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Biogeochemical Study of the Pinelands in Everglades National Park, Florida

by

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Open-File Report 95-7

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EXECUTIVE SUMMARY

Product U.S. Geological Survey Open-File Report 95-7, 1995: Final Contract Report, "Biogeochemical Study of the Pinelands in Everglades National Park, Florida."

This report presents the study design, sampling methods, and chemical analysis procedures and results for a cooperative biogeochemical study between the National Park Service and the U.S. Geological Survey in the pinelands of Everglades National Park (EVER). This study was conducted to help determine baseline ranges and spatial variability in element concentrations in South Florida slash pine (*Pinus elliottii* Engelm. var. *densa*) and the associated rockland soils. The study focused on a grid sampling of pines and soils from Long Pine Key in EVER. Long Pine Key is the principal remnant of the subtropical pinelands within South Florida. Throughout Long Pine Key, the largely second growth pines are relatively uniform in trunk diameter, but vary somewhat in canopy height. Understory height within the key varies greatly depending upon fire history. Soils throughout the pineland exhibit little development and are present as a thin veneer or in solution pockets in the oolitic limestone.

Samples were collected from 76 grid locations (grid cells were 0.75 km on a side) within Long Pine Key and neighboring pinelands in March-May 1989 (grid design). The total number of samples of each sample media was 105 which included within grid, within site, and laboratory replicates. Summary statistics and baseline 95 percent expected element concentration ranges are reported for major, minor, and trace elements in slash pine needles and rockland soils. A subset of 20 pine and soil samples from Long Pine Key were analyzed for arsenic, mercury, and stable sulfur isotope ratios (barbell design) and summary statistics are reported similarly to the grid sampling design. The results of the smaller barbell sampling design appear to be reasonably representative of the larger population of pine needles and soils within EVER. Analysis of variance results from both designs indicated that the majority of the element concentration variance was attributable to localized differences at distances of 10's to 100's of meters. This was particularly true for elements in the soils. However, normalization to aluminum content helped reduce the localized variability. Based on the analysis of variance results from the barbell design, there was little indication of significant east-west element concentration trends within the relatively small area of Long Pine Key.

Principal component models indicated that macro and micro nutrients accounted for most of the variability in pine needle chemistry, whereas elements associated with alumino-silicates and carbonates explained a majority of the variability in soil chemistry.

Contour maps of element concentrations in pine needles and element to aluminum ratios in soils are presented. Whereas the contour maps generally indicate that the element concentrations in the pines and soils are fairly uniform throughout Long Pine Key, there are some manifestations of edge or ecotonal effects at the boundaries of the key. For example, slightly higher phosphorous concentrations in pine needles and soils along the northern edge of Long Pine Key may be from agricultural/urban runoff. The former farming activity along the southern edge of the key does not appear to have influenced the pine or soil chemistry in any detectable way. No significant correlations were found between fire history and pine or soil chemistry.

In general, the pinelands do not appear to be highly contaminated with any element that was determined in this study. There is some evidence that chromium, nickel, and lead may be enriched in the soils. Also, concentrations of arsenic in soils and mercury in pine needles and soils were high enough that anthropogenic contamination may have significantly increased their natural concentrations. However, additional research is required to help define more widespread concentration trends and to estimate natural levels of these elements in the pinelands ecosystem.

Stable sulfur isotope ratio measurements were made on a limited number of pine needle and soil samples. The isotopically lighter signature of the pine needles compared to the bulk soils suggest that there are other important hydrologic or atmospheric sources of sulfur for the pines.

Baseline biogeochemical studies such as described in this report provide information critical to understanding pollutant influences and the processes controlling element translocation within the Everglades ecosystems in order to detect and ameliorate deterioration of their natural state.

Form of Product: USGS Open-File Report 95-7, Typed Report, 8½ x 11 inches, 93 pages, including 20 tables and 18 figures.

ACKNOWLEDGEMENTS

This work was performed under Interagency Agreement 0475-3-8002, Amendment #4, between the USGS and the NPS. We wish to express our appreciation to Tom Armentano, John Stenberg, Mark Bruiniger, and Lana Enlow for their assistance in the field work and to the members of the USGS Branch of Geochemistry for their assistance in chemical analysis.

CONVERSION FACTORS

Measurement values in the International (metric) System (meter/kilogram units) used in this report may be converted to the U.S. Customary System (inches/pounds units) by using the following factors:

To convert from	To	Multiply by
millimeter (mm)	inch (in)	0.03937
meter (m)	foot (ft)	3.281
	yard (yd)	1.094
kilometer (km)	mile (mi)	0.6214
hectare (ha)	acre	2.471
kilometer^2 (km^2)	mile^2 (mi^2)	0.3861
gram (g)	ounce avoirdupois (oz avdp)	0.03527
kilogram (kg)	pound avoirdupois (lb avdp)	2.205
liter (l)	quart (qt)	1.057

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INTRODUCTION

This report describes a U.S. Geological Survey-National Park Service (USGS-NPS) cooperative biogeochemical study in the pinelands of Everglades National Park (EVER). The primary objectives of this study were to:

- Determine baseline ranges in element concentrations in South Florida slash pine (*Pinus elliottii* Engelm. var. *densa* Little & Dorman)[1] and the associated soils within the pinelands of EVER;
- Determine the spatial variability of element concentrations in slash pine and the associated soils;
- Examine element concentrations and spatial trends for anthropogenic influences.

In this report, baseline ranges refer to the element concentrations in our specific sample media that was collected in the fashion described and at the time of our sampling in April 1989.

Long Pine Key, the pineland area of study in this investigation, is "the principal remnant of a vegetation complex unique in the United States and the only area in which a number of tropical and endemic taxa are likely to survive" (Olmsted and others, 1983). Baseline biogeochemical studies such as described in this report provide information critical to understanding pollutant influences and the processes controlling element translocation within the Everglades ecosystems in order to detect and ameliorate deterioration of their natural state.

EVERGLADES PINELANDS

The subtropical Everglades, most noted as the largest sawgrass marsh in the world, is actually a complex, intertwined mixture of ecosystems which are well represented, but not wholly contained or protected within the boundaries of EVER. The principal upland ecosystem within EVER is the pinelands on Long Pine Key. The pinelands occupy slightly elevated ground along the Atlantic coastal ridge. The ridge is formed from oolitic limestone (Miami Formation) and within EVER has a maximum elevation of about 5 m above mean sea level (Hoffmeister, 1974). The ridge, which extends from north of Miami south into EVER, is transected by remnant tidal channels, known as transverse glades, which effectively create islands or keys of pine forests. The slash pine forest with interspersed hardwood hammocks and a dense understory of shrubs is rooted in the extremely rough, solution-carved limestone with only a thin, discontinuous veneer of poorly developed soil.

Although pinelands once occupied more than 5000 km^2 in southern Florida, their distribution has been severely reduced as a result of development (McPherson and others, 1976; Loope and others, 1979). Within EVER, pinelands extend from Parachute Key and Pine Island on the east side of Taylor Slough westward to the most extensive stands on Long Pine Key and southwestward to the very sparse stands near Mahogany Hammock (Figure 1). The main body of Long Pine Key extends approximately 12.5 km from east to west and extends from north to south about 2-2.5 km at the eastern edge and about 5 km at the western edge. The total extent of pines in the rocklands is about 8000 ha (Olmsted and others, 1983). The very diverse flora of the rocklands, Long Pine Key, and nearby Taylor Slough have been described by Loope and

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[1] Nomenclature follows that of Avery and Loope (1983).

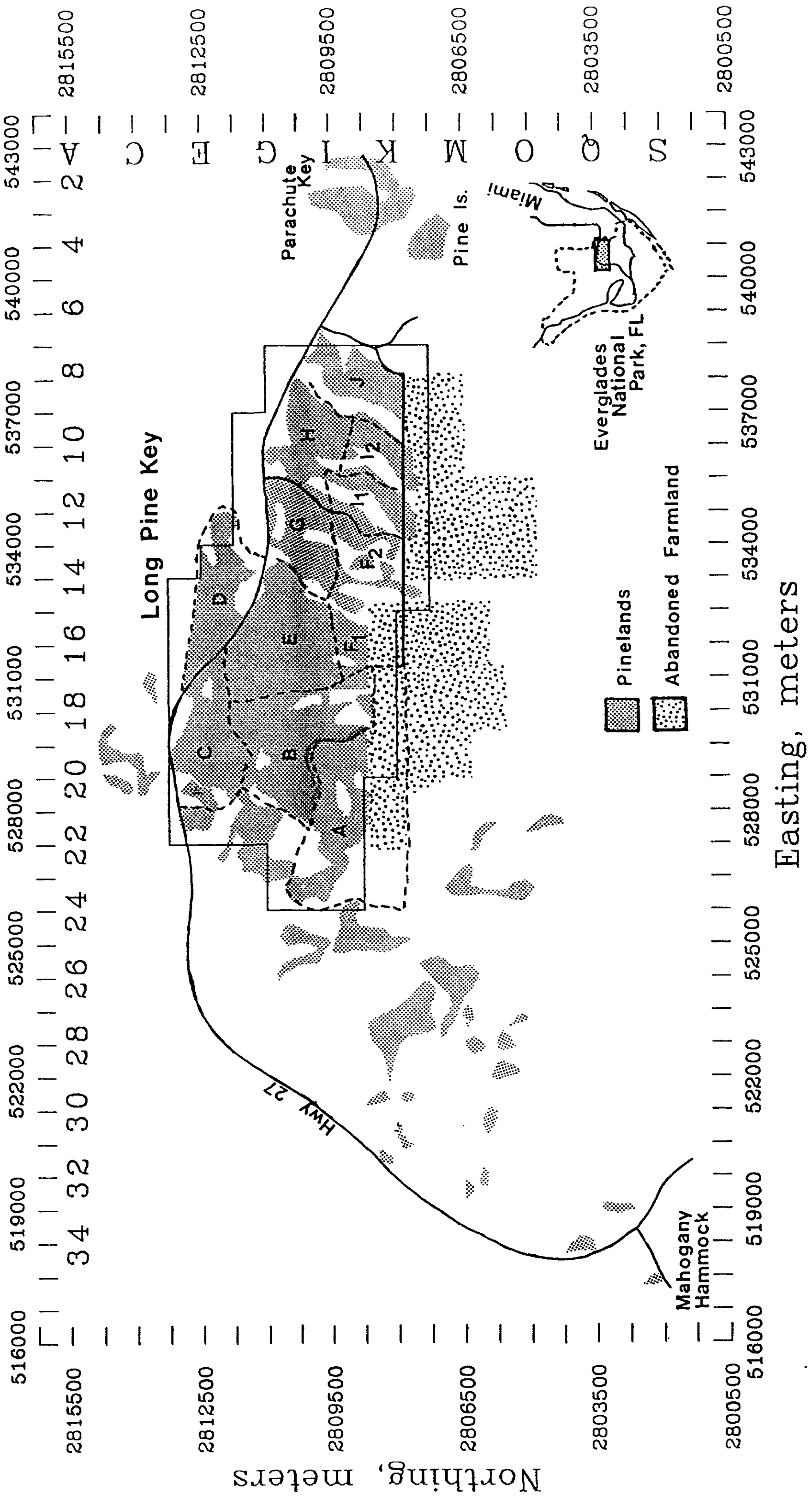

Figure 1. Pineland distribution within Everglades National Park. Long Pine Key fire management blocks are indicated by letters.

others (1979), Avery and Loope (1983), and Olmsted and others (1980, 1983). With over 200 species in the pinelands and associated prairies and hammocks, this ecosystem represents the greatest diversity of flora of any ecosystem in EVER (Olmsted and others, 1983).

The pine stands of Long Pine Key are relatively uniform second growth as a result of intensive logging from 1936-1947 with two sawmills located at the key (Olmsted and others, 1983). A combination of logging roads and modern highways form boundaries for the current fire management areas within Long Pine Key. Fire is an active natural agent in the pineland regeneration. As a result of changes in the patterns of natural fires, prescribed burning is currently ongoing in the pinelands to minimize hardwood succession. The understory of recently burned areas is typically 1-3 m tall, whereas the understory in unburned areas may exceed 6 m (Olmsted and others, 1983). Charcoal and partially burned plant material are readily obvious as components or coverings of the soil in various areas of the pinelands.

In addition to automobile traffic from park visitation, other human activities in the pinelands have included farming of the bordering prairies and transverse glades from as early as 1916 through the 1950's. In the mid fifties through 1969, rocklands of Long Pine Key were also farmed, with farming finally stopping in 1975 (Olmsted and others, 1983). The abandoned farmlands (locally referred to as the "Hole-in-the-Donut") have since been taken over by a dense stand of the exotic *Schinus terebinthifolius* (Brazilian pepper) and a few endemic hardwood species.

The pinelands have a subtropical climate with mild, dry winters and humid, wet summers. Average rainfall is 1.3-1.5 m yr^{-1} with most of it occurring between June and October (McPherson and others, 1976). The annual growth period for slash pine lasts about 10 mo (Langdon, 1963) and up to five growth flushes may occur during this period (Tomlinson and Craighead, 1972). In general, the pinelands experience fairly xeric conditions without annual inundation, whereas the average hydroperiod for the adjoining prairies and glades is 2-4 mo and 1 mo, respectively (Olmsted and others, 1983).

STUDY DESIGN

In order to meet the objectives of this study a stratified systematic design with artificial strata was chosen as the basis for collection of slash pine needles and associated rockland soils. A gridded sampling design was used for systematic sampling. By using the NPS geographical information system developed for EVER (using GRASS software), vegetational distribution maps were prepared for the slash pine ecosystem. After field examination of the pine lands, but without prior knowledge of the elemental distribution within these materials, a grid size of 0.75 km on a side was selected in order to obtain up to 100 potential sample sites within the slash pine ecosystem in EVER. The primary target area for sampling was the slash pine on Long Pine Key. This key encompasses 12 fire management blocks and is bounded roughly by a rectangle with Universal Transverse Mercator (UTM) coordinates of 2808000N, 2813000, 526000W, and 538500. Slash pine occurs in other areas of EVER such as Parachute Key, Pine Island, Paradise Key, and near Mahogany Hammock. These areas were to be sampled on the same grid pattern if they met the same site selection criteria used on Long Pine Key and there was sufficient time. In order to accomplish our mapping objective we intended to sample as many contiguous points as possible and avoid small isolated sample groupings.

The computer generated grid pattern was emplaced using UTM coordinates (Figure 2). The grid starting point was 2815500N and 543000W. This grid pattern had a random orientation with respect to the slash pine population. An unbalanced, hierarchical analysis of variance (ANOVA) design was incorporated as artificial strata into the grid sampling pattern (Severson and Tidball, 1979). At 9 randomly chosen sites replicate samples were taken at a distance of 0.1 km from a grid point on a random compass bearing and at an additional 10 randomly chosen sites replicate samples were collected from the nearby trees and soil pits. Laboratory splits were also made from 10 randomly chosen samples.

Superimposed on the grid sampling design was a barbell sampling design (Figure 3) (Severson, 1979). The samples for the grid and barbell sampling designs were the same--no additional samples were collected. The intention of the barbell design was to have a subset of samples that could be used for specific analyses that would not be done for all samples. In addition, these same sample sites were used in the Holcomb Research Institute (HRI) slash pine study (Armentano, 1991).

In the creation of the barbell sampling design there were several constraints in addition to coincidence of the grid and barbell sample locations. Sample points had to be within or near to the 12 major fire management blocks. The maximum length of the long axis was 8 km, in order to allow for complete freedom of rotation of the end axes within stands of slash pine within Long Pine Key. The long axis of the barbell design was fixed generally along the east-west trend of the key. The mid-point of the axis was also fixed within narrow constraints. The orientation of 0.75 km axes was fixed at 0°, or 90° from north in order for sample points to coincide with grid sample points.

The barbell design consisted of a long axis of 8 km fixed generally in the east-west trending orientation of Long Pine Key. At each end of the major axis was a randomly oriented axis 2 km in length at whose end was axes of 0.75 km which were fixed in orientation so that their endpoints coincided with the nearest grid intersection of the grid sampling design. At one half of the these sample locations a replicate sample was taken 0.1 km away and at one half of them a replicate sample was taken from the same site. In addition, four of the samples were split in the laboratory for replicate analyses. See Figure 4 for a schematic of the barbell design and hierarchical analysis of variance.

Final site and sample selection criteria were developed after field observations of the size class, undergrowth, and distribution patterns of slash pine in EVER. Initial general considerations were: uniformity of slash pine growth characteristics, such as density of trees, height of pruneable branches, number of whorls present, and diameter at breast height; nature of undergrowth; proximity to roads or other facilities; proximity of ecotonal areas; and accessibility. Final site selection criteria were: (1) site must be at least 50 m from an ecotonal area and 100 m from a road or man-disturbed area, (2) three healthy, mature trees with accessible branches that were within a radius of 10 m, (3) tree diameter at breast height must be at least 10 cm.

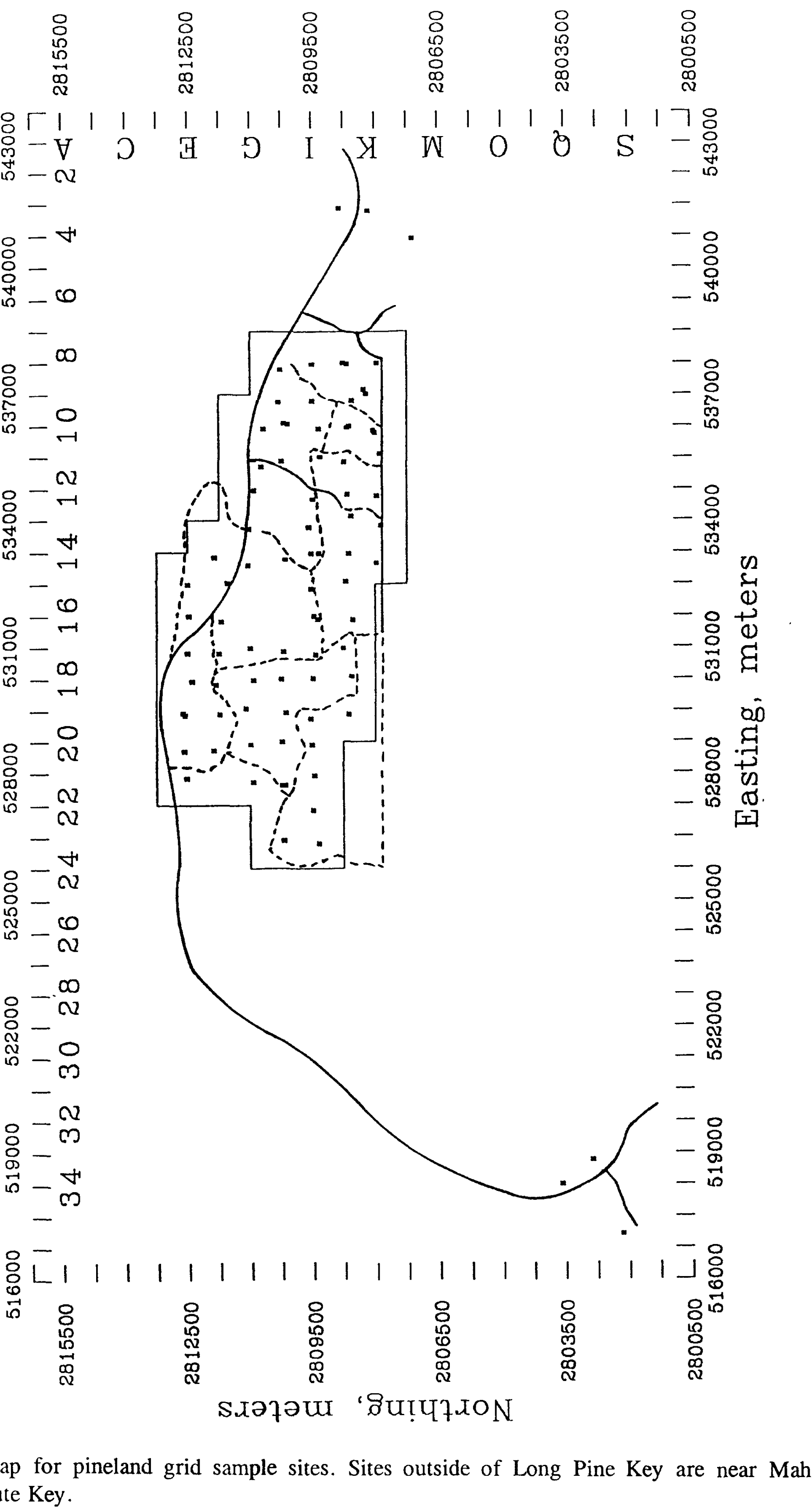

Figure 2. Location map for pineland grid sample sites. Sites outside of Long Pine Key are near Mahogany Hammock and Parachute Key.

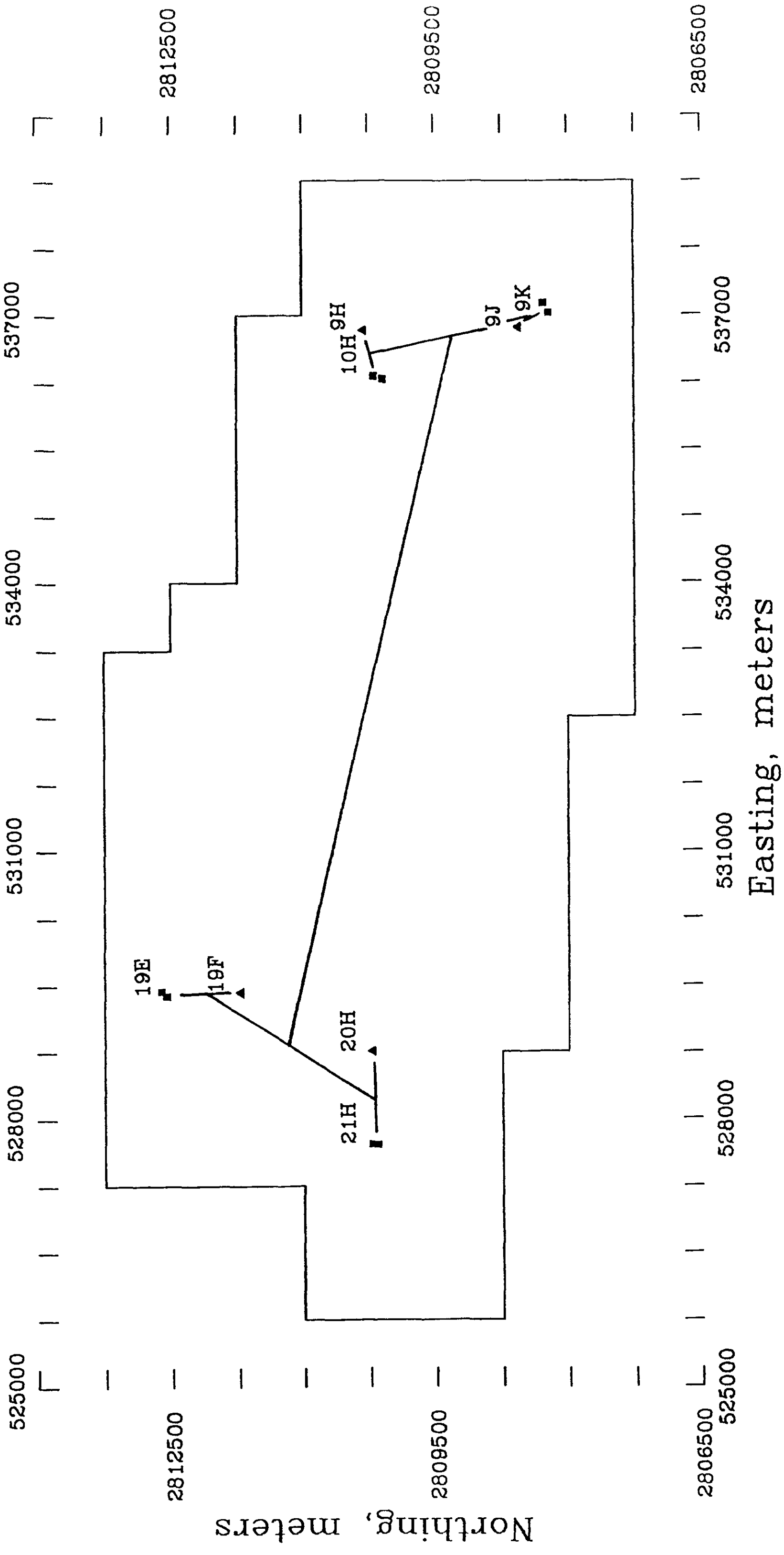

Figure 3. Location map for barbell sample sites within Long Pine Key.

