly a lifelong process, and the plant mass probably supports a more or less continual aerosol "cover," but it need not follow that the specific material composing this cover never changes. The cover will presumably experience a slow continual partial turnover. Sloughing by wind or leaching by rain, for example, may serve to intermittently and partly clean the plant prior to additional accumulation. In this way, the plant may continually extract the magnesium, phosphorus, potassium, or other nutrients required for vital functions over its lifetime.

Scores for the metabolic-constituents factor are shown in figure 10. The score for an individual ash is computed from:

$$F_{5j} = b_0 + b_1(\text{Log Ash})_j + b_2(\text{Log Al})_j + \dots + b_{26}(\text{Log Zr})_j, \quad (7)$$

where  $F_{5j}$  represents the score for factor 5 in the  $j$ th ash, the  $b$ 's represent the constant ( $b_0$ ) and the coefficients listed in the fifth column of table 5, and the variables are logs of element concentrations (expressed in the units of table 5) in the  $j$ th ash.

Variation in this factor reflects to a large extent simple variation in ash content. An ash with high concentrations of magnesium, phosphorus, or potassium (that is, a plant with relatively low ash content) will exhibit a large positive score, and an ash with low concentrations of these elements will exhibit a large negative score. Plants with relatively low ash contents seem to be fairly well restricted to eastern areas of the plant's habitat

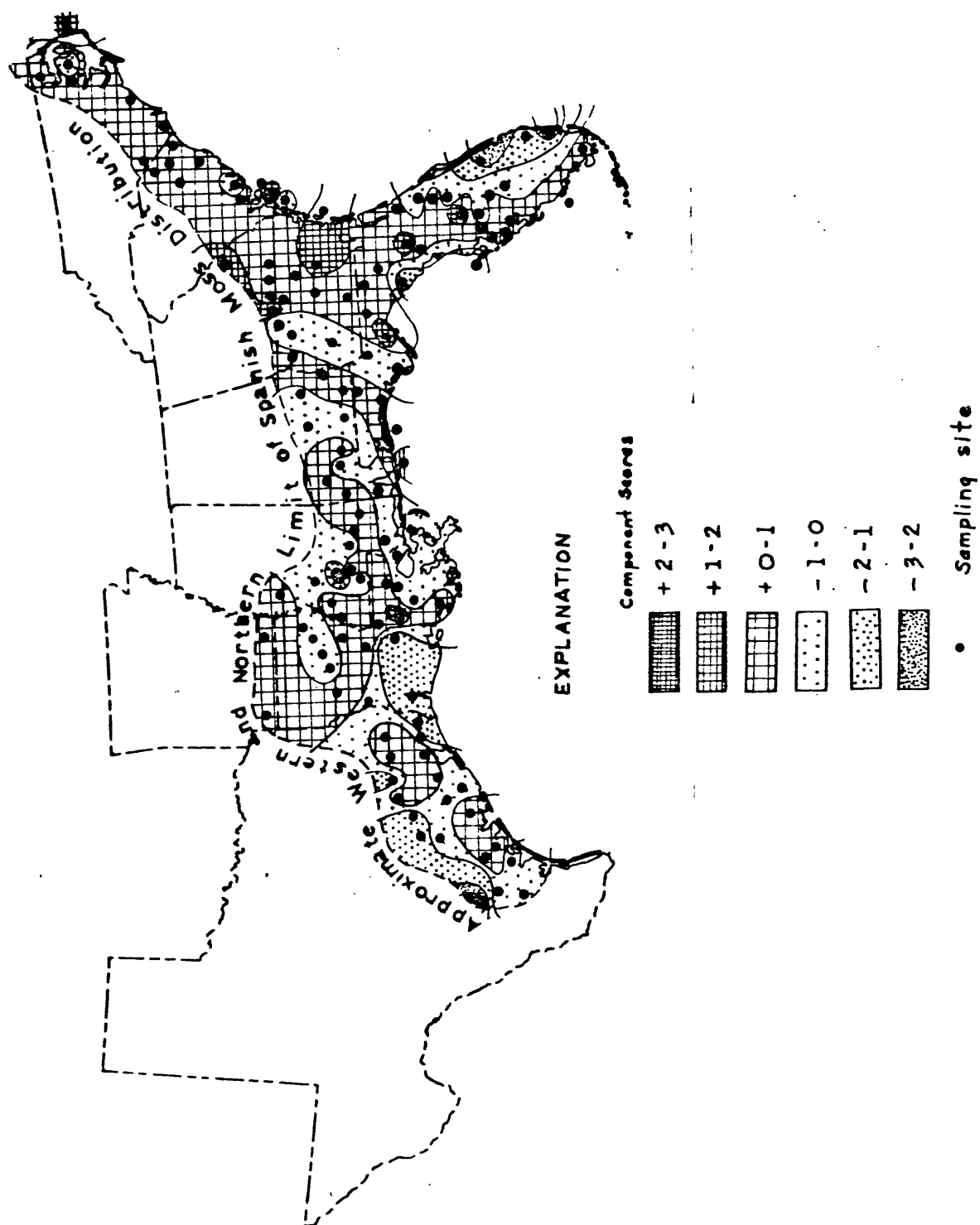


Figure 10a.--Contour map of scores for factor 5.