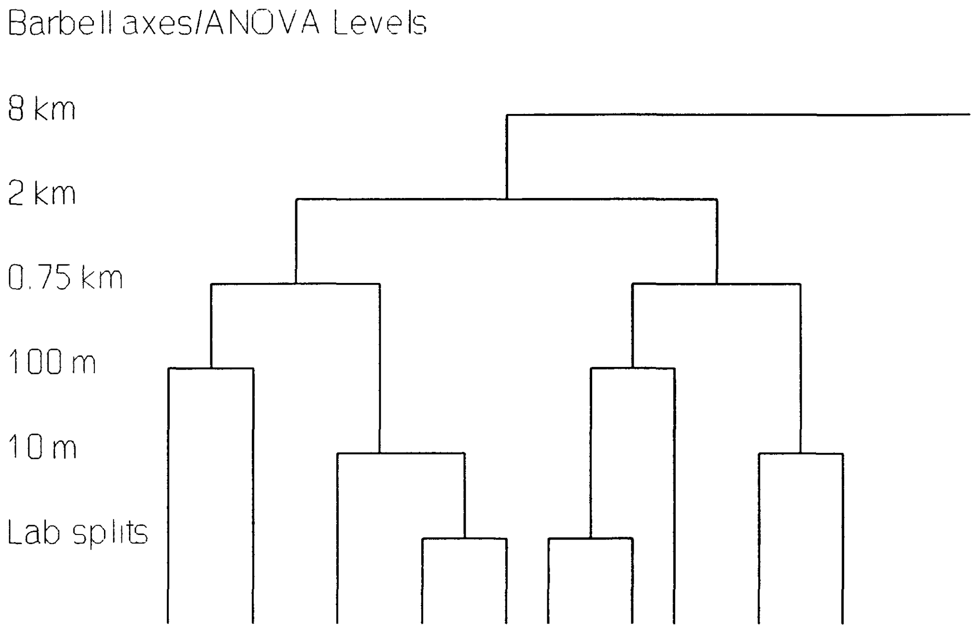

Figure 4. Schematic diagram of unbalanced, hierarchical ANOVA sampling design.

STUDY METHODS

Sample Collection

At each sample site two materials were collected: slash pine needles and rockland soil. The slash pine needles were collected and composited from three nearby trees. Branches (lower to middle portion of the canopy) were obtained using an aluminum telescopic pole pruner which had a maximum length of 15 m. Needles were removed by hand (wearing leather gloves) from the three separate branches. Needles from the middle one third of the second whorl were composited from several whorls on each of the three separate branches per tree to give a total weight of about 100 g or more. The samples were stored in Hubco cloth bags and air-dried in the field.

Soil samples were collected and composited from sites located within about 5 m of the trees sampled. Surface litter and ash, where present, were removed; and the top 10 cm of soil from an area of about 100 cm^2 was collected with a stainless steel trowel and sieved through a stainless steel screen with 1 cm^2 openings, in the field. Approximately equal volumes of soil (total about 1 kg) were collected from each of the three pits per site and homogenized in a plastic pan at the sample site. The soil samples were stored in paper bags and air-dried at the field headquarters. The soil samples were difficult to obtain because of the limited soil development in the limestone terrain and soil was generally only found in cavities in the limestone. Only shallow surface pockets were sampled. Large, deep solution cavities were avoided because their soil and moisture regimes were not necessarily representative of the more common shallow cavities.

Site replicate samples were collected and composited from a nearby set of three trees (within a radius of 10 m of the first set of trees sampled) and soil samples were collected and composited from new pits located near the second set of trees sampled.

All sample locations were within 0.1 km of the grid intersections, to the best of our field locating ability. Approximate locations were recorded on a topographic map. Where possible, exact sample locations were recorded by using LORAN-C. The LORAN unit was calibrated each morning before sampling began and rechecked at the end of each day by using the main highway (State Highway 27) bridge crossing Taylor Slough as a daily calibration point (N 25° 24.14' W 80° 36.47'). Field notes were recorded for each sample location which included field identification numbers, descriptions of the slash pines and soils sampled, general description of the site, hand drawn site map, LORAN-C location, and miscellaneous additional information such as field workers, time, and date. Slash pine descriptions included the trunk diameter at breast height (estimated to the nearest 0.5 cm) and the height of the lower canopy branches that could be sampled with the pole pruner. The latter height measurement was estimated to the nearest 1.5 m based on the number of 1.5 m extensions used with the pruner. All sampled trees were permanently marked with pre-numbered aluminum tags (100-400), a metal band (galvanized plumbers strap), and galvanized or aluminum nails.

From March 30 through April 1, 1989, the USGS and HRI field team collected the barbell design sample subset (8 sites, 16 samples total of each material). Samples of pine needles and soils were split in the field with a portion going to HRI and to the USGS. From April 3 through April 9, the USGS field team continued sampling the grid design sample locations. Thirty-eight sites were sampled in this period. From April 10 through April 14, one of the USGS field team with the assistance of EVER personnel collected samples from an additional 13 sites. From May 5 through May 16, EVER personnel collected samples at 17 sites. During this last sampling interval there was a marked increase in rainfall. With the beginning of the wet season there was a flush of new growth in the pines and because of the potential for unknown chemical changes in the pine needles further sampling was discontinued.

In all, 76 sites were sampled with 9 of the sites replicated at 100 m and 10 of the sites replicated at 10 m. Ten additional laboratory splits were made resulting in a total of 105 samples of each material. Seventy of the sites were located on Long Pine Key. Three sites were in the vicinity of Mahogany Hammock and three sites were near the headquarters and maintenance areas on Parachute Key and Pine Island, respectively (Figure 2).

Sample Preparation[2]

Prior to preparation and analysis, samples were arranged in randomized suites with a maximum of 40 samples segregated by sample type. Analytical results and coding information are permanently archived in the USGS National Geochemical Database.

Slash pine needles samples were oven dried at 40°C for 48 hrs, washed with a series of deionized water rinses, re-dried, and ground in a Wiley mill to pass a 2 mm screen. Soil samples were air-dried and disaggregated in a ceramic mortar to pass a 10 mesh (2 mm) sieve. The material passing through the sieve was further ground to pass a 100 mesh (0.15 mm) sieve by using an agate shatter box.

Sample duplicates were submitted to the laboratory within the randomized suites of samples. The duplicates were obtained by splitting the ground plant or soil material in a Jones riffle splitter and were given unique field and laboratory identification numbers.

Sample Analysis

All plant samples were ashed in Vicor crucibles by using a stepwise temperature ramp to a maximum temperature of 450°C over an 18 hr period (Peacock, 1992). One hundred milligrams of the plant ash were digested with mixed acids. After complete digestion of the plant ash, 40 major, minor, and trace elements were determined by inductively coupled plasma atomic emission spectroscopy (ICP) (Lichte and others, 1987; Briggs, 1990). Total sulfur was determined directly on 250 mg of the ground plant material by combustion at 1370°C in an oxygen atmosphere with infrared detection of evolved SO_2 (Jackson and others, 1985). Arsenic and mercury were determined on the ground plant material by using hydride-generation atomic absorption spectroscopy (HGAAS) and cold-vapor atomic absorption spectroscopy (CVAAS), respectively (Crock and Lichte, 1982; Kennedy and Crock, 1987; O'Leary and others, 1990; Welsh and others, 1990).

All soil samples were ashed and analyzed by ICP for 40 elements in the same fashion as the plants except that a larger sample size (200 mg) was digested. Total sulfur was determined in the soils by the same procedure used for the plants. Total carbon was determined by

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[2] Any use of trade names is for descriptive purposes only and does not imply endorsement by the USGS.

combustion of 0.25 to 1 g of ground material at 1370°C in an oxygen atmosphere with infrared detection of evolved CO_2 (Jackson and others, 1987). Carbonate carbon was determined by coulometric titration of acid-evolved CO_2 (Engleman and others, 1985). Organic carbon was determined by the difference of total and carbonate carbon (Jackson and Roof, 1992). Soil pH's were determined on a soil paste (1:1 soil to water) by using a conventional combination pH glass electrode (Crock and Severson, 1980).

All raw chemical analysis results as reported by the laboratory on either a dry-weight or ash-weight basis are presented in Appendix I of this report. The lower detection limits for trace elements are typically on the order of a few μg/g (see Appendix Table A3). The detection limit for elements in plant materials determined by ICP is twice as great as those for soils owing to the use of the smaller sample size. The precision for most determinations is on the order of 5-10 percent relative standard deviation or better. Analyses are reported to a maximum of three significant figures.

Stable sulfur isotope ratios in pine needles and soils were determined by Coastal Science Laboratory (Austin, TX). Samples were combusted along with a combustion aid (e.g., vacuum pump oil) under a high pressure oxygen atmosphere in a Parr bomb. The bomb with the combustion products was washed with water and barium sulfate was precipitated from the wash solutions. The stable S isotope ratio of the barium sulfate precipitate was determined by thermal ionization mass spectrometry. This procedure primarily determines the isotopic signature of organic S and water-soluble S species in the sample. For plants and non-sulfidic soils the procedure determines the isotopic signature of the total sulfur content.

The field study quality control results are summarized in Appendix I. Based on the analysis of standard reference materials, results for Na and La in pine needles and total C, organic C, Ni, and Zn in soil samples should be viewed with caution. Potential biases in the accuracy of the results for these elements do not appear to significantly affect any interpretations within this report. However, future comparisons with these data must take these apparent biases into account.

DATA ANALYSIS

Data analysis has been performed using a variety of public domain and commercial software on an IBM-compatible personal computer. The unbalanced, hierarchical analysis of variance was done using programs in the USGS Statpac library (Grundy and Miesch, 1988).

All plant and soil data have been analyzed on a dry-weight basis (i.e. air-dried). Concentrations of those elements that were determined on an ash-weight basis have been converted to a dry-weight basis prior to data analysis. All data, unless otherwise specified, have been logarithmically (base 10) transformed prior to statistical analysis. In the ANOVA and multivariate analyses qualified data, which are those results below the analytical detection limit, have been replaced with 0.7 times the detection limit prior to statistical analysis (Miesch, 1976). Elements with more than 33 percent qualified values have been excluded from any statistical analyses. In general, limited replacement of qualified values has little influence on robust statistical techniques such as ANOVA. However, appropriate caution should be used in interpreting correlation-based techniques where we have used replacement of qualified values.

The geometric means for elemental concentrations were determined as weighted averages of the transformed data owing to the unbalanced nature of the sample design. The hierarchical ANOVA levels were used for weighting such that the laboratory replicate pairs, the lowest level, were averaged first and then the 10 m site replication level pairs were averaged. All remaining higher levels in the ANOVA designs were then treated equally. The resulting data set is referred to as the "100 m" data set throughout the remainder of this report. For example, in the case of the grid sampling design, the 10 laboratory splits were averaged and then the 10 site replication pairs were averaged. This reduced the number of data points from 105 to 85 (i.e., the 100 m data set), which were then averaged to produce the overall mean. The geometric deviations were also determined from this smaller data set. The geometric deviation calculated from the hierarchically averaged data set was generally larger than the square root of the total variance calculated from the ANOVA. The former geometric deviation was used in the determination of the estimated baseline ranges. Geometric means and deviations were calculated for several elements which required replacement of some of the qualified values. This introduces a bias to these results, but reasonable comparisons can still be made.

Chemical baselines have been defined in various ways. Usually a baseline refers to a specific set of conditions and point in time (i.e. when the samples were collected) and not to historical or pre-industrial conditions. One definition of a baseline is the expected 95 percent range, which is the mean plus or minus two standard deviations. For lognormally-distributed data (Tidball and Ebens, 1976) the expected 95% range is:

(geometric mean/geometric deviation^2) to (geometric mean X geometric deviation^2)

We have defined baseline ranges for selected elements in slash pine needles and soils by using the formula presented above.

Multivariate principal component models were developed using correlation matrices generated from the hierarchically averaged data sets and varimax rotation. The number of components in the model was restricted to components with eigenvalues equal to or greater than one.

Calculation of the variance-mean-ratio and the estimated sampling density required for 80 and 95 percent confidence level geochemical-element-concentration maps followed the methods of Miesch (1976).

Spatial trends in element concentrations in pine needles and in soils were calculated using an inverse distance-squared algorithm which incorporated up to twelve nearest neighbors within a 1250 m radius (i.e., data from adjacent grids). The non-log-transformed, 100 m data set for the 70 grid sites and the nine 100 m within-cell replicates was used to generate the contours. The contours plotted were based on approximately the 10th, 30th, 50th, 70th, and 90th percentiles of the 100 m data set. Contours were smoothed by using a spline interpolation.

RESULTS AND DISCUSSION

Characteristics of the slash pine and rockland soils

The pinelands sampled varied from open stands with *Mulhenbergia* prairie species as understory to stands with dense, tall hardwood understory. Shrub species[3] commonly observed included *Ardisia escallonioides*, *Bumelia salicifolia*, *Chyrsobalanus icaco*, *Conocarpus erectus*, *Dodonaea viscosa*, *Guettarda*, *Ilex cassine*, *Lysiloma latisiliquum*, *Metopium toxiferum*, *Myrica cerifera*, *Myrsine floridana*, *Personia borbonia*, *Sabal palmetto*, *Serenoa repens*, and *Tetrazygia bicolor*. The understory in the more open stands, dominated by grasses, sedges, and palms, was typically from less than 0.5 to about 1 m high, whereas the understory dominated by shrubby hardwoods varied from about 1 m to more than 4 m high, depending on how recently the area had burned. Fire management area E (Figure 2) was an area that was largely unpenetratable because of the very dense understory that had not burned since September, 1983.

A total of 289 pine trees were sampled throughout the pinelands. At some locations the largest pines were not sampled because the lowest branches were more than 17 m high and could not be reached with the pruner. Within the pine population sampled, the diameter at breast height (dbh) ranged from 10 to 32.5 cm and had an arithmetic average and standard deviation of 18.7 ± 4.3 cm. Olmsted and others (1983) estimated the mean pine dbh to be 14-15 cm for a transect through Long Pine Key at some time around 1981. Assuming an 8 year growth period, there is an apparent annual diameter growth of about 0.5 cm. This growth rate is about half of what Langdon (1963) measured (1.1 cm yr^{-1}) for the same pine species near Fort Meyers, Florida, in the late 1950's.

The average height of pruneable branches in the lower to middle canopy of the slash pine was 10.3 ± 0.2 m with a range of 4.5-17 m. By assuming an upper canopy height of 2-5 m, the average pine height was 12-15 m which is the same as measured by Olmsted and others (1983). No estimates of mean density or mean basal area were made in this study.

An unbalanced hierarchical ANOVA of the dbh and lower canopy height was performed using ANOVA levels of "among grids", "within grids (100 m)", "site replication (a replicate set of three trees within 10 m)", and "among three trees at a site". The percentages of the total variance for each level were:

	Among grids	Within grids	10 m rep	Among trees
DBH	16%	26%	0%	58%
Ht	33%	3%	20%	43%

With the largest proportion of the variance in dbh and canopy height being attributable to differences among trees at a site, these results suggest that the pine stands sampled are relatively uniform and that there are probably greater differences among grid sites in terms of canopy height than in dbh.

The rockland soil typically exhibited relatively little development and was found as discontinuous pockets in exposed limestone solution cavities. The soil varied from a light-brown

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[3] Species were tentatively identified in the field by J. Stenberg, NPS.

to reddish-brown sandy or clayey loam to a dark-brown organic rich mat. Sand-sized limestone fragments were commonly present as was plant ash and charcoal. Numerous plant roots were common in the shallow soil pockets. The limestone substrate varied greatly in surface topography from one area to another, exhibiting areas that were relatively flat with small, shallow solution cavities and other areas that were much more rugged with larger and deeper cavities (cavities that occasionally exceeded 1 m in diameter and depth). The limestone substrate exhibited more widespread low elevations in the transverse glades, where the soil was typically marl.

Analysis of Variance and Summary Statistics

The percentage of the total variance attributable to each level in the ANOVA is presented in Tables 1 and 3 for those elements determined in the subset of 20 samples used in the barbell sampling design and in Tables 2 and 4 for those elements determined in all samples in the grid sampling design. Each table also includes the geometric means and deviations, the observed range, and the 95 percent expected baseline range.

In the slash pine needles sampled in the barbell design, only the elements Ti, Co, Hg, and La exhibited a significant portion of their total variance as laboratory error. In each case the concentrations measured were near the limit of determination for the analytical methods used and the observed concentration ranges were small. Many of the elements had a large proportion of their variance attributable to differences over very short distant increments of 10-100 m. Only K exhibited a high proportion of the variance resulting from differences from east to west within Long Pine Key. Aluminum and Ca also had a significant amount of their total variance at the 8 km ANOVA level.

In the grid sampling design, Co and La in pine needles also had a large proportion of the total variance attributable to laboratory error. For many of the other elements, a high proportion of the variance was attributable to differences between samples at the shortest distance increment, 10 m. In the case of S, Ca, K, Ba, Mn, Sr, and Zn, more than 50 percent of the variance occurred among grid cells.

For most elements in pine needles the geometric mean concentrations estimated in the barbell and grid sampling designs were within 5-10 percent. Manganese, Ni, Pb, and Zn had larger relative differences between the sampling designs with all but Ni exhibiting lower mean concentrations in the larger population. The larger population also tended to have about equal or larger deviation than the subset population.

For the soils, no element in either sampling design had a high proportion of its variance owing to laboratory error. In both designs most of the error for the majority of the elements was attributable to differences between sites only 100 m apart. In the barbell design S, Cu, and Zn had 20-30 percent of the variance resulting from east-west differences. In the grid design these same elements plus Na, P, Mn, and Pb had about the same or greater variance attributable to differences among grid cells.

Table 1. ANOVA results and summary statistics for slash pine needles (barbell sampling).

	Percentage variance[1] at each ANOVA level								Observed Range		Estimated Baseline Range	
Element	8 km	2 km	0.75 km	100 m	10 m	Lab error	Geometric mean[2]	Geometric deviation	Minimum	Maximum	Minimum	Maximum
Ash%	< 1	< 1	24	< 1	76 *	< 1	2.31	1.08	1.78	2.64	1.98	2.69
S%	< 1	27	9	< 1	54 *	10	0.10	1.10	0.09	0.12	0.08	0.12
Al µg/g	34	30	6	< 1	30	< 1	39	1.18	30	50	28	55
Ca µg/g	31	5	16	< 1	47 *	1	4400	1.17	3000	5500	3300	6000
Fe µg/g	15	27	< 1	16	34	8	39	1.11	30	48	31	48
K µg/g	67 *	12	4	< 1	16 *	< 1	1800	1.29	1300	3000	1100	3100
Mg µg/g	< 1	< 1	< 1	61	37 *	1	1600	1.14	1300	1900	1200	2000
Na µg/g	< 1	16	12	< 1	72 *	< 1	1600	1.19	970	2100	1100	2300
P µg/g	3	< 1	79 *	13	3	2	600	1.10	480	720	490	730
Ti µg/g[3]	8	1	< 1	< 1	< 1	91	2	1.17	<2	4	2	3
Ba µg/g	< 1	18	24	< 1	52 *	6	0.45	1.13	0.34	0.58	0.35	0.57
Co µg/g	< 1	7	18	< 1	34	40	0.08	1.16	0.05	0.1	0.06	0.1
Cr µg/g	14	5	< 1	54	26 *	1	0.2	1.35	0.1	0.4	0.1	0.3
Cu µg/g	7	49	< 1	31 *	< 1	12	2.4	1.09	2.0	2.7	2.0	2.8
Hg µg/g	15	< 1	49 *	< 1	4	32	0.04	1.28	0.02	0.06	0.02	0.06
La µg/g	< 1	< 1	< 1	30	25	45	0.1	1.32	0.09	0.2	0.07	0.2
Mn µg/g	< 1	81 *	< 1	5	14 *	< 1	30	2.03	10	98	7.3	120
Ni µg/g[3]	< 1	45 *	< 1	32	< 1	23	0.1	1.48	<0.09	0.2	0.06	0.3
Pb µg/g	12	< 1	< 1	62	< 1	27	0.44	1.18	0.31	0.66	0.32	0.61
Sr µg/g	13	49	10	< 1	29 *	< 1	49	1.39	25	75	25	94
V µg/g[3]	11	3	7	< 1	79 *	< 1	0.1	1.33	<0.09	0.2	0.06	0.2
Zn µg/g	< 1	< 1	7	82 *	11 *	< 1	12	1.29	7	17	7	19

[1] * significant at 0.05 probability level.

[2] n = 12 after hierarchically averaging lab replicates and 10 m site replicates, total number of samples equals 20.

[3] Ratio of samples with detectable concentrations to the total number of samples was 20/20 for all elements except: Ti = 16/20, Ni = 17/20, and V = 17/20.

Table 2. ANOVA results and summary statistics for slash pine needles (grid sampling).

	Percentage variance[1] at each ANOVA level						Observed Range		Estimated Baseline Range	
Element	Grid cell	100 m	10 m	Lab error	Geometric mean[2]	Geometric deviation	Minimum	Maximum	Minimum	Maximum
Ash%	49 *	< 1	50 *	1	2.25	1.10	1.78	3.20	1.85	2.73
S%	59 *	< 1	32 *	9	0.09	1.12	0.07	0.12	0.07	0.11
Al μg/g	29	41	27 *	4	40	1.19	30	71	28	57
Ca μg/g	67 *	< 1	32 *	1	4400	1.20	2600	7100	3100	6400
Fe μg/g	24	38	33 *	5	43	1.18	28	64	31	59
K μg/g	66 *	14	19 *	1	1700	1.28	1000	3400	1000	2700
Mg μg/g	23	16	58 *	3	1500	1.15	1100	2300	1100	1900
Na μg/g	< 1	22	77 *	1	1700	1.27	820	2900	1000	2700
P μg/g	47	41 *	3	9	540	1.12	420	720	430	670
Ba μg/g	68 *	< 1	27 *	5	0.46	1.20	0.33	0.75	0.32	0.67
Co μg/g	36 *	< 1	< 1	64	0.08	1.23	0.04	0.1	0.05	0.1
Cr μg/g	< 1	39	49 *	12	0.2	1.26	0.1	0.4	0.1	0.3
Cu μg/g	46	28	17 *	9	2.3	1.11	1.8	2.9	1.9	2.9
La μg/g	7	5	62 *	27	0.1	1.36	0.09	0.2	0.06	0.2
Mn μg/g	56	20	23 *	< 1	24	1.63	5	98	9.2	65
Ni μg/g[3]	18	< 1	68 *	14	0.2	1.49	<0.09	1	0.08	0.4
Pb μg/g[3]	36	< 1	46 *	18	0.29	1.31	<0.16	0.66	0.17	0.5
Sr μg/g	56 *	< 1	43 *	1	44	1.32	17	76	25	78
V μg/g[3]	< 1	57	35 *	8	0.1	1.43	<0.08	0.3	0.06	0.2
Zn μg/g	55	30	14 *	2	8.5	1.44	3.8	19	4	17

[1] * significant at 0.05 probability level.

[2] n = 85 after hierarchically averaging lab replicates and 10 m site replicates, total number of samples equals 105.

[3] Ratio of samples with detectable concentrations to the total number of samples was 105/105 for all elements except: Ni = 100/105, Pb = 104/105, and V = 95/105.

Table 3. ANOVA results and summary statistics for rockland soils (barbell sampling).

	Percentage variance[1] at each ANOVA level								Observed Range		Estimated Baseline Range	
Element	8 km	2 km	0.75 km	100 m	10 m	Lab error	Geometric mean[2]	Geometric deviation	Minimum	Maximum	Minimum	Maximum
Ash%	< 1	14	< 1	86 *	1 *	< 1	58.1	1.37	25.6	78.5	31.2	100[6]
C total %[3]	< 1	19	< 1	78 *	3 *	< 1	16.8	1.50	9.95	35.1	-	-
C org %[3]	< 1	25	< 1	73 *	2 *	< 1	16.1	1.50	9.17	34.9	-	-
C crbnt %	3	< 1	< 1	81	16 *	< 1	0.48	2.44	0.11	2.46	0.08	2.86
S%[4]	29	< 1	< 1	70 *	1	< 1	0.07	1.72	<0.05	0.21	0.02	0.20
pH[5]	< 1	< 1	77 *	< 1	21 *	2	7.2	0.31	6.8	7.7	6.6	7.9
Al%	< 1	< 1	< 1	98 *	2 *	< 1	7.4	1.73	2.0	13	2.5	22
Ca%	< 1	< 1	< 1	79	21 *	< 1	4.1	1.76	1.4	9.6	1.3	13
Fe%	< 1	< 1	< 1	97 *	3 *	< 1	3.7	1.69	1.2	6.3	1.3	11
K%	2	< 1	< 1	88 *	10 *	1	0.093	1.31	0.049	0.13	0.055	0.16
Mg%	3	< 1	< 1	94 *	3 *	< 1	0.48	1.56	0.16	0.82	0.20	1.2
Na%	< 1	< 1	< 1	88 *	11 *	< 1	0.052	1.23	0.038	0.085	0.035	0.078
P%	< 1	52	10	20	7	12	0.037	1.28	0.030	0.070	0.023	0.061
Ti%	< 1	< 1	< 1	98 *	2 *	< 1	0.43	1.82	0.097	0.82	0.13	1.4
As μg/g	< 1	< 1	< 1	98 *	2 *	< 1	11	1.65	4.7	20	4.0	30
Ba μg/g	6	11	< 1	70	13 *	< 1	52	1.42	22	81	25	100
Be μg/g	< 1	9	< 1	90 *	1	< 1	2	1.86	0.5	4	0.6	8
Ce μg/g	< 1	5	< 1	94 *	2 *	< 1	86	1.85	21	200	25	290
Co μg/g	< 1	12	< 1	82 *	6 *	< 1	5	1.68	2	11	2	15
Cr μg/g	< 1	3	< 1	95 *	2 *	< 1	140	1.73	41	240	48	430
Cu μg/g	22	< 1	25	< 1	44 *	9	6.6	1.37	3.0	11	3.5	12
Eu μg/g[4]	< 1	< 1	< 1	94 *	< 1	6	2	2.01	<0.9	3	0.4	7
Ga μg/g	< 1	< 1	< 1	97 *	3 *	< 1	13	1.74	4	23	4	39
Hg μg/g	1	< 1	< 1	67	17	16	0.21	1.93	0.08	0.50	0.06	0.78
La μg/g	< 1	2	< 1	97 *	2 *	< 1	42	1.75	11	79	14	130
Li μg/g	< 1	< 1	< 1	99 *	1 *	< 1	80	1.70	22	130	28	230
Mn μg/g	< 1	17	3	59	21 *	< 1	370	2.20	73	1200	76	1800
Nb μg/g	< 1	< 1	< 1	99 *	1 *	< 1	14	2.03	2.3	28	3.5	59
Nd μg/g	< 1	4	< 1	95 *	2 *	< 1	41	1.70	12	76	14	120
Ni μg/g	< 1	1	< 1	97 *	3 *	< 1	41	1.76	11	72	13	130
Pb μg/g	3	< 1	56	6	33 *	1	48	1.20	31	81	33	69
Sc μg/g	< 1	3	< 1	96 *	1	< 1	13	1.81	3	23	4	43
Sr μg/g	< 1	6	< 1	79	15 *	< 1	300	1.67	120	810	110	840
Th μg/g	< 1	2	< 1	97 *	1 *	< 1	12	1.88	3	23	4	43
V μg/g	< 1	4	< 1	93 *	3 *	< 1	78	1.75	25	150	25	240
Y μg/g	< 1	< 1	< 1	98 *	2	< 1	41	1.82	10	74	12	140
Yb μg/g	< 1	5	< 1	91 *	3	< 1	3	1.91	0.8	6	0.9	10
Zn μg/g	33	9	< 1	51 *	6 *	1	12	1.47	6.7	26	5.6	26

[1] * significant at 0.05 probability level.

[2] n = 12 after hierarchically averaging lab replicates and 10 m site replicates, total number of samples equals 20.

[3] Baseline range was not estimated due apparent biases in concentration measurement.

[4] Ratio of samples with detectable concentrations to the total number of samples was 20/20 for all elements except: S = 15/20, and Eu = 18/20.

[5] Arithmetic mean and deviation.

[6] Maximum value set equal to 100, calculated value equals 108.

Table 4. ANOVA results and summary statistics for rockland soils (grid sampling).

	Percentage variance[1] at each ANOVA level						Observed Range		Estimated Baseline Range	
Element	Grid cell	100 m	10 m	Lab error	Geometric mean[2]	Geometric deviation	Minimum	Maximum	Minimum	Maximum
Ash%	< 1	85 *	14 *	1	64.2	1.24	25.6	86.1	41.7	98.9
S%[3]	41	28	28 *	3	0.06	1.69	<0.05	0.35	0.02	0.19
Al%	< 1	90 *	10 *	< 1	8.5	1.53	2.0	16	3.7	20
Ca%	13	58	29 *	< 1	3.9	2.08	0.97	25	0.89	17
Fe%	< 1	88 *	12 *	< 1	4.4	1.55	1.2	8.3	1.8	10
K%[3]	< 1	76 *	22 *	2	0.096	1.35	<0.04	0.17	0.053	0.18
Mg%	< 1	87 *	13 *	< 1	0.55	1.39	0.16	0.92	0.28	1.0
Na%	29	49 *	16 *	6	0.054	1.22	0.038	0.13	0.036	0.081
P%	86 *	< 1	10 *	4	0.034	1.33	0.016	0.14	0.021	0.067
Ti%	< 1	87 *	12 *	1	0.5	1.60	0.1	0.9	0.2	1.3
Ba μg/g	10	55	34 *	1	56	1.40	21	120	28	110
Be μg/g	< 1	92 *	< 1	8	2	1.65	0.5	4	0.9	6
Ce μg/g	< 1	87 *	13 *	1	98	1.61	21	200	38	250
Co μg/g	< 1	82 *	17 *	1	6.5	1.51	1.8	13	2.8	15
Cr μg/g	< 1	87 *	12 *	1	170	1.50	41	290	75	380
Cu μg/g	28	< 1	57 *	15	7	1.33	3	18	4	12
Eu μg/g[3]	< 1	92 *	3	5	2	1.64	<0.8	4	0.8	5
Ga μg/g	< 1	87 *	12 *	1	14	1.53	4	27	6	34
La μg/g	< 1	88 *	12 *	< 1	48	1.53	11	87	21	110
Li μg/g	< 1	87 *	13 *	< 1	93	1.52	22	170	40	210
Mn μg/g	20	61 *	18 *	< 1	340	1.86	73	1400	99	1200
Nb μg/g[3]	< 1	67	30 *	3	18	1.80	<1.6	33	5.4	57
Nd μg/g	< 1	89 *	11 *	< 1	46	1.49	12	81	21	100
Ni μg/g	< 1	87 *	13 *	< 1	48	1.56	11	87	20	120
Pb μg/g	33	< 1	59 *	9	46	1.26	15	81	29	74
Sc μg/g	< 1	90 *	9 *	< 1	15	1.58	3	28	6	37
Sr μg/g	< 1	72 *	27 *	< 1	260	1.57	93	810	110	640
Th μg/g	< 1	87 *	12 *	1	14	1.63	3	27	5	37
V μg/g	< 1	89 *	10 *	< 1	92	1.59	23	170	36	230
Y μg/g	< 1	88 *	12 *	1	50	1.63	10	99	19	130
Yb μg/g	< 1	89 *	7	4	4	1.66	0.8	8	1	10
Zn μg/g	29	36	29 *	6	13	1.42	4	26	6	26

[1] * significant at 0.05 probability level.

[2] n = 85 after hierarchically averaging lab replicates and 10 m site replicates, total number of samples equals 105.

[3] Ratio of samples with detectable concentrations to the total number of samples was 105/105 for all elements except: S = 74/105, K = 104/105, Eu = 94/105, and Nb = 103/105.

In comparing mean concentrations between the grid samples and the barbell design subset, the major elements Al, Fe, and Mg had about 15 percent (relative) higher concentrations in the larger population. This is probably owing to a slightly higher non-carbonate mineral matter abundance in the larger population. Most trace elements also exhibit a slightly higher or about equal concentration in the grid samples than in the barbell subset. In contrast to what was observed for the pine needles, the larger population generally exhibited a smaller geometric deviation than the barbell subset for most elements. Calcium is a notable exception.

In general, it appears that the results from the barbell sampling design are reasonably representative of the larger population of pine needles and rockland soils within EVER. The ANOVA results from both designs indicate that a high proportion of the variance for most elements in both sample media is attributable to very localized differences at distances of 10's to 100's of meters. There is little indication from the barbell design results that there are any highly significant east-west biogeochemical trends in the relatively small area of Long Pine Key.

Future comparisons with the baseline 95 percent expected concentration ranges should be made with the estimated ranges given in Tables 2 and 4, that is the ranges estimated from the larger pineland population in the grid study. For the few elements that were determined only in the barbell sample subset, based on the results for other elements that were determined in both sampling designs, the estimated baseline ranges appear to be reasonablely representative of the pinelands as a whole and these data should be useful for future comparisons also.

Baseline studies such as described here are critical to assessing temporal changes in element content of ecosystem components. In other areas, lichens have been used frequently as biomonitors to examine trends in atmospheric deposition. For example, Lawry and Hale (1981, 1988) have used lichens to demonstrate changes in Pb deposition over several decades in the Northeastern US. From 1970 through 1985, Perkins and Millar (1987, 1988) monitored the temporal changes in fluoride content of lichens as indicators of emissions from a nearby aluminum plant. Monitoring with lichens from 1983 to 1988 has demonstrated an apparent improvement in air quality in South west Louisiana (Walther and others, 1990). The Dutch had a national lichen monitoring survey that was performed at 5 yr intervals to help identify pollution sources (Sloof and Wolterbeek, 1991). It has been estimated that in Europe over 5000 lichen samples are analyzed annually for biomonitoring purposes (Quevauviller and others, 1993). As a result of the number of analyses that are performed, interlaboratory comparison exercises have been done to improve the quality of trace element determinations in lichens (Quevauviller and others, 1993). Other media have been used also to monitor temporal changes in environmental conditions. For example, Keller and others (1994) used beech leaves as a bioindicator over a period of two decades near a waste incinerator in Switzerland. Herrick and Freeland (1990) have identified an apparent decrease in Pb content of forest soils in the Northeastern US through temporal sampling. However, they note that "concentration differences may, to a lesser extent, reflect differences in sampling techniques." Just as differences in sampling and analysis techniques may affect our ability to detect temporal changes in element content of a specific sample media, natural causes may have dramatic influences that are difficult to quantify. Hurricane Andrew did significant damage to the EVER pinelands in August 1992. Thus, any future reevaluation of the chemistry of these pinelands must take into account the potential influence of this singular event that occurred after our measurements were made.

Inter-element relationships in pine needles and in rockland soils

Exploratory principal component analysis was performed on a subset of variables determined in slash pine needles and rockland soils from the barbell and grid sampling designs in order to reduce the dimensionality and examine the latent variables or components inherent in the data. Our objective was to obtain a "simple structure" of easily interpretable components that explained an acceptable amount of the total variance. Models with five components that explained 70-94 percent of the total variance were derived for both sample media. Those elements used in the models and their component loadings are listed in Tables 5-8. Those elements that have high loadings on an individual component are the elements that are most highly correlated with each other in multi-dimensional space. Positive and negative loadings are arbitrarily assigned and only represent inter-element relationships, not absolute concentrations.

The models for the barbell and grid sampling designs were based on data sets with prior hierarchical averaging of the laboratory and 10 m site replicates ($n=12$ and $n=85$, respectively). The models for the barbell design include all elements used in the grid design models plus one or more additional elements that were only measured on the barbell subset of samples. The models produced from each design were generally similar. Because of the greater number of samples, the emphasis in interpretation has been placed on the grid design model.

For the pine needles, no individual component explained a high proportion of the total variance. The most significant two or three components each explained about 20 percent of the variance. One component was comprised mainly of Al, Fe, and a few trace elements and a second component was made up of ash yield, Ca, K, and Na. Calcium, in particular, K, and Na are major constituents of the plant ash. Similar element associations have been observed in other plant species (Jackson and Gough, 1991). In the barbell design model, component III had a positive association of K, Hg, and Pb, and accounted for about as much variance as the first two components. The other components in the two models account for most of the variance in 1-3 elements on each component. The last two components in both models have many of the same elements, but in different combinations on the components.

The rockland soils have highly varying amounts of silicates, limestone, and organic matter. This is reflected in the principal component models for both sampling designs by one predominant component that accounts for about 65 percent of the total variance. This component exhibits positive correlations among the major silicate-forming elements, Al, Fe, K, Mg, and Ti, and their associated trace elements. Of the trace elements only Cu, Hg, and Zn do not load significantly on this component. Lead loads on a component with Na in both models and on a carbonate component in the grid model, in addition to a moderate loading on the silicate component. Calcium and Sr are inversely related to the silicate elements on this component. In the barbell design model this is also true for organic C.

Another much less important component in the models is a limestone component with a carbonate C, Ca, and Sr association. Magnesium is not related to this component, but probably is related to the silicate component because the oolitic limestone is low-magnesium calcite (Gleason, 1972). In the models there are also S-P and Na-Pb components. In the barbell model, soil pH is also associated with the S-P component and inversely associated with the least significant Hg component. In the grid model, only Cu has a major loading on the fifth component.

In these latter components, the S-P association is potentially related to their anionic form in these soils and nutrient cycling and the Na-Pb association may be related to lead chloride complexes (chloride was not measured). The inverse pH-Hg association may result from a number of factors, singly or in concert. Soils higher in organic matter and/or clays tend to have higher mercury content (Adriano, 1986). In the rockland soils increased calcite content would increase the soil pH and decrease the relative amount of organic matter or clay. Soils with greater alkalinity have been observed to have higher Hg volatilization losses (Landa, 1979). However, it should be noted that this apparent association may also be an artifact of the model. This component of the model accounts for 74 percent and 35 percent of the Hg and pH variances, respectively, but in two-dimensional space the correlation coefficient (for non-standardized variables) between Hg and pH ($r=-0.26$) was not significant ($p=0.001$).

Table 5. Varimax rotated component loadings for pine needles (barbell sampling).

	Component Loadings > 0.50				
Element	Component I	Component II	Component III	Component IV	Component V
Ash	0.90				
S				-0.89	
Al		0.75			
Ca	0.87				
Fe		0.83			
K			0.78		
Mg					0.84
Na	0.82				
P	0.73				
Ba		0.81			
Cr	-0.50	0.60			
Cu		0.86			
Hg			0.98		
Mn				0.70	
Ni		0.54		0.79	
Pb			0.65		
Sr			-0.76		
Zn					0.89
Eigenvalue	3.8	3.6	3.5	2.7	2.0
% of total variance	21.3	20.2	19.3	15.0	11.4
Cumulative % variance	21.3	41.5	60.8	75.8	87.2

Table 6. Varimax rotated component loadings for pine needles (grid sampling).

	Component Loadings > 0.50				
Element	Component I	Component II	Component III	Component IV	Component V
Ash		0.70			
S			0.79		
Al	0.91				
Ca		0.90			
Fe	0.74				
K		-0.83			
Mg				0.64	
Na		0.54			
P			0.75		
Ba	0.71				
Cr	0.80				
Cu			0.69		
Mn				0.74	
Ni					0.80
Pb	0.58				
Sr		0.80			
Zn				0.63	
Eigenvalue	3.4	3.4	2.2	1.6	1.4
% of total variance	20.2	19.7	13.0	9.3	8.0
Cumulative % variance	20.2	39.9	52.9	62.2	70.2

Table 7. Varimax rotated component loadings for rockland soils (barbell sampling).

	Component Loadings > 0.50				
Element	Component I	Component II	Component III	Component IV	Component V
Ash	0.97				
C organic	-0.96				
C carbonate		0.94			
S	-0.69		0.66		
pH			0.52		-0.59
Al	0.98				
Ca	-0.59	0.75			
Fe	0.96				
K	0.89				
Mg	0.96				
Na				0.90	
P			0.93		
Ti	0.98				
As	0.89				
Ba	0.80				
Ce	0.97				
Co	0.98				
Cr	0.98				
Cu		0.48[*]			
Ga	0.97				
Hg					0.86
La	0.98				
Li	0.96				
Mn	0.82				
Nb	0.97				
Nd	0.99				
Ni	0.98				
Pb	0.55			0.75	
Sc	0.98				
Sr	-0.75	0.53			
Th	0.98				
V	0.97				
Y	0.98				
Zn			0.72		
Eigenvalue	23.0	2.7	2.6	2.2	1.5
% of total variance	67.8	7.8	7.8	6.3	4.4
Cumulative % variance	67.8	75.6	83.4	89.7	94.1

[*] Highest loading for Cu on any component.

Table 8. Varimax rotated component loadings for rockland soils (grid sampling).

	Component Loadings > 0.50				
Element	Component I	Component II	Component III	Component IV	Component V
Ash	0.82				
S	-0.43*	-0.82			
Al	0.97				
Ca	-0.60		-0.73		
Fe	0.96				
K	0.65				
Mg	0.86				
Na				0.95	
P		-0.91			
Ti	0.95				
Ba	0.68				
Ce	0.93				
Co	0.95				
Cr	0.97				
Cu					0.95
Ga	0.97				
La	0.96				
Li	0.96				
Mn	0.53	0.51			
Nb	0.91				
Nd	0.97				
Ni	0.96				
Pb	0.46*		0.58	0.49*	
Sc	0.98				
Sr	-0.75		-0.52		
Th	0.97				
V	0.96				
Y	0.96				
Zn		-0.79			
Eigenvalue	18.7	2.6	1.9	1.8	1.5
% of total variance	64.6	9.1	6.6	6.1	5.2
Cumulative % variance	64.6	73.7	80.3	86.4	91.6

*Loadings which explain less than 25% of an element's total variance.

Plant-soil element relationships

Element concentrations in soil frequently are not well correlated with plant concentrations because the total concentrations in soil do not necessarily reflect what is available to plants and because of plant preferential uptake or exclusion of elements, differences among plant tissues, or seasonal translocation of elements. In the pinelands, we found several weak to moderate correlations between elements in the pine needles and the rockland soils. The significant ($p=0.001$) Spearman's non-parametric rank correlation coefficients are shown in Table 9. The correlations largely appear related to nutrient and micronutrient uptake. Sulfur, P, Cu, Mn, and Zn are nutrients that may have been anthropogenically added to soils in this environment. Thus trends for these elements in soils may be reflected in major nutrient concentrations in pines, but would be difficult, if not impossible, to detect by examining pine needles alone because of the many confounding factors related to nutrient cycling.

Spatial element concentration trends

Spearman's rank correlation coefficients were examined for elements versus easting and northing as a crude test for spatial trends within the EVER data. Several elements exhibited weak correlations (≥ 0.37 to ≤ 0.55, $p=0.001$). Calcium in pine and S, P, and Zn in soil had positive correlations with both easting and northing, whereas K in pine and Ba in soil had negative correlations. Sodium in soil was also negatively correlated with northing. The meaningfulness of these correlations is unclear, although the trends are somewhat reflected in the element contour maps presented below.

The ability to accurately and reproducibly map element concentration trends is dependent upon the scale of variability within the sample population and the sampling density. The ANOVA results indicated that for many elements in pine needles there was a significant fraction of the total variability among grid cells. On the other hand for the rockland soils, most of the variance was attributable to differences within grids at distances of 10-100 m. The high degree of sample heterogeneity over short distances suggests that biogeochemical maps produced with these data may not be highly stable, that is reproducible. Map stability has been examined by two methods which use the hierarchical ANOVA results. The number of samples required within a mappable unit for a given map confidence level and the variance mean ratio (V_m), that is the ratio of variance among map units to within units, have been calculated using the techniques of Miesch (1976) and subsequent modifications of Severson and Tidball (1979). The latter modifications take into account the unbalanced design in the calculation of the V_m and assume that finite population corrections are negligible.

Based on the data already collected, the number of samples required to produce a map at the 80 and 95 percent confidence levels for each element in pine needles and soils is shown in Table 10. Generally, for pines, our maps would be stable at the 80 percent confidence level if we sampled three or four times within each grid. For soils, for the few elements that are mappable, four or more samples would be required. On average we sampled 1.4 times per grid; less than required to produce stable maps at the 80 percent confidence level.

A second approach to evaluate map stability examines the ratio of variance among map units to within units. The variance among 0.75 km grids was ratioed to the sum of the variances (corrected for unbalancing) at each lower level (≤ 100 m). It has been empirically determined that ratios of V_m that are ≥ 1 tend to reproduce true spatial trends (Miesch, 1976). Using this criteria, stable maps could be produced for ten of the twenty elements in pine, but only for P in soils. If mappable units for soils were assigned to 100 m distances instead of 0.75 km grids (i.e. the sum of the variances at the upper two levels are ratioed to the sum of the lower two levels), the recalculated V_m indicated that most elements could be mapped and the maps would faithfully reproduce the true spatial trends. However, sampling at 100 m grid intervals is impractical, and undoubtedly unnecessary when what these data seem to suggest is that there are no distinct regional trends in the soil geochemistry.

As an alternative approach for the soils, all elements were normalized to Al in an attempt to reduce local variability without additional sampling. The element/Al ratio was calculated for each sample (non-log transformed) and hierarchically averaged to produce the 100 m data set. The ANOVA results for this data set generally had a greater proportion of the total variance at the grid level. The adjusted results (Table 10) suggest that 2-3 samples would be required per 0.75 km grid cell to produce maps at the 80 percent confidence level, whereas the V_m indicated that the current Al-ratioed results would produce stable maps for all elements but Be, Cr, and Eu.

Table 9. Spearman rank correlation coefficients[1] for elements in pine needles and soils.

	Pine needles						
Soil	Ash	Ca	Fe	K	Mn	Ba	Sr
S	0.49	0.51		-0.47	-0.42		
K	-0.42	-0.39		0.39			
Mg	-0.39						
Na							
P		0.49		-0.44			
Ba				0.40			-0.36
Ce	-0.41	-0.35			0.42		
Cu		-0.35		0.52			
Eu	-0.36						
La	-0.36						
Mn	-0.50	-0.44	-0.36		0.62	-0.39	
Nd					0.35		
Zn		0.48		-0.52			

[1] significant at $p=0.001$, $r \geq 0.345$, $n=85$.

Table 10. Estimated sample density and variance mean ratios for 0.75 km grid cell for elements in pine needles and soils and element:Al ratio in soils.