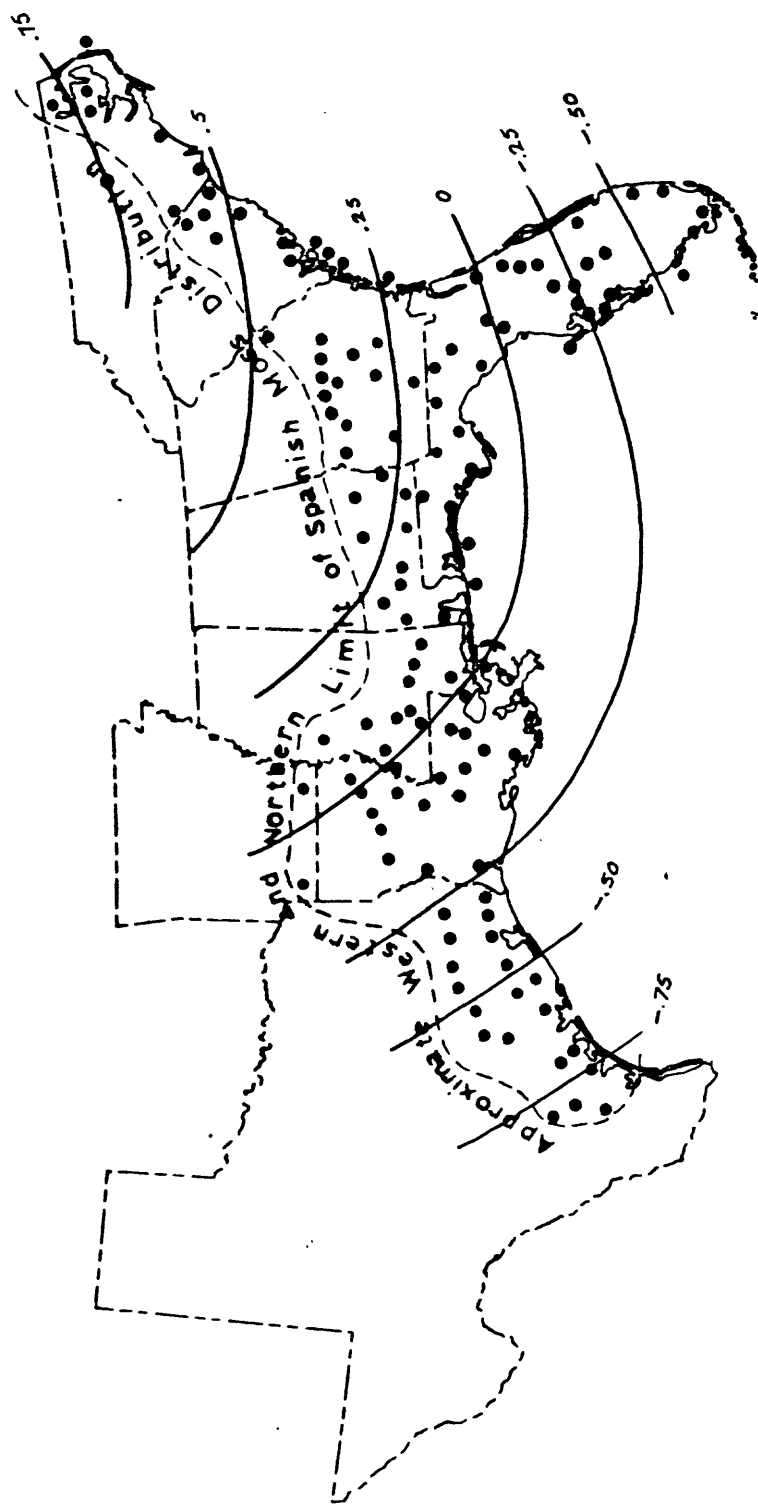


Figure 10b.--Regional trend in scores for factor 5.

(fig. 10). The highest score on factor 5 is for a plant collected on the Gulf Coast in Alabama, and the lowest score is for a sample from southern Texas.

The scores for this factor were examined by stepwise trend analysis using the same 15 potential regressors as before. The best predictor equation for the regional variation is:

$$T_5 = -424.8 - 0.00001353(\text{LONG})^3 - 109.3(\text{Log LAT})(\text{Log LONG}) + 218.6(\text{Log LAT} + \text{Log LONG}), \quad (8)$$

where  $T_5$  stands for an estimate of the score, LAT stands for north latitude, and LONG stands for west longitude.

The trend equation in (8) accounts for a small, but statistically significant, 13.9 percent of the total variation shown in figure 10. This trend indicates that the ratio of accumulated materials to the content of metabolic elements tends to increase to the southeast and southwest. The data at hand are insufficient to determine whether such an effect reflects a broad-scale, but weak, variation in atmospheric dust levels, or a similarly weak regional variation in metabolic activity of some kind.