Pine needles				Soils				Soils--element:Al		
element	n_r-80%[1]	n_r-95%	V_m	element	n_r-80%	n_r-95%	V_m	n_r-80%	n_r-95%	V_m
Ash %	3	5	1.2	Ash %	-[2]	-	-	3	5	2.6
S%	3	4	1.9	S%	3	6	0.9	2	2	1.2
Al %	4	9	0.5	Al %	-	-	-			
Ca %	3	4	2.7	Ca %	7	22	0.2	3	5	2.8
Fe %	4	11	0.4	Fe %	-	-	-	2	3	1.8
K %	3	4	2.5	K %	-	-	-	2	3	1.3
Mg %	4	12	0.4	Mg %	-	-	-	2	3	6.7
Na %	-	-	-	Na %	4	9	0.5	2	2	1.3
P %	3	5	1.1	P %	2	3	8.8	2	3	2.5
Ti %				Ti %	-	-	-	3	5	2.3
Ba μg/g	3	4	2.9	Ba μg/g	8	28	0.1	2	3	1.3
Be μg/g				Be μg/g	-	-	-	4	8	<0.1
Ce μg/g				Ce μg/g	-	-	-	3	4	3.6
Co μg/g	3	7	0.9	Co μg/g	-	-	-	2	3	1.1
Cr μg/g	-	-	-	Cr μg/g	-	-	-	3	5	0.1
Cu μg/g	3	6	1.1	Cu μg/g	4	9	0.5	2	3	1.0
Eu μg/g				Eu μg/g	-	-	-	4	9	0.7
Ga μg/g				Ga μg/g	-	-	-	3	5	2.3
La μg/g	11	39	0.1	La μg/g	-	-	-	3	4	3.8
Li μg/g				Li μg/g	-	-	-	2	3	4.3
Mn μg/g	3	4	1.6	Mn μg/g	5	13	0.3	3	4	4.0
Nb μg/g				Nb μg/g	-	-	-	4	10	1.3
Nd μg/g				Nd μg/g	-	-	-	3	5	2.9
Ni μg/g	5	15	0.3	Ni μg/g	-	-	-	3	4	2.3
Pb μg/g	3	7	0.8	Pb μg/g	4	8	0.6	2	2	1.1
Sc μg/g				Sc μg/g	-	-	-	3	6	1.2
Sr μg/g	3	4	1.7	Sr μg/g	-	-	-	2	3	1.3
Th μg/g				Th μg/g	-	-	-	3	5	2.0
V μg/g	-	-	-	V μg/g	-	-	-	2	3	1.0
Y μg/g				Y μg/g	-	-	-	3	5	2.5
Yb μg/g				Yb μg/g	-	-	-	3	4	1.1
Zn μg/g	3	5	1.5	Zn μg/g	4	9	0.5	2	3	3.9

[1] n_r = estimated number of samples required within a 0.75 km grid cell for 80% or 95% confidence level.

[2] dash indicates negative variance components and inability to calculate estimates.

Contour maps were produced for elements or element ratios in pine needles and rockland soils by using only the 70 grid cells on Long Pine Key. For pine needles, contour maps for 10 elements that had V_m ratios greater than one are shown in Figures 5-8. The element contour maps are divided amongst the figures based on which principal component they loaded most highly on and are ordered within each figure based on decreasing magnitude of their component loading (see Table 6).

For the pine needles, of the elements that loaded highly on principal component I only Ba had a high enough V_m to produce a contour map (Figure 5). Barium concentrations tended to be highest along the northern edge of Long Pine Key. Contour maps for Al, Fe, and Pb, although unstable, generally indicated a similar trend. For component II, Ca, K, Sr, ash, and Na loaded highly and only Na was not mappable. Contour maps were relatively similar for Ca, Sr, and ash with concentrations tending to increase in a northwest direction (Figure 6). Potassium had an inverse trend as expected from its inverse correlation with the other elements on the component. Sulfur, P, and Cu were mappable for component three (Figure 7). However, the range of S concentrations in the needles is very small and the contour map indicates a relatively uniform distribution throughout the key. Phosphorus was generally higher at the outer edge and in the vicinity of one transverse glade near the center of the key. The highest P concentrations were at the SW and SE extremes of the key. Copper, like S, exhibited a very narrow range of concentrations with less than one microgram per gram difference between the 10th and 90th percentiles. Although the range of concentrations was small, the contours generally are similar in pattern to P. For component IV, Mn and Zn were mappable (Figure 8), but Mg in the needles was not. The Mn concentrations tended to be high along the southern boundary, and in the NW and SE corners of the key. The Zn concentration trends were somewhat similar to those of Mn. Zinc was generally high in the eastern-central portion of the Long Pine Key.

Element concentration contour maps for Al and P were produced for the rockland soils in a fashion similar to those for the pine needles. Contour maps were produced also for the ratios of 15 elements to Al in the soils (Figures 9-13). The maps are ordered based on the principal component loadings of the individual elements (see Table 8). No estimate of map stability could be made for Al in the soils because of negative variance components in the ANOVA results. However, the Al map is presented in Figure 9 and it is probably as reliable as any of the element/Al ratio maps.

The central portion of Long Pine Key generally has the highest Al concentrations (Figure 9). Areas where the Al concentration is lower tend to have higher ash and Ca to Al ratios (Figures 9 and 11). Carbonates, organic matter, and/or plant ash (charcoal) undoubtedly represent a larger proportion of the soil matrix that was sampled in these areas. For elements such as Fe, Ni, V, Ti, and Mg that are highly correlated with Al and highly loaded on principal component I, the element/Al ratios vary relatively little throughout the key. Strontium was also loaded fairly highly on component I but inversely to Al. Hence, the map of Sr/Al ratios tends to magnify the spatial variability of these two elements and there is a greater range observed for this ratio than for most other element/Al ratios. Potassium/Al ratios were fairly uniform throughout the key, whereas Mn/Al ratios tended to be highest in the SE corner of the key.

Phosphorus, an element that loaded on component II, generally had the highest concentrations in the NW portion of the key and along the northern edge (Figure 10). Sulfur/Al and Zn/Al ratios were somewhat similar.

Calcium was the primary element loaded on principal component III. The Ca/Al ratios were highest in the vicinity of the NW and NE corners of the key (Figure 11). Although Pb was inversely loaded on this component compared to Ca, the Pb/Al and Ca/Al maps exhibit somewhat similar patterns.

Sodium and Cu loaded highly on the fourth and fifth components, respectively. The maps of the ratios of these two elements to Al (Figures 12 and 13) have highs in the NW and NE portions of the keys; patterns that are similar to a number of other elements on other components.

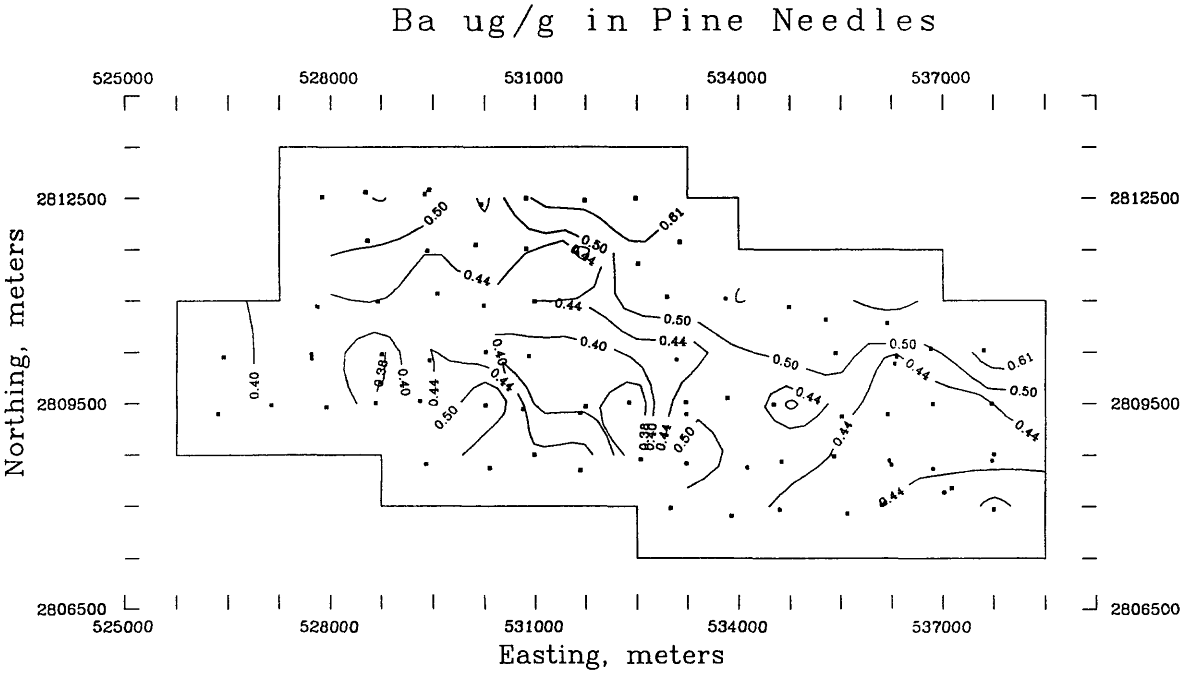
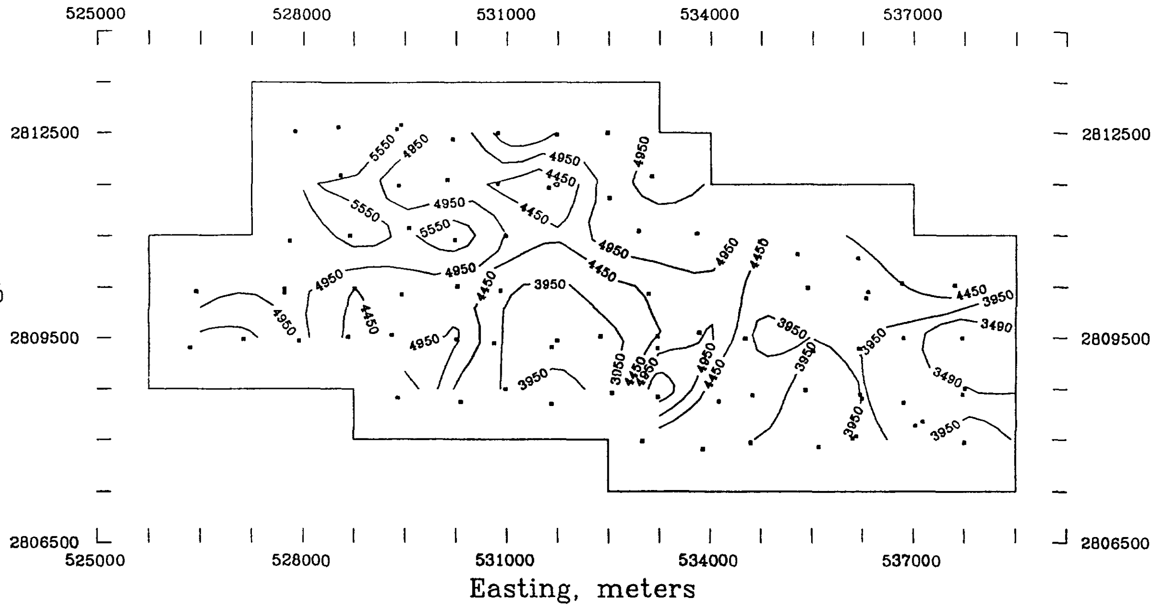
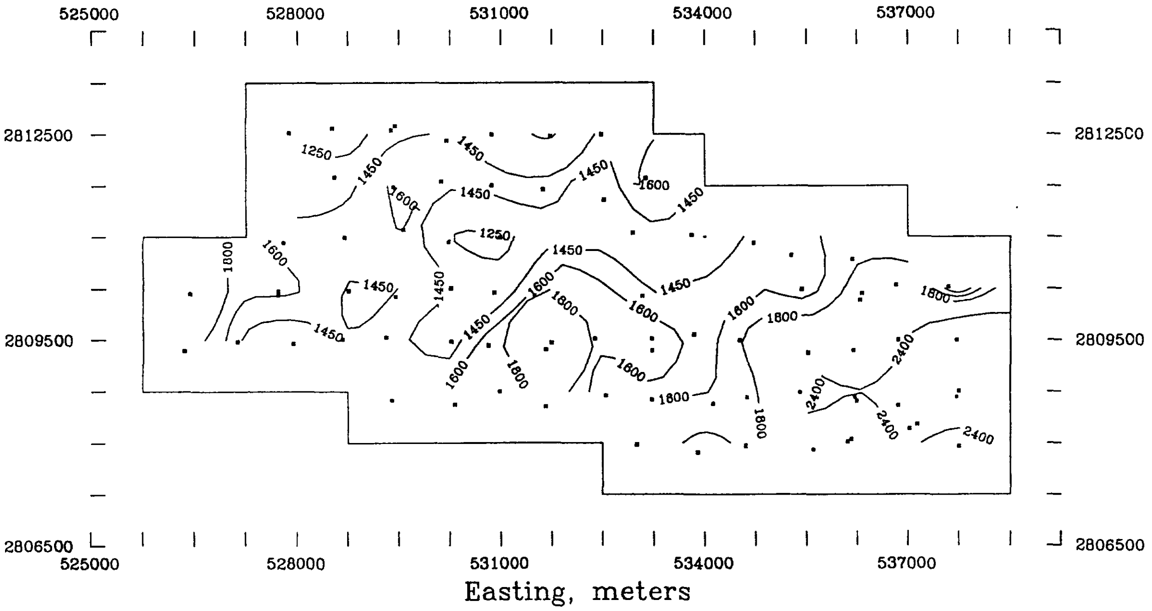


Figure 5. Distribution map of Ba concentration in pine needles (Principal Component I).

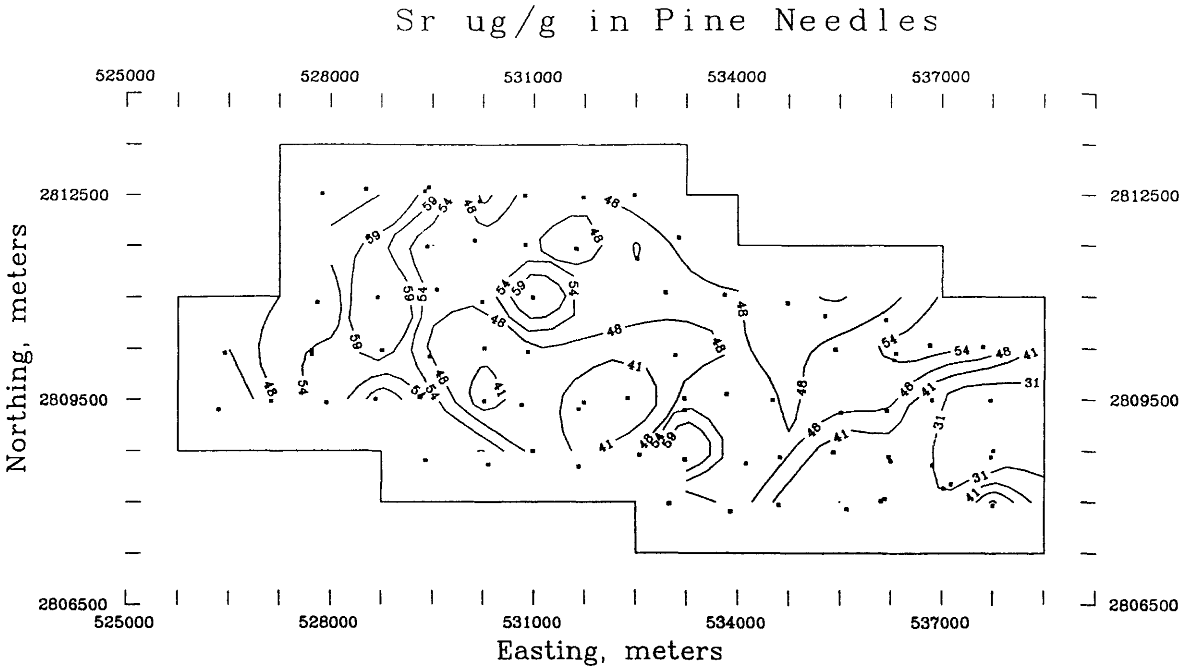


Ca ug/g in Pine Needles



K ug/g in Pine Needles

Figure 6. Distribution map of Ca, K, Sr, and ash concentrations in pine needles (Principal Component II).



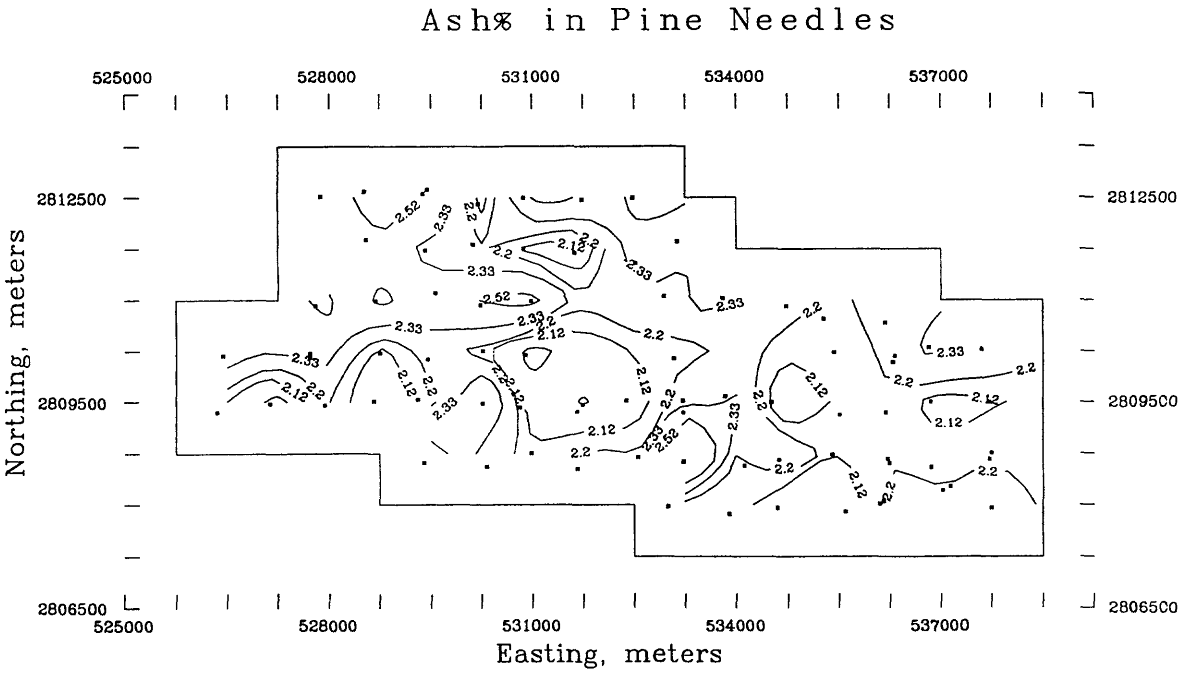
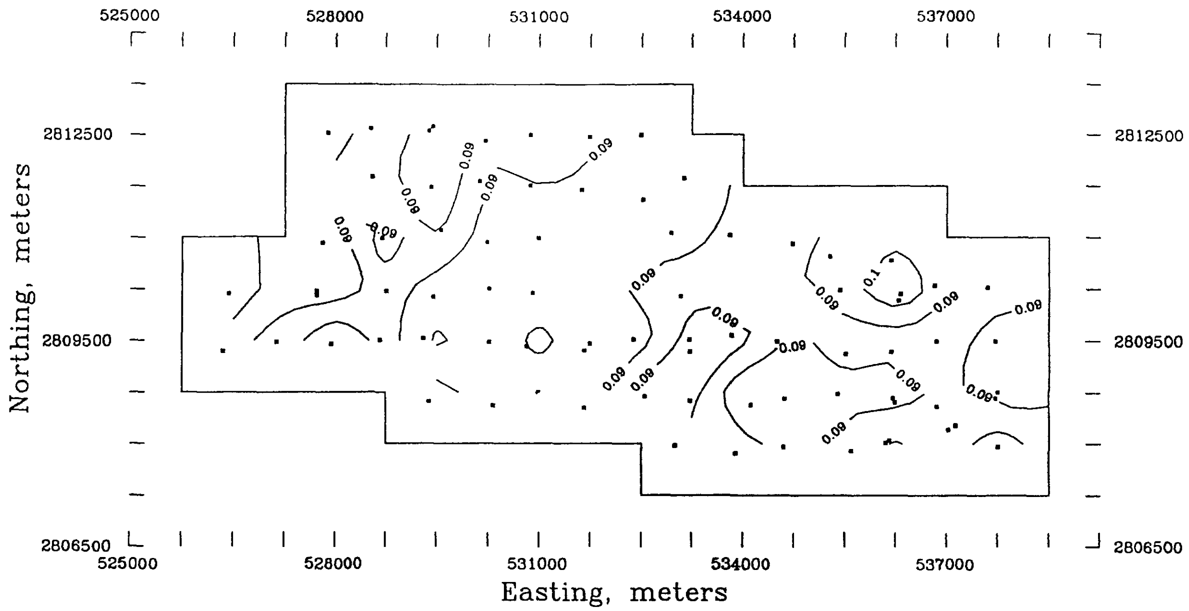


Figure 6. Continued.

S% in Pine Needles



P ug/g in Pine Needles

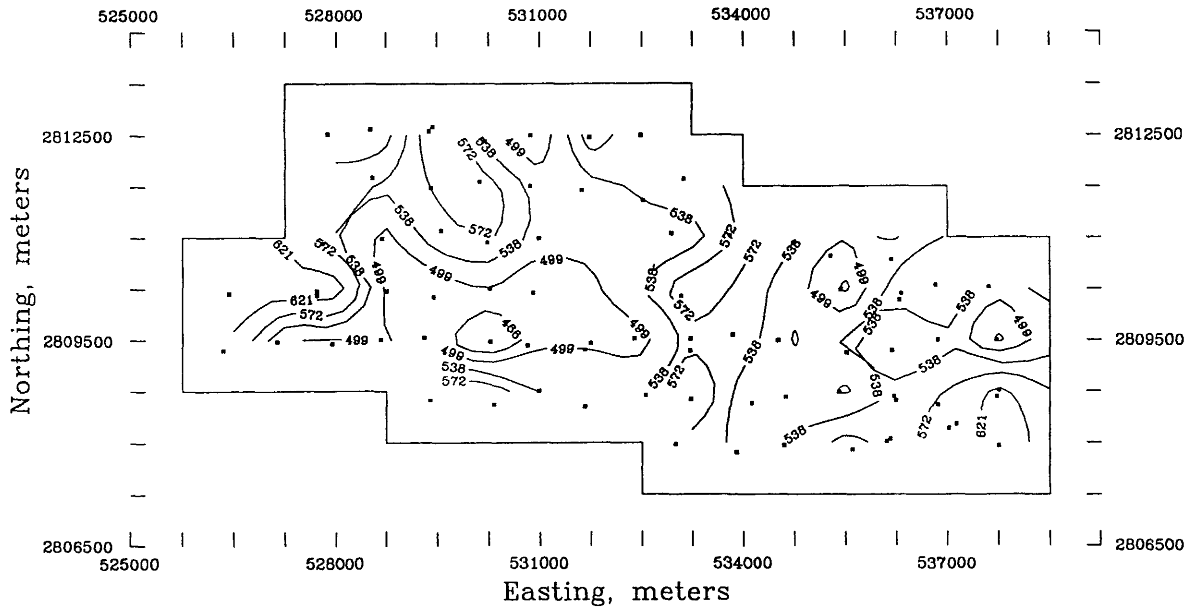


Figure 7. Distribution map of S, P, and Cu concentrations in pine needles (Principal Component III).