A few other metals appear to be associated in a weak way with the metabolic constituents. Logarithms of manganese, zinc, and cadmium are positively associated with factor 5 (table 3), suggesting that these metals may be related to metabolic activity in the plant. Log calcium is negatively associated with factor 5, but as pointed out previously, the role of calcium is complex and poorly understood; the weak relation between log calcium and factor 5 remains unexplained.

#### SUMMARY AND CONCLUSIONS

This study was done to test the utility of Spanish moss as a chemical monitor of the local atmosphere. The increase of sodium in samples near the ocean and the enormous amounts of lead in samples along highways demonstrate the feasibility of using the plant as a natural air monitor. The factor analysis described in this report has resulted in a specific descriptive model of chemical variation in ash of Spanish moss. The model appears to be mathematically adequate, in that five independent factors describe nearly three-fourths of the total observed variation, and also empirically informative, in that the factors have aided in identifying some major compositional phases accumulated by living tissue. Some of these phases were expected (lead-rich vehicular exhaust, for example), and others were not (two kinds of airborne soil dust, for example).

The concentrations of magnesium, phosphorus, and potassium in Spanish moss relate inversely to the amount of ash and reflect largely physiological demand. The specific atmospheric sources of these three elements are unknown, but if, as we have theorized, they occur in clean tissue in constant amounts, then their observed variations in ash result from simple dilution by accumulated aerosols. Although accumulation of airborne substances, as pointed out earlier, likely involves something more than simple filtration of air, the chemical variation observed in ash is most easily interpreted in just such a filtration sense.

The accumulated material apparently consists of a number of compositional phases, and each appears to be reflecting one or more distinct sources, some of which are thought to be natural and others artificial or anthropogenic. The naturally occurring material forms the bulk of the airborne substances and seems to consist largely of particulates of soil, sea salt, and perhaps limestone. The strong inverse relation between soil-related elements and the salt and limestone-related elements in ash suggests a competition for depositional sites on plant tissue. Such a competition could reflect a similarity in average size or surface properties of the naturally occurring substances.

Variation in metals thought to be artificially introduced into the atmosphere reflects a variety of urban and industrial sources, at least one of which is lead-rich vehicular exhaust, and a second of which may be vanadium-rich heating fuel. Because variability in the technological metals is only weakly related to variability in the natural particulates, the accumulation of the anthropogenic and natural materials appears to be, for all practical purposes, independent of each other. This may reflect a lack of site competition in element accumulation between the two kinds of materials. If the artificial substances are aerosols of a different size or shape (or perhaps gaseous) than the naturally occurring particulates, the living tissue may be interacting with these two differing materials independently. For example, Friedlander (1973, fig. 2), in a study in Pasadena, Calif., showed that automotive exhaust aerosols were mostly less than 1 micrometer in diameter, whereas atmospheric soil and dust particulates were mostly greater than 1 micrometer in diameter.

An additional difference between the two kinds of materials is that the natural particulates appear to vary regionally in their source composition (figs. 5 and 6), whereas the artificial aerosols do not (figs. 8 and 9). Natural sources, like soil dust or sea salt, are relatively uniform in composition and occur continuously over large areas, but anthropogenic sources act as many highly diverse and widely distributed point sources, so that resulting atmospheric concentrations may fluctuate widely over relatively short distances. Failure to find regional trends in data points spaced at about a 50-km interval (figs. 8 and 9) suggests that anthropogenic point sources significantly contribute to the local atmospheric load for distances on the order of a few hundred kilometers or less.

Of the total chemical variation observed in ash of Spanish moss, about 37 percent appears to reflect variation in local atmospheric levels of naturally occurring materials (factors 1 and 2), about 23 percent appears to reflect variation in local atmospheric levels of artificially introduced materials (factors 3 and 4), about 11 percent is due to simple dilution of metabolically controlled elements by accumulated dust (factor 5), and the remaining 29 percent reflects variation from unknown sources, the most important of which is probably related to sampling and laboratory errors. Probable sources of the 25 elements in Spanish moss discussed in this study are listed in table 6.

Table 6.--Sources of elements in Spanish moss

Element	Most probable source, or sources
Aluminum--	Soil dust.
Barium----	Soil dust.
Boron-----	Various industrial sources.
Cadmium---	Automotive exhaust?
Calcium---	Cement manufacture?, road aggregate?
Chromium--	Automotive exhaust?, soil dust.
Cobalt----	Soil dust.
Copper----	Automotive exhaust?
Gallium---	Soil dust.
Iron-----	Soil dust.
Lead-----	Automotive exhaust.
Lithium---	Various industrial sources.
Magnesium-	Unknown.
Manganese-	Soil dust.
Nickel----	Various industrial sources.
Phosphorus	Unknown.
Potassium-	Unknown.
Sodium----	Sea water.
Strontium-	Cement manufacturing?, road aggregate?
Titanium--	Soil dust.
Vanadium--	Fossil fuels.
Ytterbium-	Soil dust.
Yttrium---	Soil dust.
Zinc-----	Automotive exhaust?
Zirconium-	Soil dust.

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