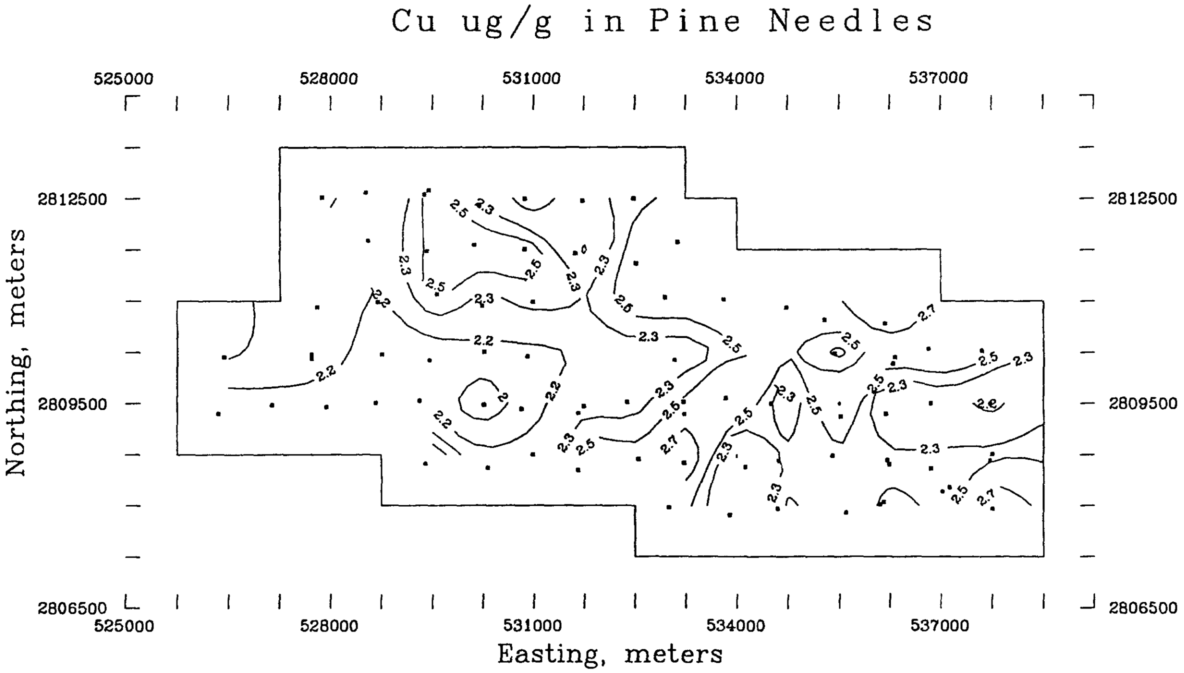
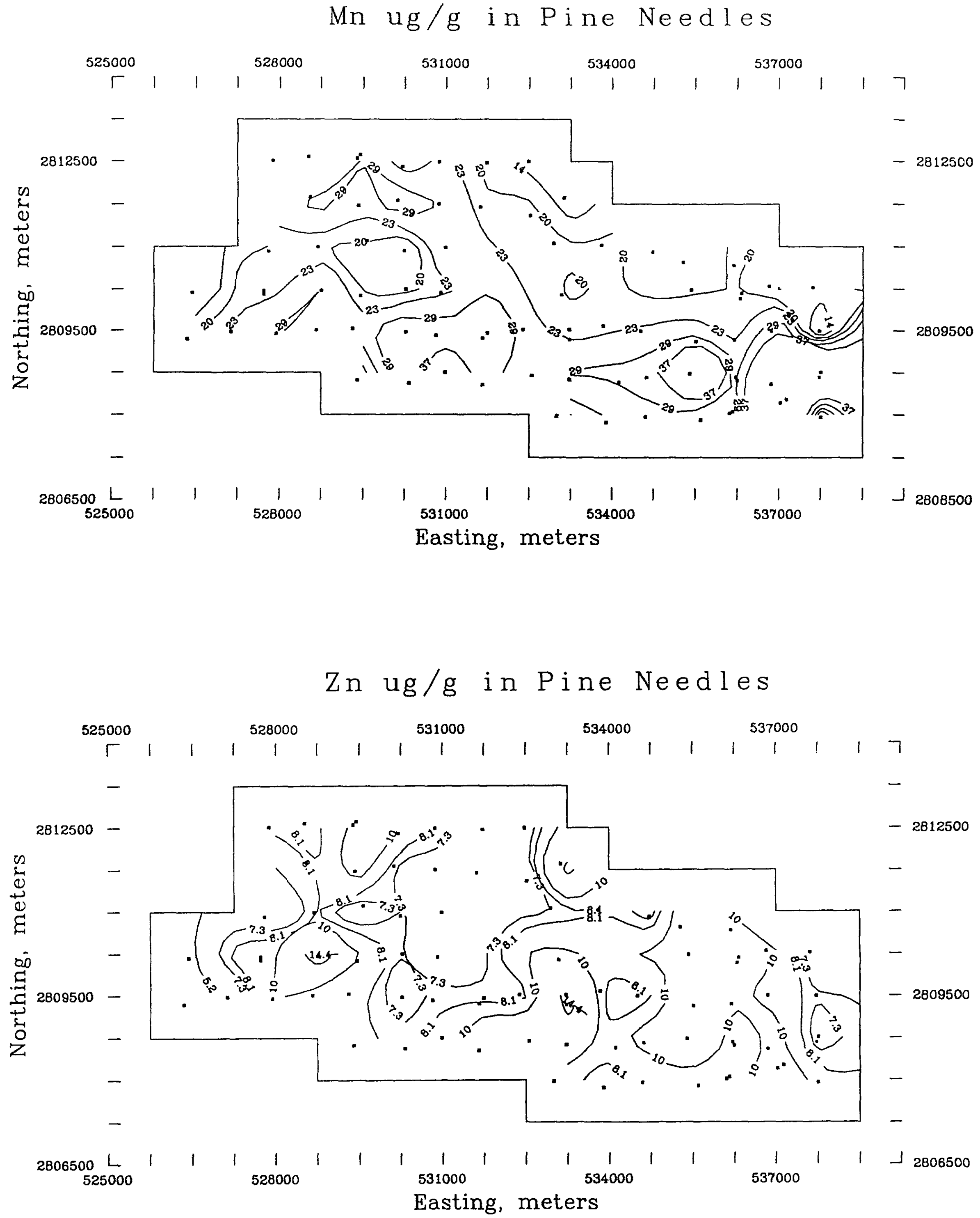


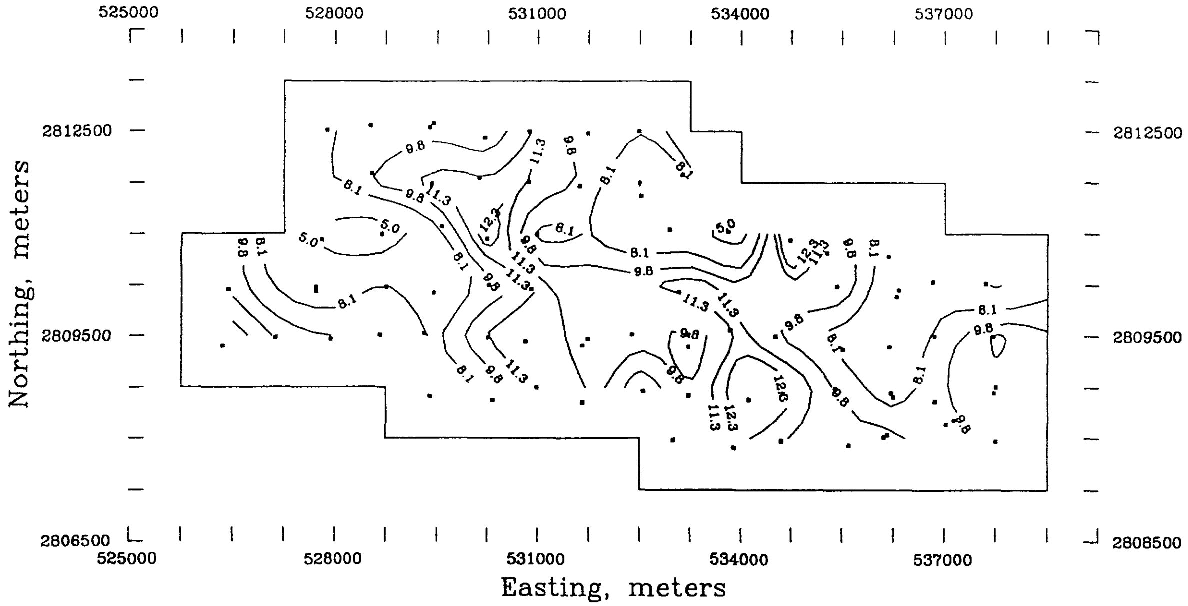
Figure 7. Continued.


Mn ug/g in Pine Needles

Zn ug/g in Pine Needles

Figure 8. Distribution map of Mn and Zn concentrations in pine needles (Principal Component IV).

Al% in soil



Ratio of Fe% to Al% in soil

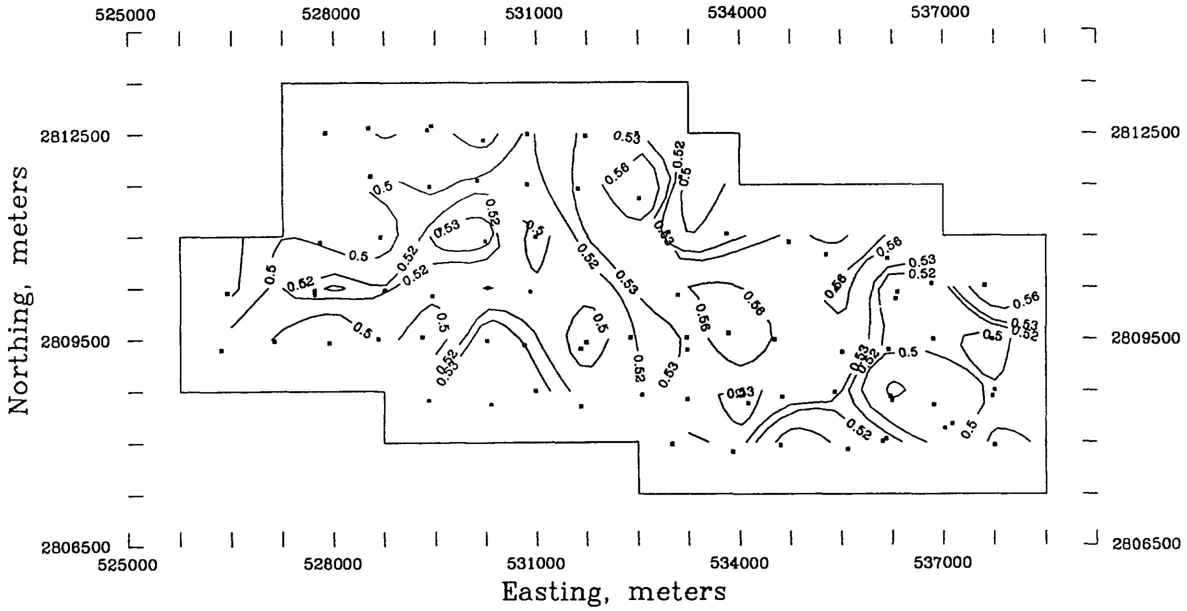
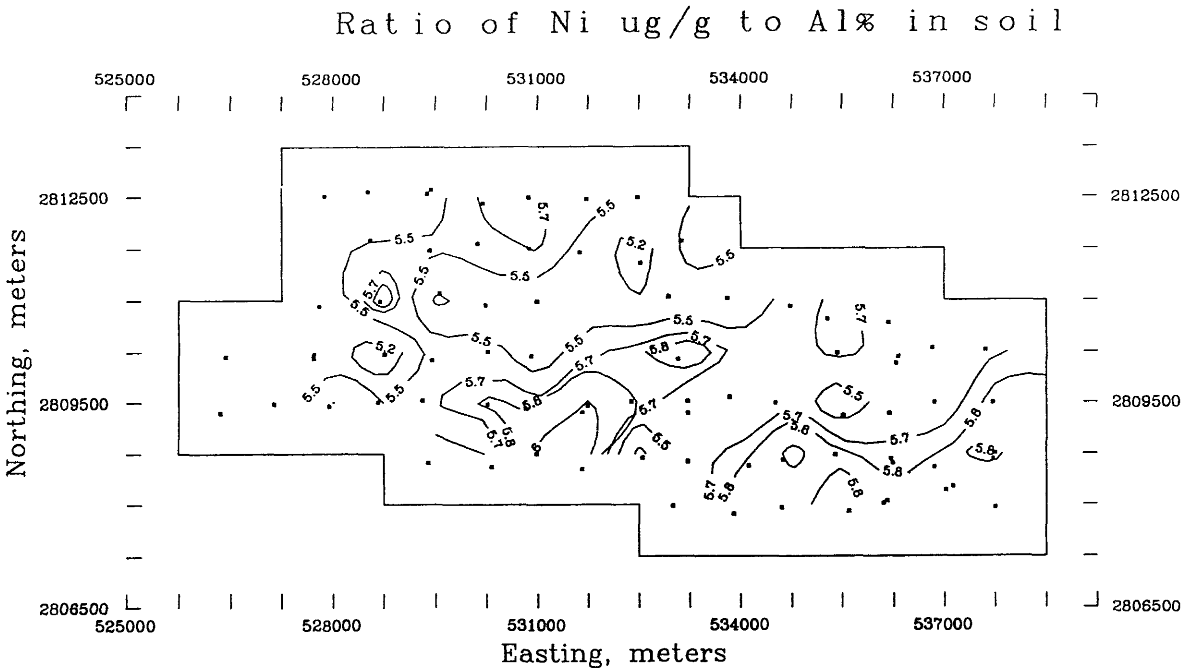
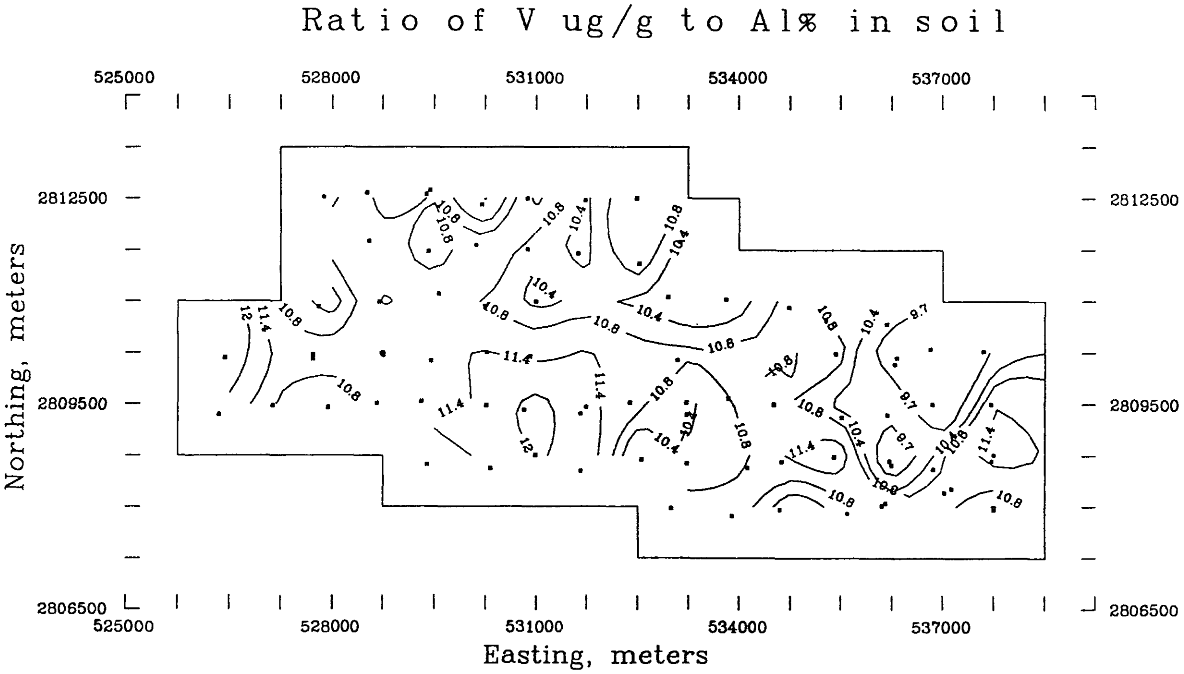


Figure 9. Distribution map of Al concentration and Fe/Al, Ni/Al, V/Al, Ti/Al, Mg/Al, ash/Al, Sr/Al, K/Al, and Mn/Al concentration ratios in rockland soils (Principal Component I).

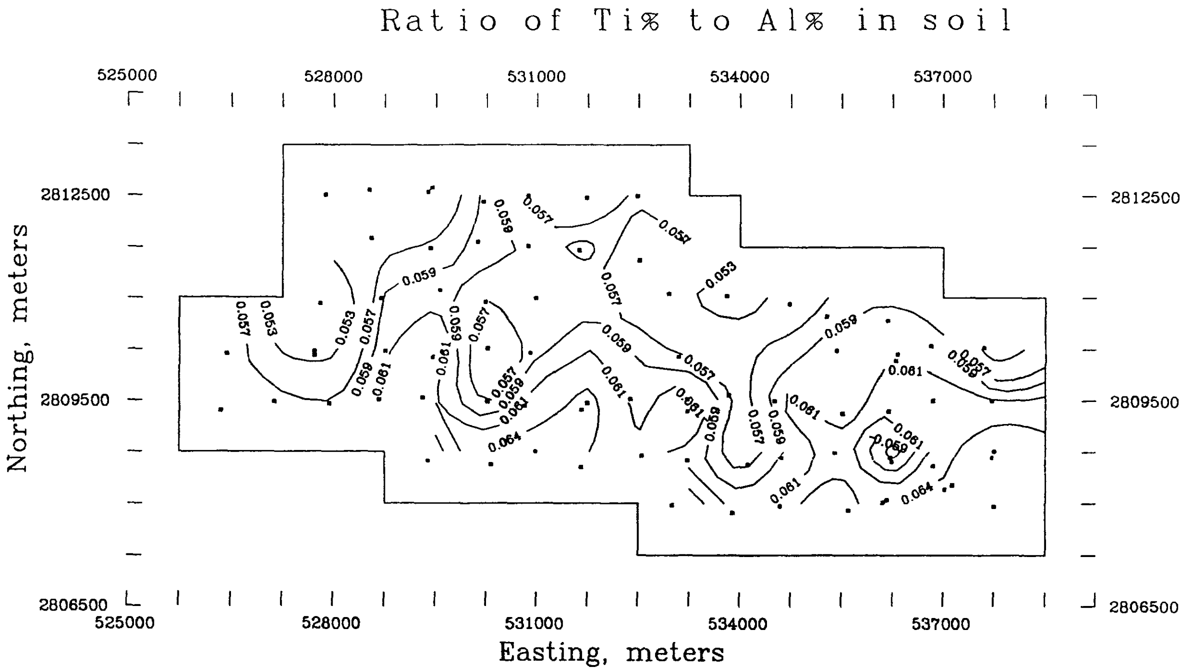


Ratio of Ni ug/g to Al% in soil



Ratio of V ug/g to Al% in soil

Figure 9. Continued.



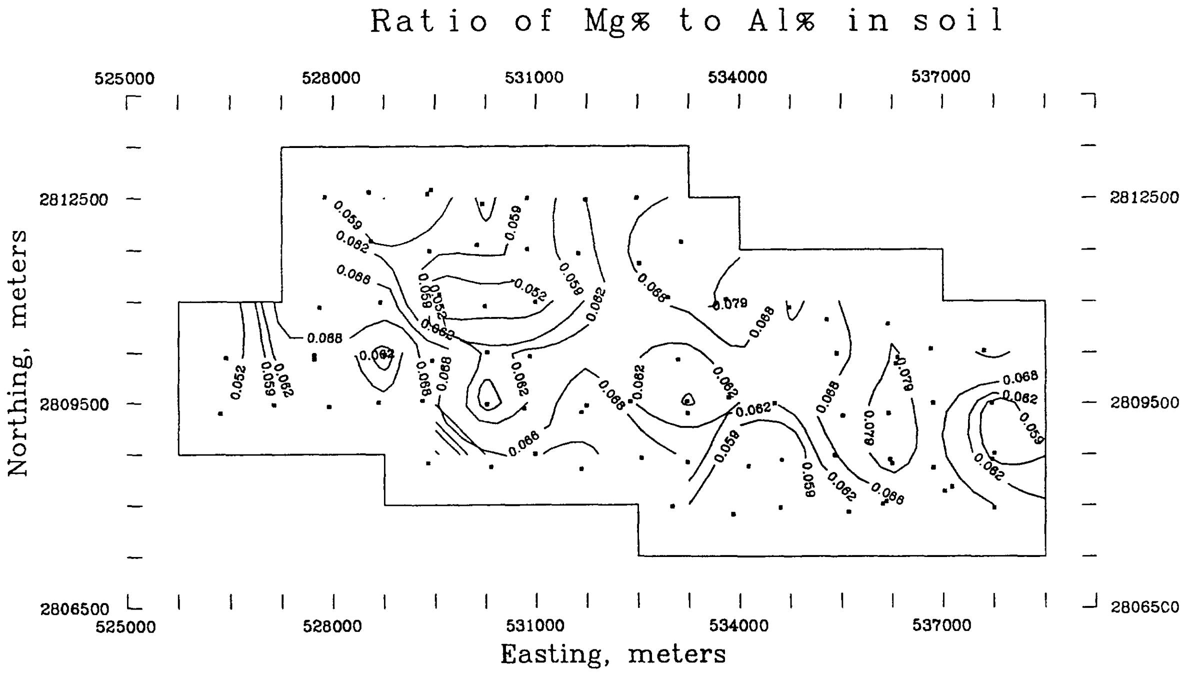
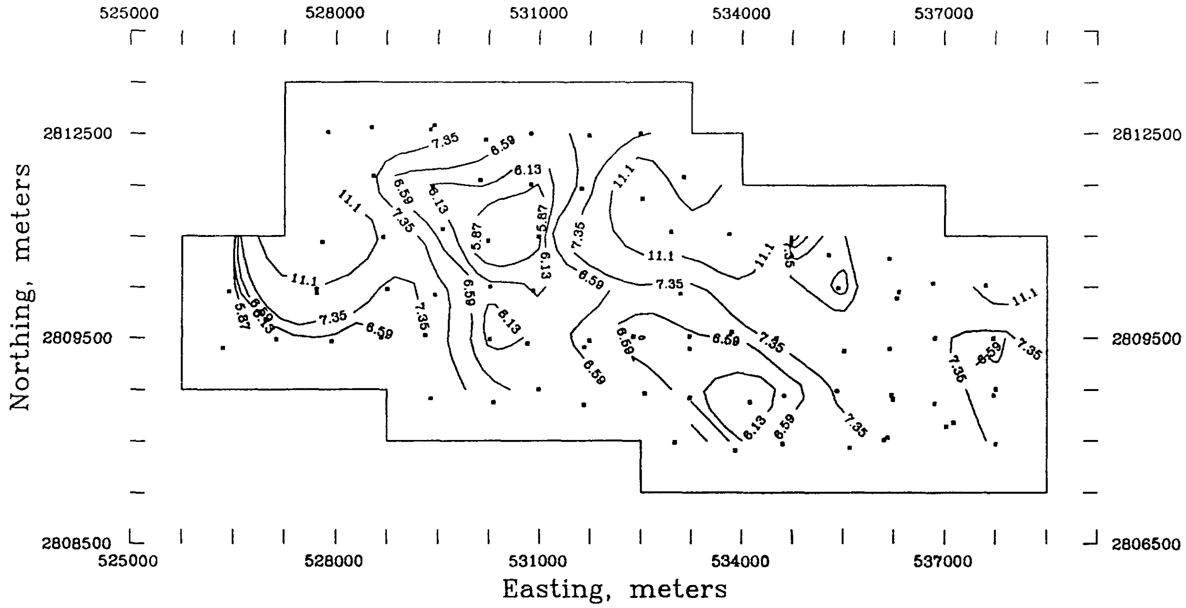


Figure 9. Continued.

Ratio of Ash% to Al% in soil



Ratio of Sr ug/g to Al% in soil

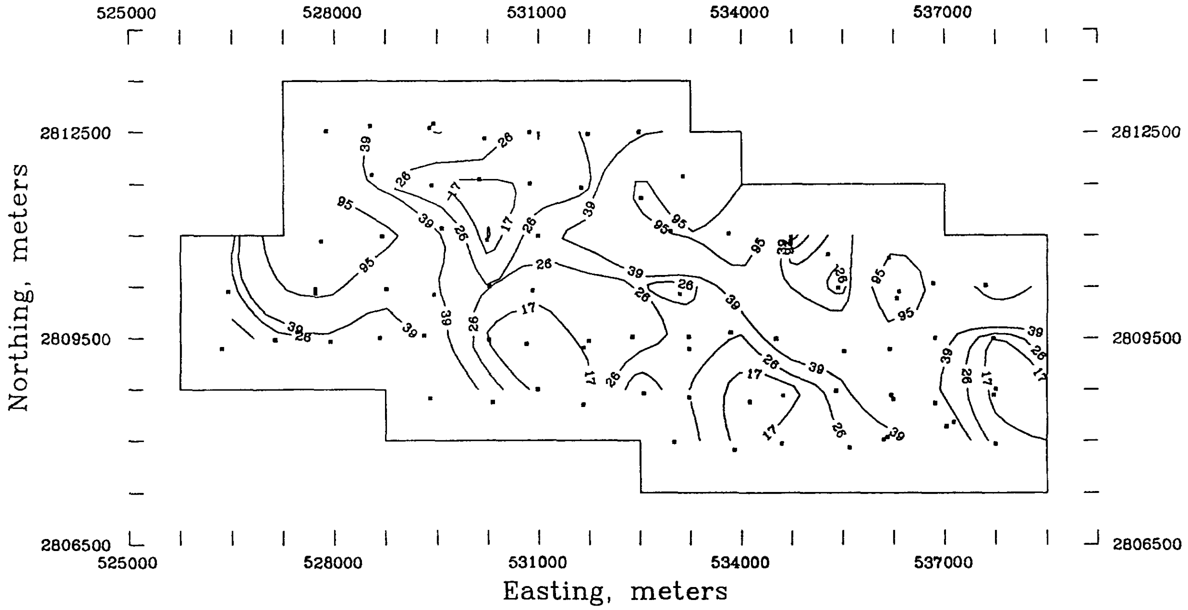


Figure 9. Continued.

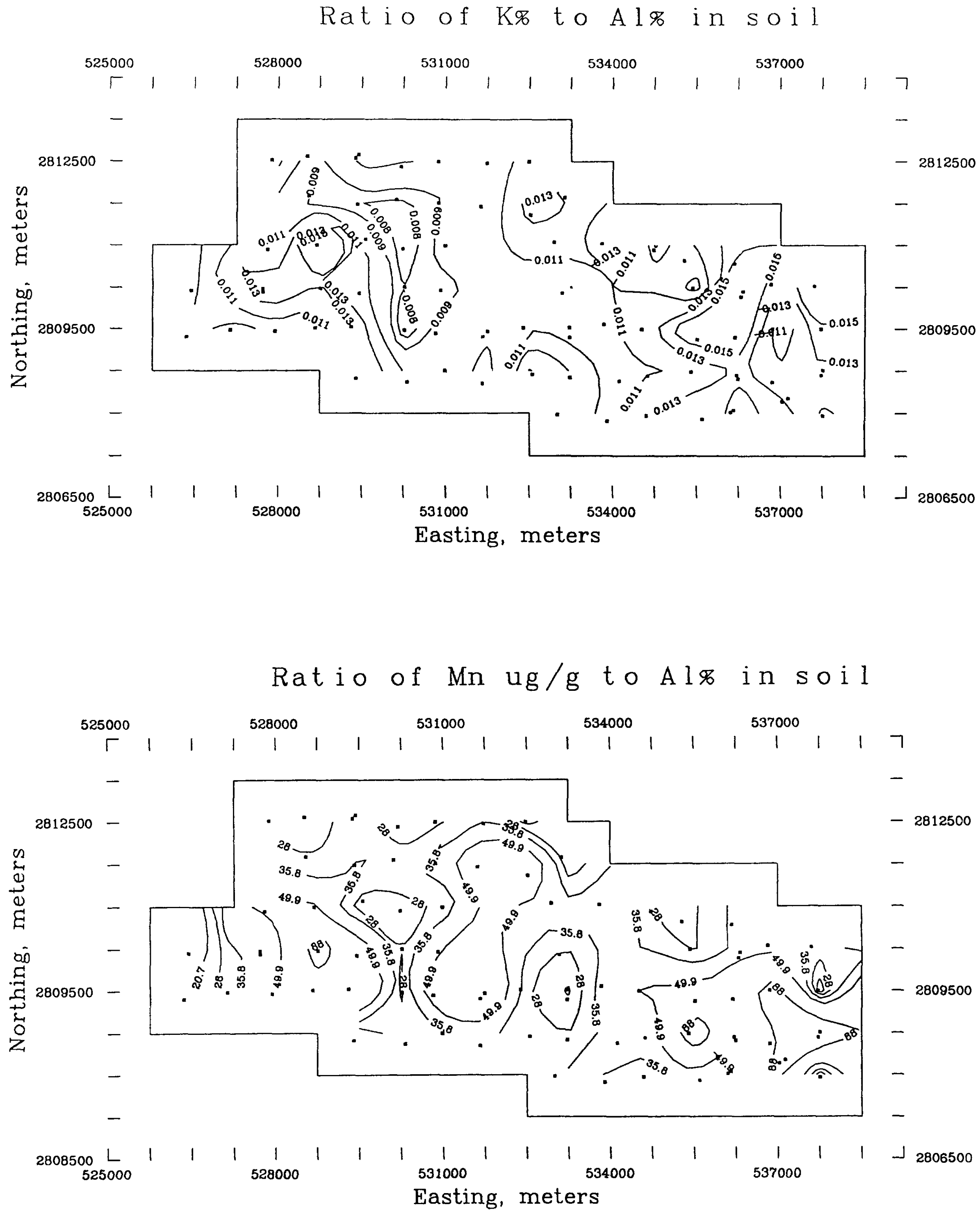
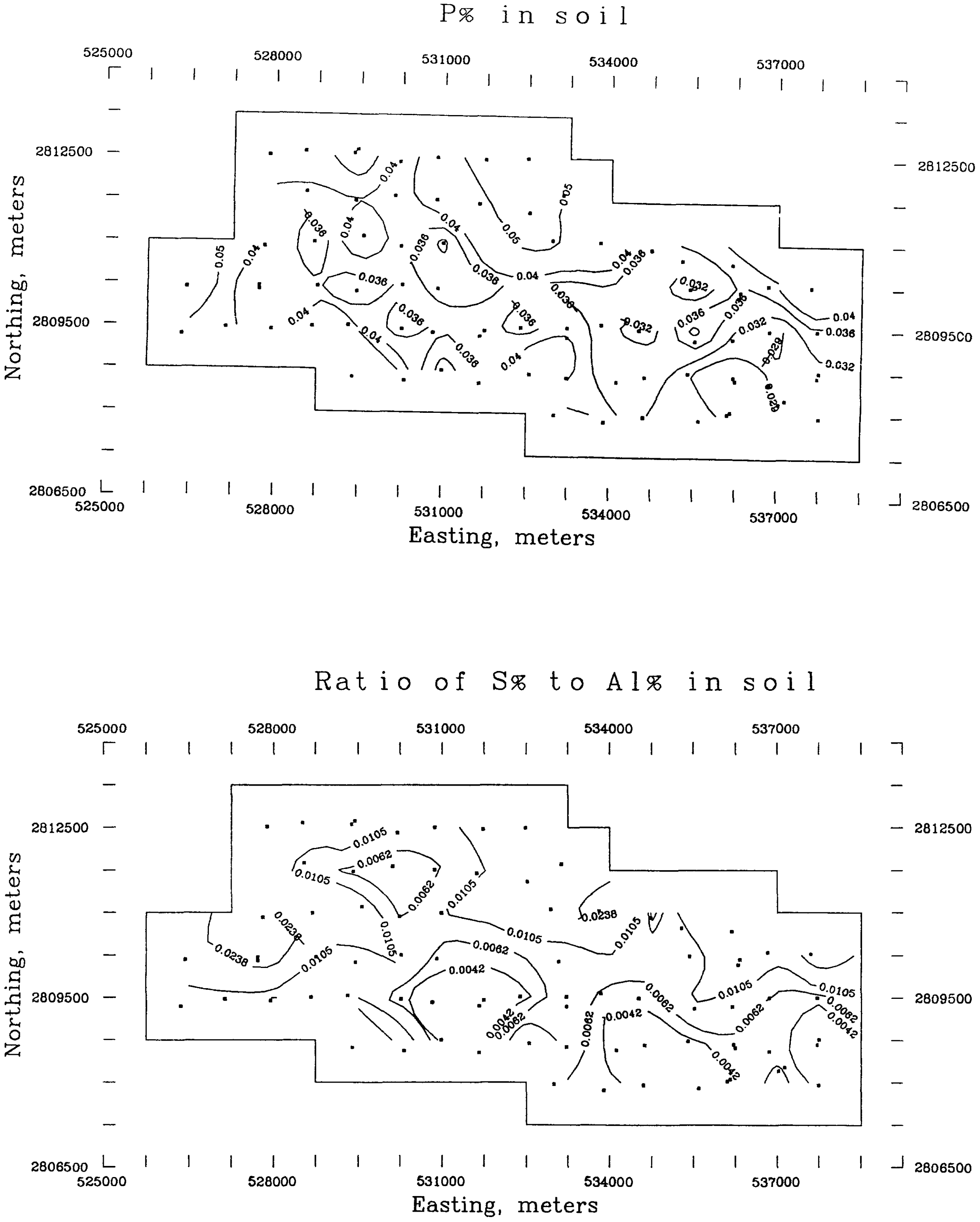


Figure 9. Continued.


P% in soil

Ratio of S% to Al% in soil

Figure 10. Distribution map of P concentration and S/Al, and Zn/Al concentration ratios in rockland soils (Principal Component II).

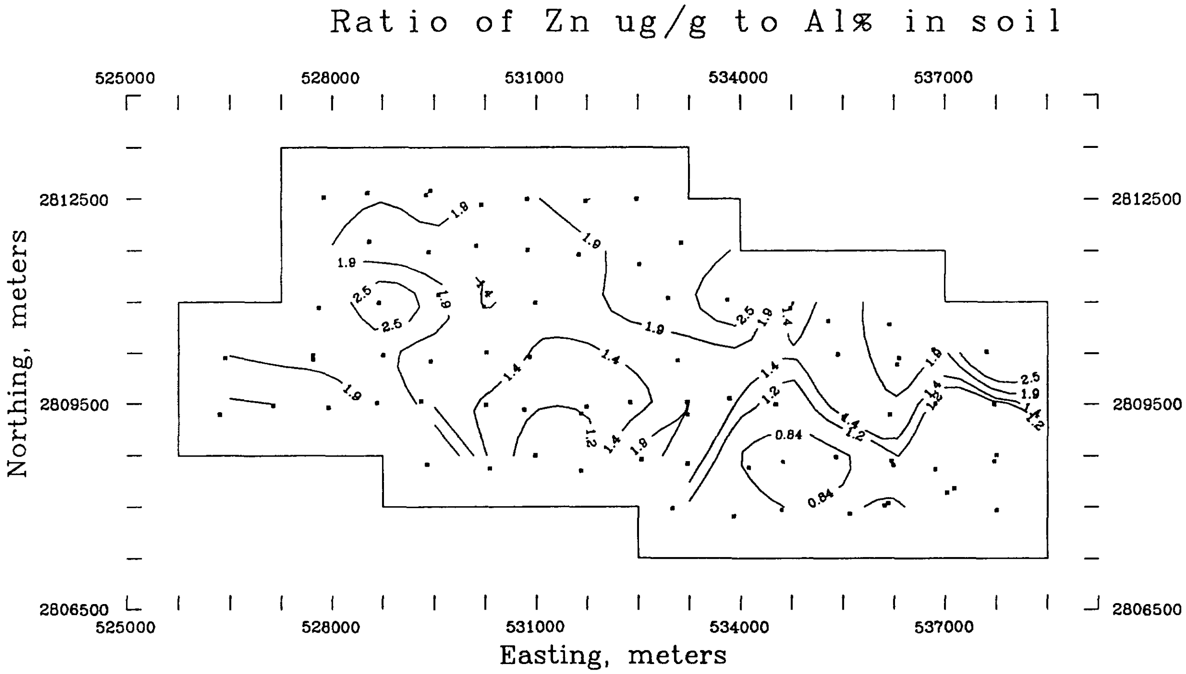
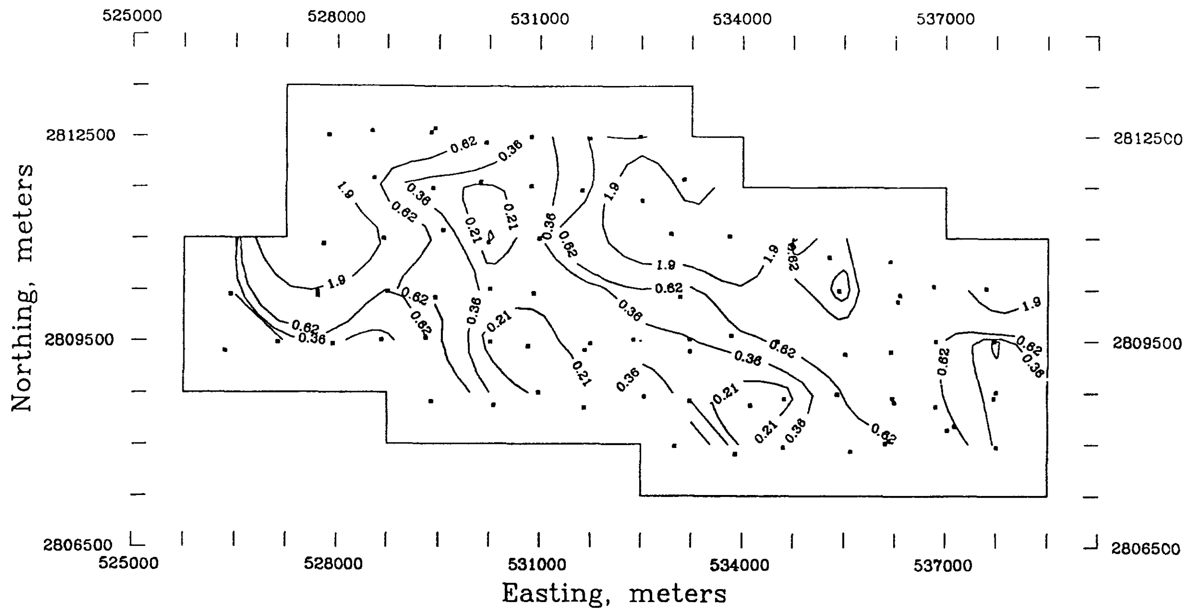


Figure 10. Continued.

Ratio of Ca% to Al% in soil



Ratio of Pb ug/g to Al% in soil

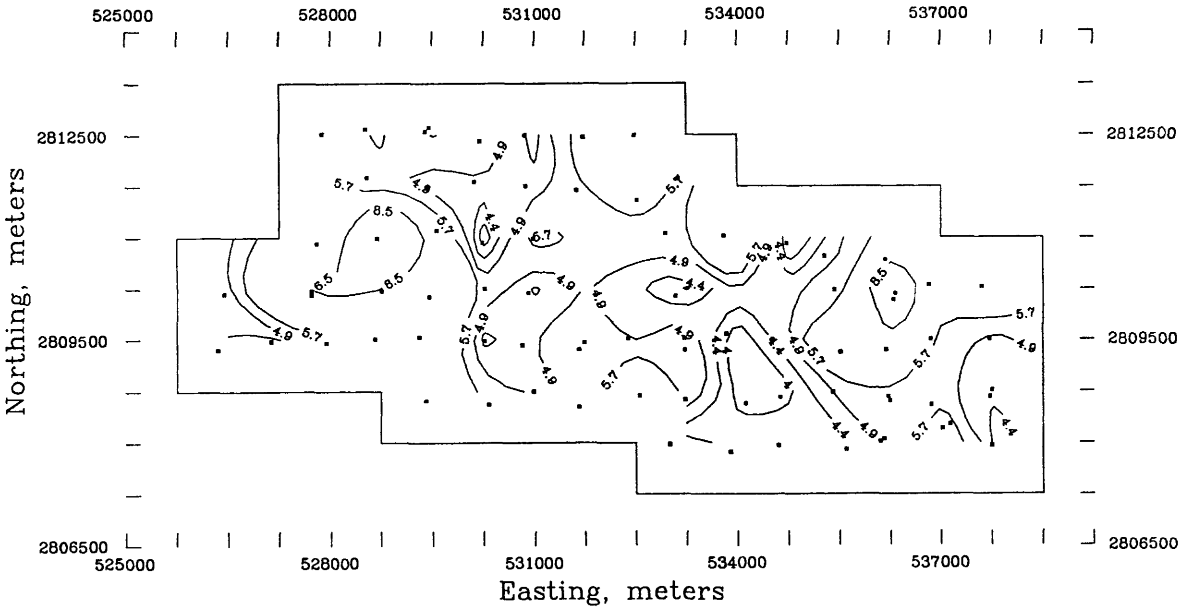


Figure 11. Distribution map of Ca/Al, and Pb/Al concentration ratios in rockland soils (Principal Component III).

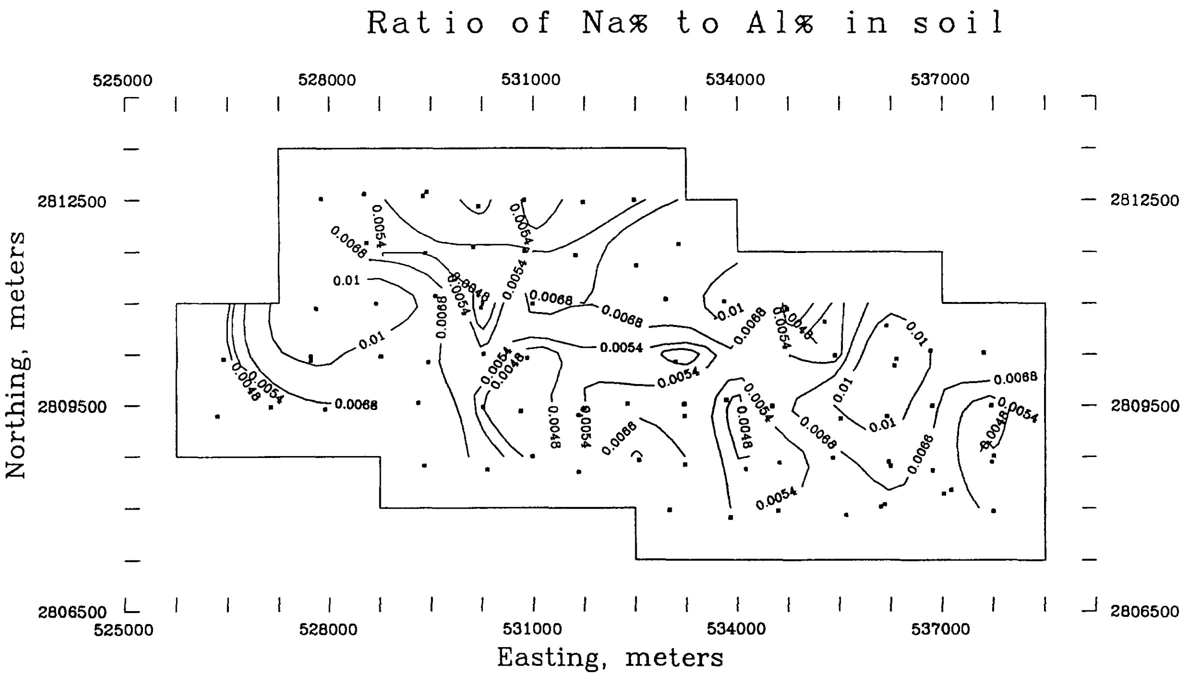


Figure 12. Distribution map of Na/Al concentration ratio in rockland soils (Principal Component IV).

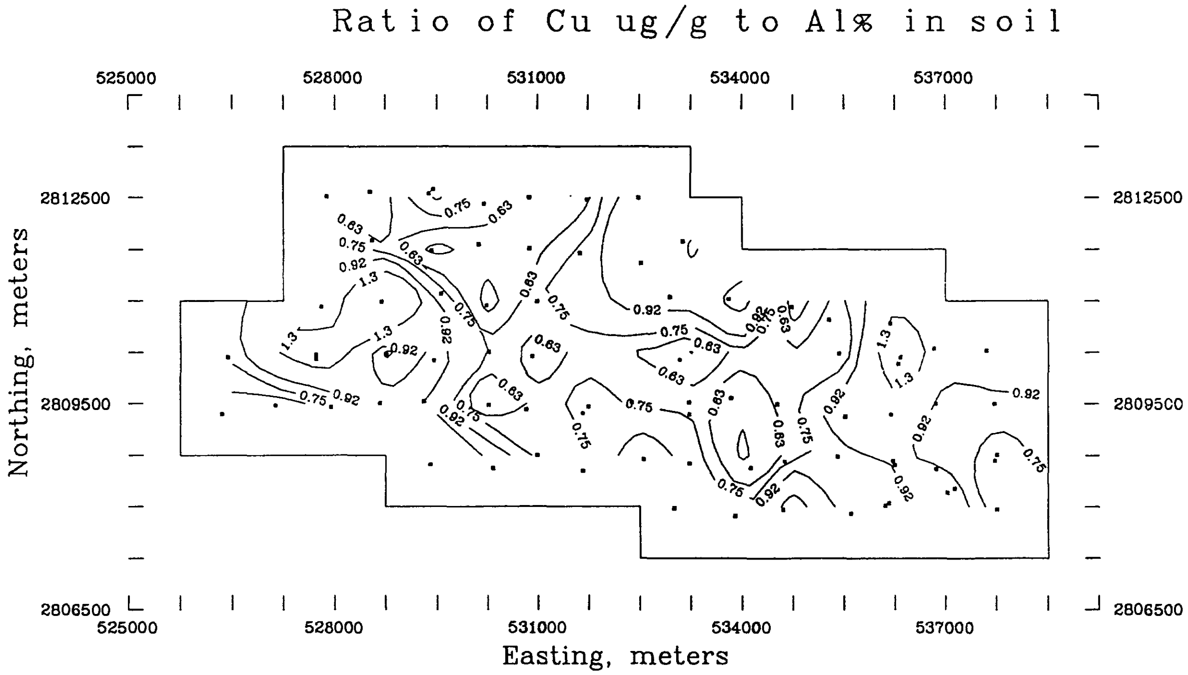


Figure 13. Distribution map of Cu/Al concentration ratio in rockland soils (Principal Component V).

Interpreting the spatial trends is difficult. The Long Pine Key area is small and trends in the data are hard to discern. The trends that have been discussed above seem to indicate that ecotonal areas near the edges of the key or in the vicinity of glades may be somewhat different than more interior portions of the key. These edge affects may be a result of differences in elevation, surface topography of the limestone substrate, and hydrologic inputs. Minor elevation differences of less than 50 cm have been measured for transitions from pinelands to glades (Olmsted and others, 1983). Surface water flow is generally from north to south in this portion of EVER. As a result, the higher pine needle and soil P content along the northern edge of the key may be from agricultural/urban runoff that has been a problem in more northern portions of EVER (Reddy and others, 1993), but there is not direct evidence for that in this work. The proximity of the former farming activity along the southern edge of the key does not appear to have influenced the pine or soil chemistry in any detectable way. However, the drainage from these lands was probably more to the south away from the pinelands.

Because fire is a critical agent in this ecosystem and Long Pine Key has had an active fire management program for some time (Hofstetter, 1984), fire history was examined as a potential influence on the spatial trends in the pine and soil chemistry. Long Pine Key has been divided into 12 main fire management blocks which have been burned on a rotating basis about every five years. Our sample sites were classified as to fire history based on the last prescribed burn for a given block (EVER draft fire management plan, 1989, J. Stenberg, personal communication). For classification, all sites within a fire block were assumed to have been burned during a prescribed burn, although an entire block was never uniformly burned. Spearman's rank correlation coefficients were calculated for years since last burn versus element concentrations in pine needles and soils. No significant correlations were found between fire history and pine or soil chemistry ($p=0.001$). This may be the result of fire being a constant agent throughout the ecosystem and the fact that most sites had experienced one or more rainy seasons since the last burn. The rapid leaching away of the more soluble salts in the fire ash may have tended to make most of the sites appear relatively uniform with respect to fire history.

Element enrichment in pine needles and rockland soils

The mean element concentrations in slash pine needles from this study have been compared with concentrations observed in a very limited sampling of slash pine from South Dade County, Florida (Gough and others, 1986), with a more extensive sampling of loblolly pine (*Pinus taeda*) from a small barrier island near Charleston, South Carolina (Gough and others, 1993), and with a different slash pine subspecies (*Pinus elliottii* Engelm. var. *elliottii*) from northern Florida that had been treated for 16 years with municipal garbage composted with sewage sludge (Jokela and others, 1990). As seen in Table 11, with the exception of S, Ca, and Sr, the mean concentrations of elements in the EVER rockland pines were within or below the observed ranges for elements in slash pine at three locations in the urban and agricultural areas of South Dade County. The mean S concentration in the rockland pines was only slightly higher than the maximum observed in slash pine at three locations in South Dade County. Calcium and Sr also averaged higher in our larger study within EVER. Lead in the EVER pines was almost five times lower than the minimum observed in the nearby urban area. Copper and zinc were also lower in the EVER pines.

In comparison with a different pine species, the EVER slash pine needles had about the same mean concentrations for many elements as the South Carolina loblolly pine needles. The elements, Ca and Sr, that are associated with the limestone terrain are clearly enriched in the slash pine compared to the loblolly pines growing in sandy soils. Sodium is also enriched in the slash pines several-fold, despite the closer proximity of the loblolly pines to the ocean. Chromium, Cu, Ni, and Zn were about equal to or lower in the slash pine than the loblolly pine. Lead was slightly higher in the slash pine.

Arsenic and mercury were also determined in the barbell subset of the slash pine samples, but not in any of the other pine studies. Arsenic was below the analytical limit of determination (i.e., <0.05 μg/g) for all twenty samples in the barbell subset. Our detection limit is near the minimum of the observed As concentration range (0.009 - 1.5 μg/g) for vegetation grown in uncontaminated soils (Kabata-Pendias and Pendias, 1992). Thus, As contamination from industrial or agricultural emissions does not appear to be significant at this time.

Table 11. Comparison of element concentrations in EVER slash pine needles with other pine data.

	Slash Pine, FL			Loblolly Pine, SC[3]
	EVER[1]	So Dade County Urban/Agricultural[2]		
Element	Geometric mean	Minimum	Maximum	Geometric mean
Ash%	2.25	1.7	2.3	3.2
S%	0.09	0.016	0.082	0.12
Al μg/g	40	46	76	170
Ca μg/g	4400	2000	4200	2100
Fe μg/g	43	41	56	49
K μg/g	1700	1200	5200	3800
Mg μg/g	1500	1100	2000	1400
Na μg/g	1700	480	2500	480
P μg/g	540	320	560	1500
Ba μg/g	0.46	0.44	0.76	0.30
Co μg/g	0.08	0.04	0.08	0.13
Cr μg/g	0.19	<0.26	0.40	0.26
Cu μg/g	2.3	3.4	7.9	2.9
La μg/g	0.1	-	-	0.12
Mn μg/g	24	11	140	190
Ni μg/g	0.18	-	<0.52	0.19
Pb μg/g	0.29	1.4	3.8	0.25
Sr μg/g	44	5.0	28	4.9
V μg/g	0.1	-	<0.56	≤0.19[4]
Zn μg/g	8.5	12	44	30

[1] From Table 2, n = 85.

[2] Observed range from Gough and others (1986), n = 6, sampling of 2 trees at 3 locations.

[3] From Gough and others (1993), n = 59.

[4] Maximum observed range.

The mean Hg concentration in the pine needles was 0.04 μg/g with a range of 0.02-0.06 μg/g. The mean Hg concentration in grains and other foodstuffs from uncontaminated sites is typically 0.01-0.02 μg/g or lower (Kabata-Pendias and Pendias, 1992). Mercury in alfalfa and grasses has been observed at 0.04-0.05 μg/g (Kabata-Pendias and Pendias, 1992). The slash pine Hg concentration is somewhat higher than the foodstuffs, but about the same as in grasses. The slash pine Hg concentration is also lower than the concentration generally found in a wide variety of plant species that are grown in contaminated areas (Kabata-Pendias and Pendias, 1992). For example, pine needles from mining and metal producing areas and from volcanic areas (typically areas with naturally elevated Hg levels) in Italy ranged from 0.2-11.4 μg/g and 0.007-0.027 μg/g, respectively (Kabata-Pendias and Pendias, 1992). Pine needles from volcanic areas in Hawaii were somewhat higher than in Italy with a range of 0.031-0.33 μg/g (Kabata-Pendias and Pendias, 1992). Without additional data, it is difficult to assess if the slash pine Hg concentrations are elevated above natural background values, but the pines do not appear to be highly contaminated.

In general, for the pines there appears to be little, if any enrichment of elements that can be clearly attributed to anthropogenic sources. Copper, Pb, and Zn appear to be lower than found in a limited sampling of pines in the nearby agricultural/urban area. Chromium, Ni, and V also may be lower in EVER. As noted above, additional data needs to be gathered before Hg enrichment can be adequately assessed.

In a similar fashion to the pines, the EVER rockland soil data were also compared with other soil data sets. Very limited data are available for comparison. Element concentrations in EVER soils have been compared with mineral soils from 14 locations in South Dade County (locations with generally greater soil development than in EVER, Gough and others, 1986) and with 541 soils from the Eastern U.S. (Shacklette and Boerngen, 1984) (Table 12). The latter samples were collected from largely native, undisturbed soils between 1961 and 1975. Because of the large differences in Al concentration in the EVER and Eastern U.S. soils, the element to Al ratios have also been examined for these data sets.

For the EVER soils, only a few elements, Fe, Mg, Ce, Co, Nb, Nd, and V, had mean concentrations greater than the maximum observed in the South Dade County soils. However, more than twenty elements had greater mean concentrations in the EVER soils than the Eastern U.S. soils. This is not surprising, because most of these elements are highly correlated with soil Al concentrations and the EVER Al concentration was about 2.5 times greater than Al in the Eastern soils. When comparing element/Al ratios, more than half the elements were depleted in the EVER soils. Calcium, Li, and Sr, elements that would be expected to be elevated in a marine carbonate terrain, were enriched two- to four-fold in the EVER soils. Chromium, Ni, and Pb were also enriched between 1.3 and 2 times, whereas Zn was lower by more than a factor of ten in the rockland soils. Sulfur in the EVER soils was also lower than in the Eastern soils.

Arsenic and Hg were determined in the EVER soils on the barbell subset of samples at eight grid locations. The EVER geometric mean As concentration was 11 μg/g with an observed range of 4.7-20 μg/g. Eastern U.S. soils had a more than two-fold lower mean concentration of 4.8 μg/g (Shacklette and Boerngen, 1984). However, the EVER soil barbell As/Al ratio was 1.49 which was about equal to the Eastern soils ratio of 1.46. The mean concentration of As in soils throughout the world is about 7 μg/g (Adriano, 1986). Agricultural soils (potato crops)

Table 12. Comparison of element concentrations in EVER rockland soils with other soil data.

	Mineral Soils, FL			Eastern US[3]	Pearson correlation coefficient	Element/Al ratios[4]	
Element	EVER[1] Geometric mean	So Dade County[2] Minimum	Maximum	Geometric mean	(M:Al)	EVER	Eastern US
Ash%	64.2	-	-	-	0.70	7.6	-
S%	0.06	<0.005	0.25	0.10	-0.46	0.007	0.030
Al%	8.5	0.07	9.4	3.3	-	-	-
Ca%	3.9	1.1	35	0.34	-0.73	0.46	0.10
Fe%	4.4	0.12	3.9	1.4	0.98	0.52	0.42
K%	0.096	<0.05	0.19	1.2	0.69	0.011	0.36
Mg%	0.55	0.08	0.48	0.21	0.89	0.065	0.064
Na%	0.054	0.02	0.24	0.25	0.10	0.0064	0.076
P%	0.034	0.006	0.19	0.020	-0.11	0.004	0.0061
Ti%	0.5	<0.005	0.54	0.28	0.99	0.059	0.085
Ba μg/g	56	15	120	290	0.69	6.6	88
Be μg/g	2	<1	2	0.55	0.95	0.24	0.17
Ce μg/g	98	<4	85	63	0.95	12	19
Co μg/g	6.5	1	6	5.9	0.94	0.76	1.8
Cr μg/g	170	2	220	33	0.99	20	10
Cu μg/g	7	<1	57	13	0.14	0.82	3.9
Eu μg/g	2	-	-	-	0.92	0.24	-
Ga μg/g	14	<4	16	9.3	0.99	1.6	2.8
La μg/g	48	<2	48	29	0.97	5.6	8.8
Li μg/g	93	<2	110	17	0.99	11	5.2
Mn μg/g	340	51	810	260	0.53	40	79
Nb μg/g	18	<4	15	10	0.94	2.1	3.0
Nd μg/g	46	<4	43	46	0.96	5.4	14
Ni μg/g	48	2	53	11	0.99	5.6	3.3
Pb μg/g	46	4	130	14	0.62	5.4	4.2
Sc μg/g	15	<2	15	6.5	0.99	1.8	2.0
Sr μg/g	260	83	1200	53	-0.79	31	16
Th μg/g	14	<4	15	7.7	0.98	1.6	2.3
V μg/g	92	<2	76	43	0.98	11	13
Y μg/g	50	<2	57	20	0.96	5.9	6.1
Yb μg/g	4	<1	4	2.6	0.94	0.47	0.79
Zn μg/g	13	<4	64	65	0.37	1.5	20

[1] From Table 4, n = 85.

[2] From Gough and others (1986), n = 28, sampling of 2 soil pits at 14 locations.

[3] From Shacklette and Boerngen (1984), n = 70 to 541.

[4] Element geometric mean/Al geometric mean.

in Florida exhibited As concentrations of 8 and 18-28 μg/g for non-treated and As pesticide and defoliant treated soils, respectively (Adriano, 1986). Arsenic contaminated soils tend to range from ten to hundreds of micrograms per gram (Kabata-Pendias and Pendias, 1992). Thus, it appears that the EVER soils are not highly contaminated with As, but that As in some of the EVER soils may be elevated above natural concentrations.

Mercury concentrations in the EVER soils ranged from 0.08-0.5 μg/g with a mean concentration of 0.21 μg/g. Shacklette and Boerngen (1984) estimated a mean concentration of 0.081 μg/g with a range of 0.01-3.4 μg/g for 534 Eastern soil samples. Mercury in noncontaminated soils is generally in the range of 0.05-0.3 μg/g, although histosols and other organic-rich soils may have higher Hg content on the order of 0.4 μg/g (Kabata-Pendias and Pendias, 1992). The mercury concentration in the limited number of EVER soil samples analyzed may be bimodally distributed (Figure 14). The arithmetic mean concentration for samples in the lower portion of the distribution ([Hg] < 0.25 μg/g) was 0.13 ± 0.03 μg/g (n=10) and in the upper portion was 0.44 ± 0.06 μg/g (n=6). The samples with the higher Hg concentrations appear to be randomly scattered throughout Long Pine Key with differences in concentration occurring at 10-100 m (Figure 15).

The difference in Hg concentration between sample splits varied from 0.02 to 0.13 μg/g with an average of 0.08 μg/g for the four pairs analyzed. The analysis of standard reference soils gave acceptable results for Hg. Thus, analytical error does not appear to be a major contributor to these differences in soil Hg concentrations. Although differences in soil organic matter are a common cause for differences in Hg concentrations, the pineland soil Hg concentrations do not correlate with any other soil parameter measured. Nevertheless the higher concentrations of Hg in the EVER soils appear to be elevated sufficiently to suspect anthropogenic contamination. Additional research is required to truly evaluate whether the Hg is present at naturally occurring levels.

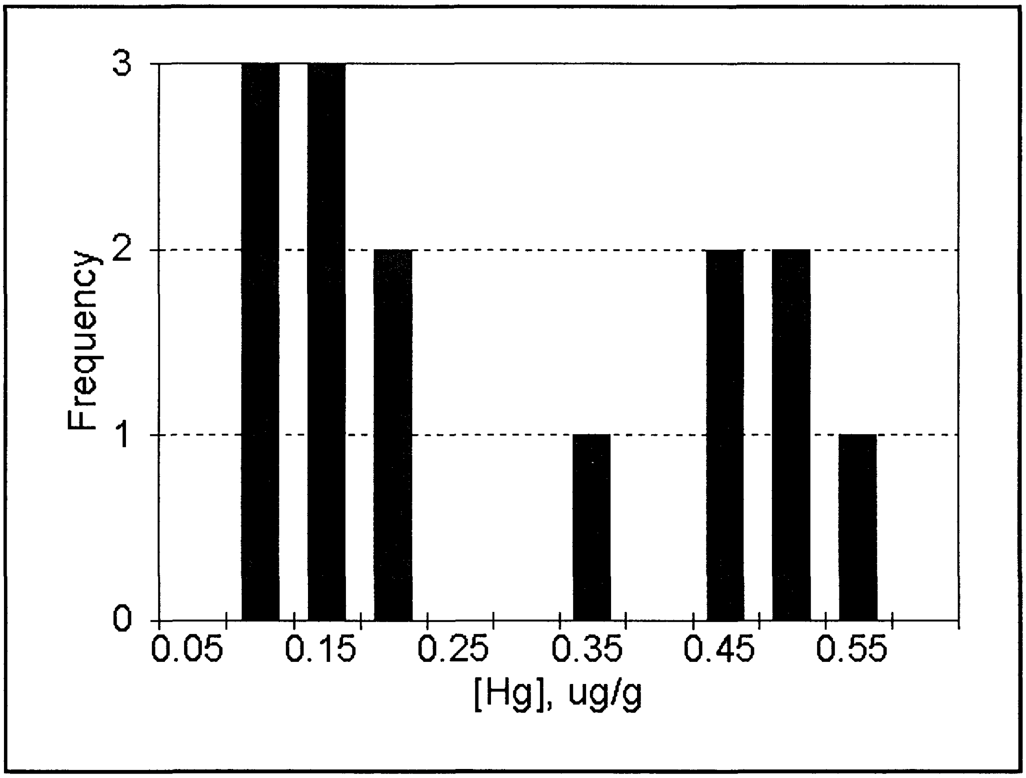


Figure 14. Frequency distribution of Hg concentration in rockland soils.

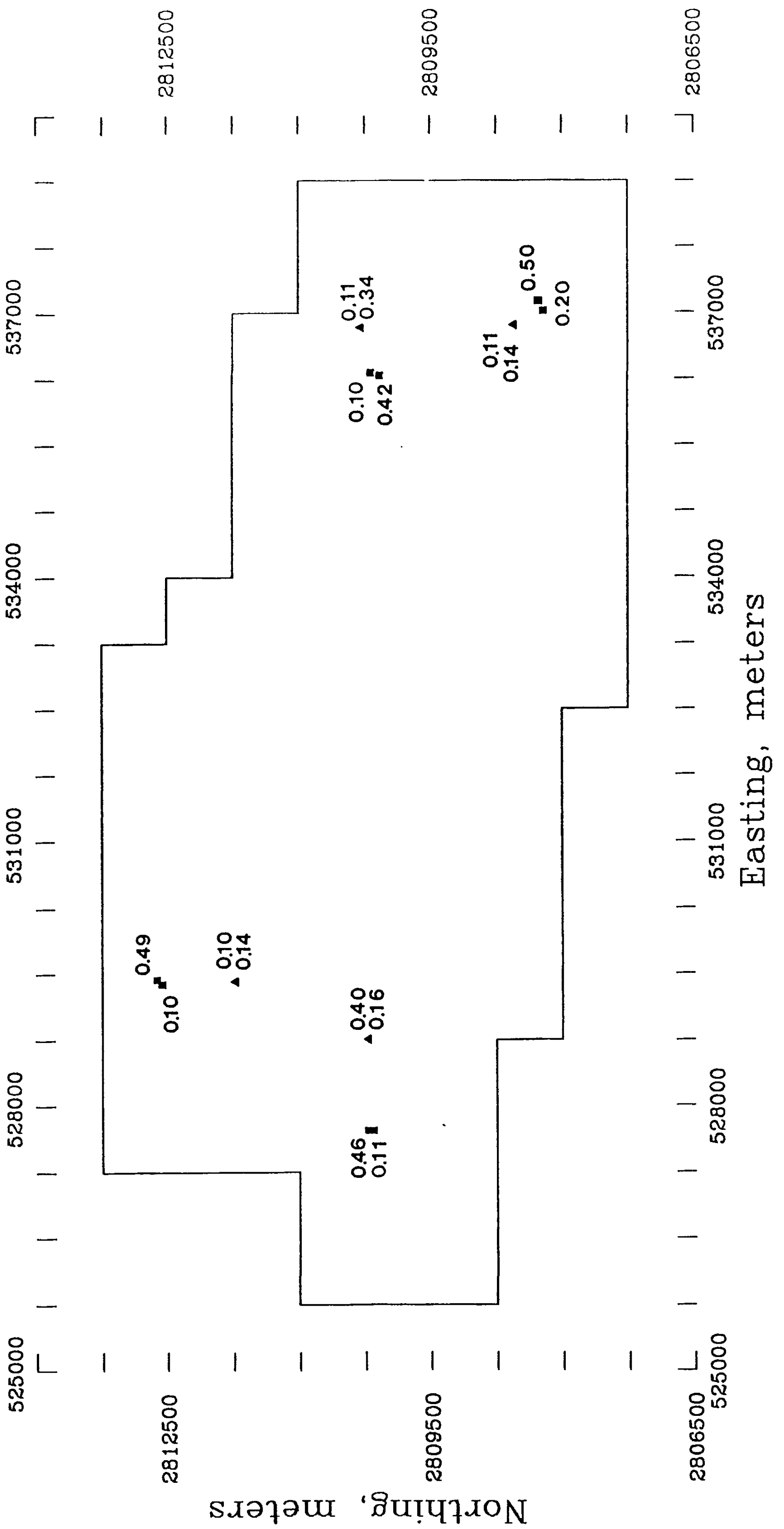


Figure 15. Distribution map of Hg concentration in soils from barbell sampling (■ = 100 m replicates, ▲ = 10 m replicates).

Stable sulfur isotope ratios

The use of stable sulfur isotope ratios in ecosystems is a unique method for studying biogeochemical processes and sulfur distribution from different sources. Because of differences in reaction rates, many biological reactions fractionate the stable sulfur isotopes and produce a wide range of sulfur isotope ratios in nature. Biologically mediated anaerobic sulfate reduction is the major sulfur isotope fractionating process. The sulfate reduction process produces sulfide that is enriched in ^{32}S and residual sulfate that is enriched in ^{34}S. Because of the importance of anaerobic sulfate reduction in the global sulfur cycle, a wide range of sulfur isotope ratios occur in natural inorganic and organic products. It is the difference in the sulfur isotope ratios in nature that makes sulfur isotope ratio measurements useful in environmental studies[4] (Jackson and Gough, 1989; Krouse, 1989).

In order to use stable S isotope ratios to understand biogeochemical processes or atmospheric dispersion of S, the isotopic ratios of the different S sources must be known, the isotopic ratios of the S sources must be different from each other, and potential isotopic fractionation processes during physical and chemical transformations must be well understood (Calhoun and Bates, 1989). Despite the stringent restrictions that these three conditions place on the use of S isotope ratios, a large number of environmental studies have made successful use of S isotope ratios to define anthropogenic influences and to elucidate biogeochemical processes. Jackson and Gough (1989) have reviewed the application of stable sulfur isotope ratios for use in air pollution studies with respect to the South Florida environment.

In this study, stable S isotope ratios were determined on 10 pine needle and 9 soil samples. The samples were primarily selected from sites used in the barbell sampling. The $\delta^{34}S$ isotope ratios in the pine needles had a range of +1.1 to +4.1‰ with an average of +2.6 ± 1.1‰. The soils had somewhat isotopically heavier ratios with a range of +2.9 to +9.8‰ and an average of +7.0 ± 2.1‰. The distribution of samples and their isotope ratios are shown in Figures 16 and 17. There are no readily identifiable spatial trends in the isotope ratios for either the pine needles or the soils. For the eight sites where we were able to determine the stable S isotope ratios on both the pine needles and the soils, we found no strong relationship between the isotope ratios in the two media (Figure 18).

The isotopic signature for the pine needles implies that the pines are taking up sulfur from ground water, rain, soil solution, and/or the atmosphere that is isotopically lighter than the bulk soil. Pines have been found to generally have isotopic signatures intermediate between soil and atmospheric sources of sulfur (Krouse and others, 1984). Anthropogenic sources of S arise largely from fossil fuel combustion. The isotopic signature of most fuels tend toward lighter $\delta^{34}S$ values as a result of their biogenic origin. Based on studies of the isotopic ratios of SO_2 in populated areas, Calhoun and Bates (1989) suggest that anthropogenic emissions of S are

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[4] The sulfur isotope ratio is measured in the sample relative to the isotope ratio in a meteoritic troilite standard. The enrichment factor determined is expressed as $\delta^{34}S$ in parts per thousand (‰) or per mil.

$$\delta^{34}S\ ‰ \quad \left[\frac{(^{34}S/^{32}S)_{sample}}{(^{34}S/^{32}S)_{meteorite}} \quad 1\right] x\ 1000$$

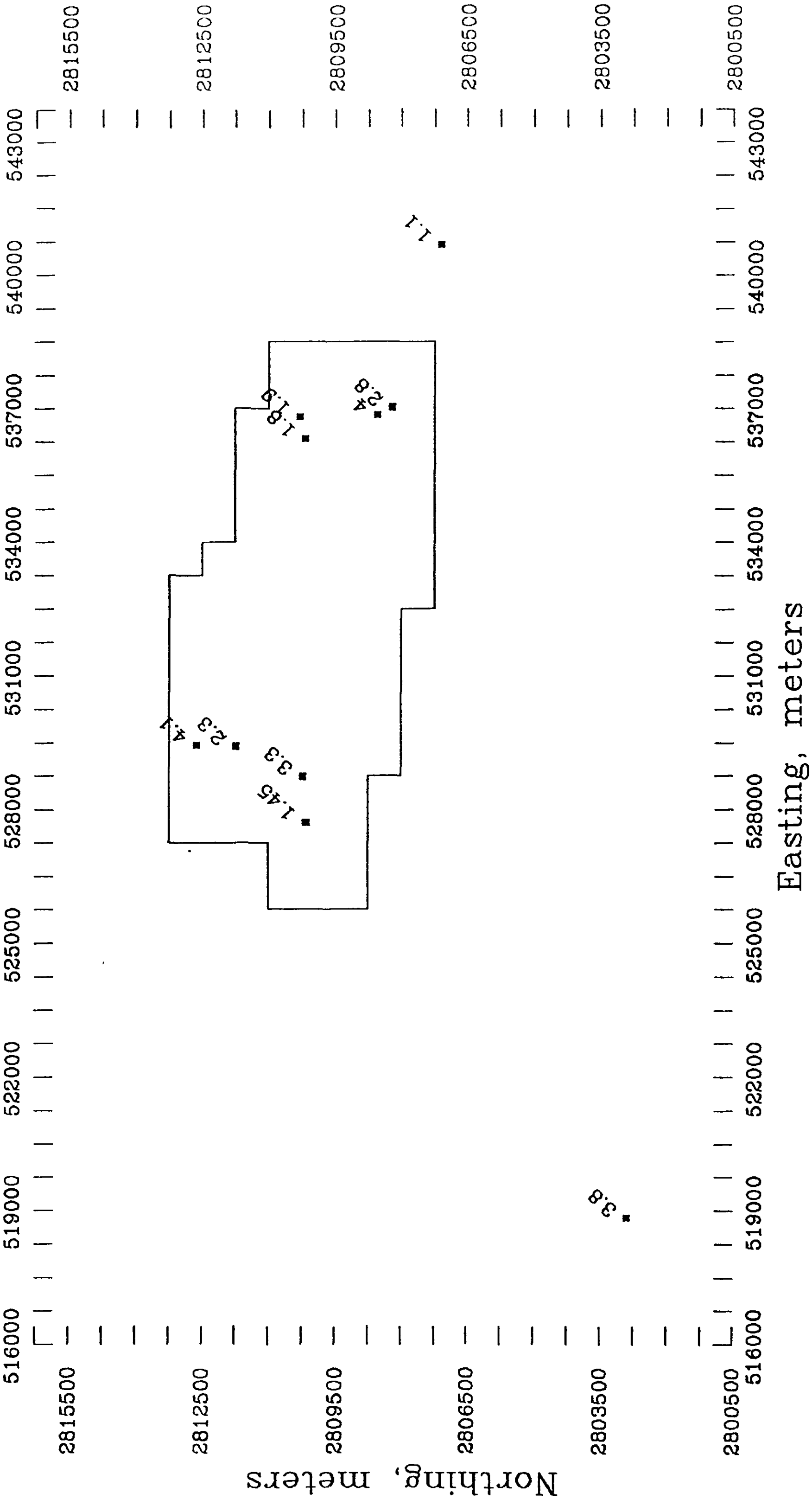

Figure 16. Stable S isotope ratios ($\delta^{34}S$‰) in pine needles.

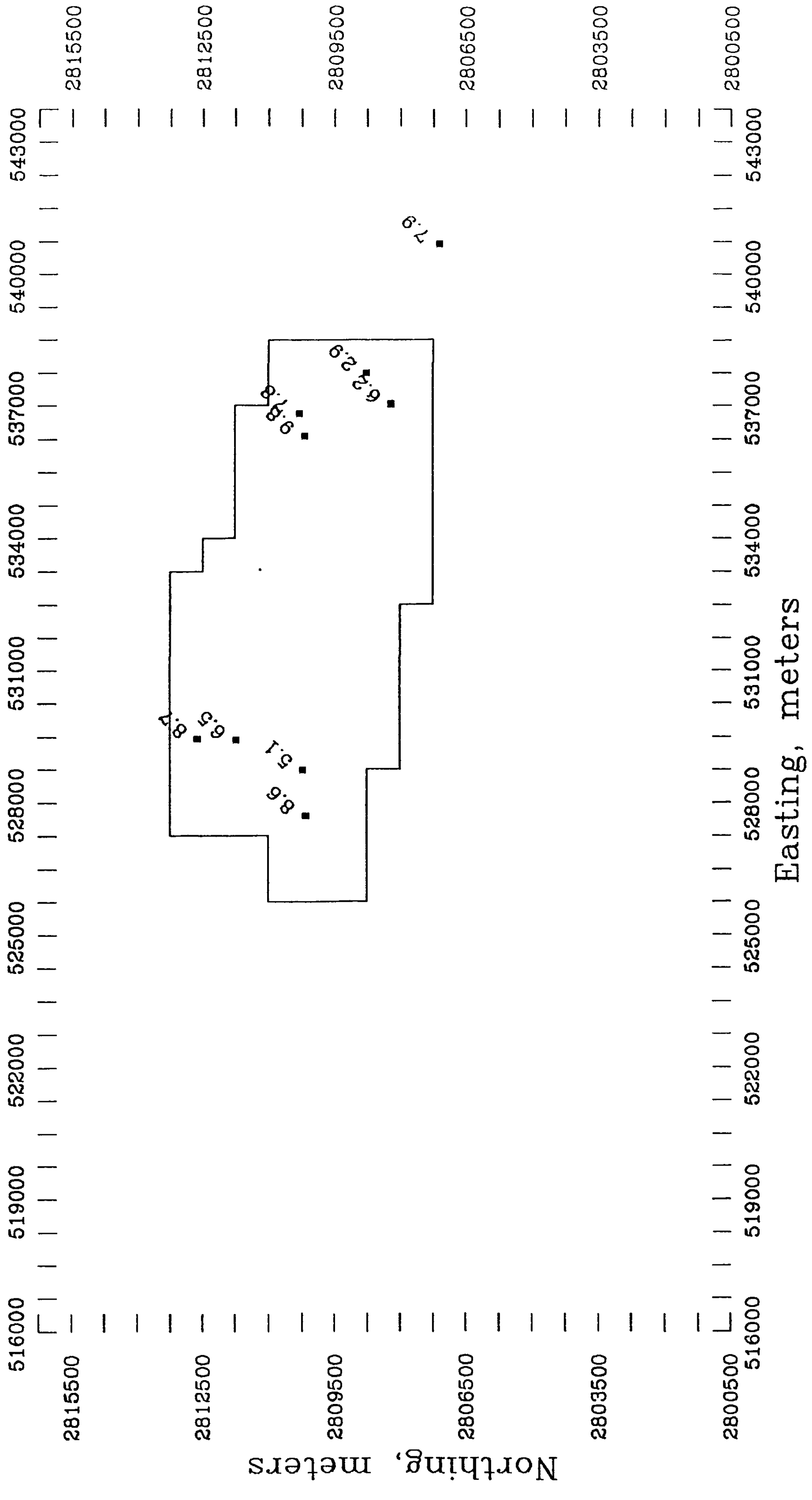

Figure 17. Stable S isotope ratios ($\delta^{34}S$‰) in rockland soils.

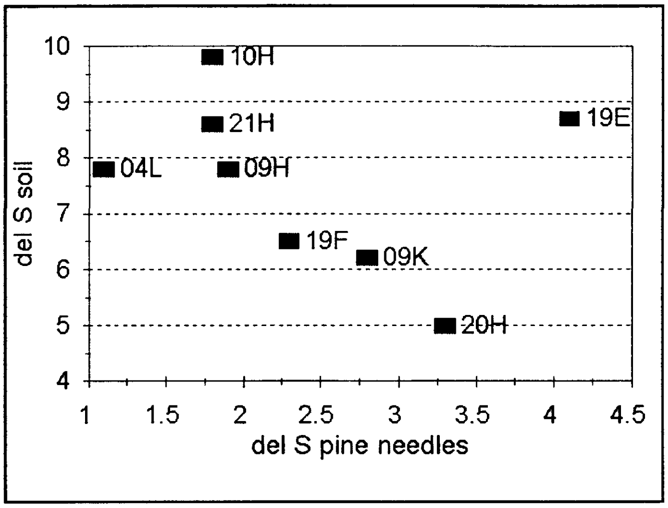

Figure 18. Stable S isotope ratios ($\delta^{34}S$‰) in soils versus pine needles (grid locations are to the right of each point).

likely to have $\delta^{34}S$ values of -2 to +6‰ prior to atmospheric oxidation. Continental rainfall typically has isotopic signatures of about +2 to +10‰, whereas oceanic rainfall generally has a heavier signature closer to that of seawater (Jackson and Gough, 1989). In this study, stable sulfur isotope ratios for other sources of S than the soils were not measured.

Gough and others (1986) previously measured sulfur isotope ratios in slash pine needles at three locations, in organic rich soils at three locations, and in mineral soils at six additional locations in South Dade County. All soil samples were collected at different locations than the pine samples. The locations extended from about the eastern edge of EVER eastward to the coast. The range and average $\delta^{34}S$ isotope ratio for the pines were +10.1 to +18.3‰ and +13.8 ± 3.3‰, respectively. For the organic-rich soils the range of isotope ratios was +9.0 to +16.8‰ with an average of +13.2 ± 3.9‰. The range and average for the six mineral soils were +7.0 to +16.8‰ and +10.9 ± 2.2‰.

The isotope ratios, in this study, for the pines and the soils were more negative than the results observed by Gough and others (1986) for sites in South Dade County. In general, sites closer to the coast may exhibit a more positive sulfur isotope ratio owing to greater influence from sea salt spray. Sea water sulfate typically has an isotope ratio of about +21‰ (Rees and others, 1978; Chukhrov and others, 1978). However, if proximity to the ocean were the only factor, samples from coastal islands would have heavy isotopic signatures close to that of seawater (Chukrov and others 1978; Krouse, 1989). One sample of slash pine needles from Big Pine Key (latitude 24°41'43", longitude 81°22'19", Florida Keys, Monroe County, FL) was also collected during the same time period as the remainder of the samples in this study. The stable S isotope ratio for the Big Pine Key sample was +4.0‰. The isotope ratios for loblolly pine needles sampled on a barrier island and nearby coastal locations in South Carolina were about +2‰ (Jackson and others, 1993). Thus, it does not appear that differences in proximity to the ocean is a reasonable explanation for the disparities between this study and our earlier work.

Although possible, it seems unlikely that the average isotope ratio in the pine needles would be different by more than 10‰ between the two studies despite the differences in sample location and the intervening 6 yrs. There was also a difference of 4-6‰ for the soil samples. Laboratory biases between the two commercial laboratories that performed the stable isotope measurements may be a significant contributing factor. An isotopic shift of this magnitude is possible owing to environmental causes if there has been an equal shift in the hydrologic or atmospheric sources of S input into this environment. At this time, further research is required to evaluate whether there has been a significant shift in stable sulfur isotope ratios of the pines and soils. We doubt that is the case and suspect that laboratory biases may play a significant role in explaining the differences between the studies. Regardless of the differences between the studies, the data from this study suggest that there is an isotopically light hydrologic or atmospheric source of S for the pines compared to the bulk soil S.

SUMMARY AND CONCLUSIONS

- The largely second growth pinelands sampled in EVER were relatively uniform throughout the study area in regard to tree diameter. The greatest differences from one area to another were mainly in canopy and understory height. Soils throughout the pinelands exhibited little development and were present as a thin veneer or in pockets of the oolitic limestone.
- The ANOVA results indicated that the majority of element concentration variance was attributable to localized differences at distances of 10's to 100's of meters. This was particularly true for most elements in the soils. The barbell and grid study designs gave similar results in terms of spatial scales of variability.
- For most elements in the pines and soils, the barbell subset of samples produced mean concentrations that were within 5-10 percent of the means obtained from the larger grid study sampling. Thus, the concentration of several elements that were determined only in the barbell sample subset is likely to be relatively representative of the concentration in the larger pineland population. Baseline 95 percent expected concentration ranges were estimated for most elements that were determined in pine needles and rockland soils. Thus, the study objective regarding determining baselines element concentration ranges in pine needles and soils was met.
- Any future reevaluation of the chemistry of these pinelands must take into account the potential influence of Hurricane Andrew (August 1992) that occurred after our measurements were made.
- Principal component models generated for the pines, indicated that macro nutrients and micro nutrients accounted for most of the variance in the models, but no single component accounted for more than about 20 percent of the variance. Similar models for the soils demonstrated that Al and other major and trace elements that would be associated with silicate minerals explained most of the variability in the soils. A second, less important component of the soil models, was related the calcium carbonate content of the soils. There were some weak correlations between element concentrations in the pines and soils that may be related to nutrient uptake, but in general bioavailablity and nutrient cycling confound our ability to detect relationships.

- Spatial trends in element concentrations within Long Pine Key were examined by using contour maps. Two measures of map stability, both of which were based on the ANOVA results, gave equivocal results for stability of the maps of element concentration in the pines. Because of high localized variability in element concentrations, contour maps were produced for only 10 elements in pines and the reproducibility of these maps is unclear.
- The map stability indicators for elements in the rockland soils showed that only P was mappable unless the soil variability was reduced by normalizing to the Al content. Maps were produced for P, Al, and 15 elements ratioed to Al in the soils. As with the pines, the stability or reproducibility of these maps is unclear.
- One of our major objectives was to map the spatial distribution of elements in pine needles and soils. Biogeochemical maps were produced for a variety of elements in pine needles and soils. Although the map stability indicators gave equivocal results as to the confidence levels of the maps produced, the maps generally indicate that there are not dramatic differences in element concentrations in pine needles or soils within the pinelands that are obviously related to natural or anthropogenic influences
- Whereas the contour maps generally indicate that the element concentrations in the pines and soils are fairly uniform throughout Long Pine Key, there are some subtle manifestations of edge or ecotonal effects. For example, the somewhat higher P content in pine needles and soils along the northern edge of the key may be a result of agricultural/urban runoff. However, there is not direct evidence of that in this work. The previous farming activity along the southern portion of the key has not obviously influenced the pine or soil chemistry. Also, there is no evidence that fire history has had a significant effect on spatial trends in plant or soil chemistry.
- Most elements in the pines and rockland soils do not appear to be greatly anthropogenically enriched, but there are very limited data for comparison. For the pines, Cu, Pb, and Zn were lower than in a very limited sampling of more urban Dade County locations in a previous study. For the soils, Cr, Ni, and Pb may be enriched and S and Zn depleted compared to Eastern soils in general. Some elements, such as As in soils and Hg in the pines and soils, exhibited concentration levels that potentially indicate anthropogenic contamination. These elements, in particular, merit further study to adequately assess anthropogenic enrichment.
- Evaluation of element concentration levels and spatial trends for potential anthropogenic influences was one of the objectives of this project that was completed as outlined above. However, the evaluations were based on comparisons with data from other areas. These evaluations were hampered by the lack of prior background or baseline chemical data from EVER for comparison.
- Stable S isotope ratios were isotopically lighter in the pine needles than in the soils. This suggests that an isotopically lighter hydrologic or atmospheric source of S is significantly influencing the isotope signature of the pines compared to the bulk soils. Stable S isotope ratios in the pines and soils were isotopically lighter than found in an earlier study. Laboratory biases between the studies are suspected as a possible source of the differences.

- In general, the pinelands of EVER are relatively uniform in element concentrations and do not appear to be highly contaminated with any element that was measured in this study. Arsenic, Hg, and P concentrations in pines and/or soils and S isotope ratios merit additional research because their concentrations and regional patterns suggest anthropogenic influences.

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Appendix I: Chemical Analysis Results

INTRODUCTION

This appendix lists all chemical analysis results as reported by the laboratory for the pineland biogeochemical study at Everglades National Park (EVER). *Pinus elliottii* (slash pine) and rockland soils were analyzed as part of this study. The chemical analysis results, which are found in this appendix, are interpreted in other sections of this report. For interpretation purposes all chemical analysis results that were reported on an ash-weight basis as shown in this appendix were mathematically converted to a dry weight basis with maintenance of the appropriate number of significant figures. Also included in this appendix are summaries of quality control results from the analysis of National Institute of Standards and Technology (NIST, formerly the National Bureau of Standards) and Canadian Certified Reference Materials Project (CCRMP) standard reference materials that were submitted to the laboratory in each suite of plant and soil samples. All samples were analyzed in the Denver laboratories of the U.S. Geological Survey Branch of Geochemistry with the exception of the sulfur isotope analyses (Coastal Science Laboratories, Austin, Texas). Quality assurance (QA) and control (QC) practices and most of the analysis methods are provided in more detail in the quality assurance manual for the Branch of Geochemistry (Arbogast, 1990).

CHEMICAL ANALYSIS RESULTS

Table A1 describes the sample field number encoding schemes used for each sample type collected and Table A2 provides a summary of all samples collected. The lower detection limits for all elements and species determined are shown in Table A3. The chemical analysis results for the plant and soil samples are shown in Tables A4 and A5. Stable sulfur isotope ratios for the selected plant and soil samples that were analyzed are shown in Table A6.

Chemical analysis results for ash yield, sulfur, arsenic (by HGAAS), mercury, and forms of carbon are reported on a dry-weight basis, whereas all elements that were determined by ICP are reported on an ash-weight basis. As used in this report, dry-weight basis refers to air drying at ambient temperature for soils and at 40°C for plants; and not to a moisture free basis (i.e., drying at 105°C). This weight basis conforms to laboratory protocols for data reporting and data storage in the archival database. Elements listed in Table A3 that were below the detection limit for all samples were omitted from Tables A4 and A5 and blanks in the tables indicate elements that were not determined.

Arsenic was determined in selected samples by HGAAS and in all samples by ICP. The ICP-arsenic determination was performed on an ashed sample. Some arsenic was potentially lost during ashing. Thus, the ICP-arsenic results have not been used in the interpretative sections of this report, however, they are included in the raw data tables.

Table A1. Sample field number encoding.

Field number = A12B345

- A = sample type
  - P = *P. elliottii* needles
  - S = Soils
- 12 = sample grid number (03-35)
- B = sample grid letter (E-S)
- 3 = within grid replication at 100 m (1 or 2)
- 4 = among trees or soil pits site replication at 10 m (1 or 2)
- 5 = laboratory split (1 or 2), not used in the field

Example: P18G111 = *P. elliottii* needles collected at grid cell 18G.

Table A2. Summary of grid locations sampled.

Collection Sequence	Collection Date	Grid #	Split #	Replicates 100 m	10 m	Lab
1	03/30	9K	11			
2	03/30	9K	21	1		
3	03/30	9J	11			1
4	03/30	9J	12		1	
5	03/31	21H	11			
6	03/31	21H	21	1		
7	03/31	20H	11			
8	03/31	20H	12		1	1
9	03/31	19F	11			
10	03/31	19F	12		1	
11	04/01	10H	11			
12	04/01	10H	21	1		
13	04/01	9H	11			
14	04/01	9H	12		1	1
15	04/01	19E	11			
16	04/01	19E	21	1		1
17	04/03	33R	11			
18	04/03	20F	11			
19	04/03	18F	11			
20	04/04	10K	11			
21	04/04	10K	21	1		
22	04/04	11K	11			
23	04/04	12K	11			
24	04/04	13J	11			
25	04/04	12J	11			1
26	04/04	12I	11			1
27	04/05	11J	11			1
28	04/05	11I	11			1
29	04/05	9I	11			
30	04/05	10J	11			
31	04/05	10J	21	1		
32	04/05	10I	11			1
33	04/05	13I	11			
34	04/05	11H	11			
35	04/06	14J	11			
36	04/06	14I	11			
37	04/06	14I	21	1		
38	04/06	14H	11			
39	04/06	15I	11			
40	04/06	15J	11			
41	04/06	16I	11			
42	04/06	16I	21	1		
43	04/06	17I	11			
44	04/07	8K	11			
45	04/07	8J	11			
46	04/07	8J	21	1		
47	04/07	8J	22		1	1
48	04/07	16F	11			
49	04/07	17F	11			
50	04/07	17F	12		1	
51	04/07	17G	11			
52	04/07	17H	11			
53	04/08	16J	11			
54	04/08	17J	11			
55	04/08	18J	11			
56	04/08	19I	11			
57	04/09	23I	11			
58	04/09	23H	11			
59	04/09	22I	11			
60	04/09	21G	11			
61	04/09	21E	11			
62	04/10	11G	11			
63	04/10	12G	11			
64	04/10	13G	11			
65	04/10	13K	11			
66	04/12	18G	11			
67	04/12	19G	11			
68	04/12	19G	12		1	
69	04/12	20G	11			
70	04/12	20I	11			
71	04/12	20I	12		1	
72	04/13	14F	11			
73	04/14	15F	11			
74	04/14	15F	12		1	
75	04/14	21I	11			
76	04/14	21I	12		1	
77	04/14	19H	11			
78	04/14	14K	11			
79	05/05	8H	11			
80	05/05	14G	11			
81	05/05	17E	11			
82	05/05	20E	11			
83	05/08	18I	11			
84	05/08	19J	11			
85	05/09	16E	11			
86	05/09	18E	11			
87	05/09	18H	11			
88	05/10	10G	11			
89	05/10	15E	11			
90	05/15	8I	11			
91	05/15	3J	11			
92	05/15	3K	11			
93	05/16	34Q	11			
94	05/16	35S	11			
95	05/16	4L	11			

Table A3. Lower determination limits[1] for the analysis of plants and soils.

Inductively-Coupled Plasma Emission

Element	Plants	Soils	Element	Plants	Soils
Al %	0.1	0.05	Ga µg/g	8	4
Ca %	0.1	0.05	Ho µg/g	8	4
Fe %	0.1	0.05	La µg/g	4	2
K %	0.1	0.05	Li µg/g	4	2
Mg %	0.1	0.05	Mn µg/g	8	4
Na %	0.01	0.005	Mo µg/g	4	2
P %	0.01	0.005	Nb µg/g	8	4
Ti %	0.01	0.005	Nd µg/g	8	4
Ag µg/g	4	2	Ni µg/g	4	2
As µg/g	20	10	Pb µg/g	8	4
Au µg/g	16	8	Sc µg/g	4	2
Ba µg/g	2	1	Sn µg/g	20	10
Be µg/g	2	1	Sr µg/g	4	2
Bi µg/g	20	10	Ta µg/g	80	40
Cd µg/g	4	2	Th µg/g	8	4
Ce µg/g	8	4	U µg/g	200	100
Co µg/g	2	1	V µg/g	4	2
Cr µg/g	2	1	Y µg/g	4	2
Cu µg/g	2	1	Yb µg/g	2	1
Eu µg/g	4	2	Zn µg/g	4	2

Other Methods

Element	Plants	Soils
C total%	-	0.05
C crbnt%	-	0.01
S total%	0.05	0.05
As µg/g (HGAAS)	0.05	0.1
Hg µg/g	0.01	0.01

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[1] Lower determination limits are given for the weight basis used in the analysis (e.g., for plants the limits are for ash basis for ICP analyses and for dry, unashed material for the other methods).

Table A4. Element concentrations in pine needles.

				%, dry-weight		μg/g, dry-weight		Percent, ash-weight basis							
Field #	Lab #	Lat	Long	Ash	S	As	Hg	Al	Ca	Fe	K	Mg	Na	P	Ti
P03J111	D328360	252350	803518	2.23	0.09			0.22	17.8	0.20	9.2	7.05	8.78	2.07	0.01
P03K111	D328344	252328	803520	2.20	0.08			0.21	20.2	0.20	7.2	7.13	7.64	1.89	0.01
P04L111	D328431	252254	803544	2.59	0.09			0.17	14.2	0.17	7.7	6.06	8.83	2.01	<0.01
P08H111	D328359	252437	803734	2.30	0.09			0.26	21.6	0.24	5.1	5.54	8.95	2.22	0.02
P08I111	D328377	252412	803730	2.11	0.08			0.18	12.4	0.21	15.4	6.27	7.46	2.18	0.01
P08J111	D328394	252348	803729	2.18	0.08			0.20	15.8	0.20	15.5	6.34	6.40	2.90	<0.01
P08J211	D328428	252345	803730	2.04	0.08			0.23	15.8	0.20	14.5	6.36	7.45	2.68	0.01
P08J221	D328380	252345	803730	2.01	0.08			0.21	18.1	0.22	12.4	7.17	5.19	2.53	0.01
P08J222	D328414	252345	803730	2.00	0.08			0.20	17.9	0.21	12.4	7.06	5.16	2.70	<0.01
P08K111	D328411	252322	803729	2.28	0.10			0.17	19.3	0.21	8.8	7.18	7.28	2.80	0.01
P09H111	D328226	252438	803802	2.56	0.10	<0.05	0.03	0.18	19.6	0.18	6.4	6.37	7.47	2.25	0.01
P09H121	D328230	252438	803802	2.34	0.10	<0.05	0.05	0.17	17.9	0.18	9.5	5.82	8.56	2.55	0.01
P09H122	D328238	252438	803802	2.37	0.09	<0.05	0.03	0.17	18.4	0.17	9.2	5.75	8.26	2.50	0.01
P09I111	D328426	252412	803801	2.05	0.09			0.18	17.7	0.17	11.8	6.73	6.54	2.57	<0.01
P09J111	D328225	252341	803801	2.19	0.09	<0.05	0.06	0.23	17.8	0.22	11.4	6.27	8.04	2.79	0.02
P09J112	D328240	252341	803801	2.18	0.09	<0.05	0.05	0.23	17.4	0.20	11.0	6.02	7.81	2.67	0.01
P09J121	D328239	252341	803801	1.98	0.09	<0.05	0.04	0.20	15.4	0.20	15.0	6.89	5.69	2.85	0.01
P09K111	D328237	252330	803755	2.16	0.09	<0.05	0.04	0.23	16.1	0.18	11.0	7.63	5.83	2.71	0.01
P09K211	D328236	252332	803751	2.44	0.09	<0.05	0.05	0.20	17.3	0.17	12.3	7.67	6.22	2.55	0.01
P10G111	D328353	252450	803825	2.22	0.10			0.32	21.5	0.29	7.2	7.01	6.40	2.10	0.02
P10H111	D328231	252434	803820	2.25	0.12	<0.05	0.04	0.16	17.2	0.16	8.8	8.44	5.92	2.47	0.01
P10H211	D328244	252431	803821	2.19	0.10	<0.05	0.03	0.17	20.6	0.17	7.9	6.20	7.25	2.69	0.01
P10I111	D328433	252407	803825	2.18	0.08			0.14	17.9	0.15	8.4	7.28	8.18	2.29	<0.01
P10I112	D328349	252407	803825	2.18	0.09			0.15	18.1	0.16	8.7	7.36	8.18	2.14	<0.01
P10J111	D328401	252345	803824	2.19	0.08			0.18	17.7	0.18	11.9	7.29	5.96	2.62	<0.01
P10J211	D328346	252343	803823	2.18	0.08			0.14	19.4	0.13	9.0	8.24	3.76	2.19	<0.01
P10K111	D328409	252324	803828	2.38	0.09			0.19	20.3	0.23	6.8	7.41	7.38	2.32	0.01
P10K211	D328423	252325	803826	2.16	0.10			0.17	17.7	0.19	9.4	7.70	5.72	2.59	<0.01
P11G111	D328405	252452	803857	2.18	0.10			0.26	18.6	0.24	7.1	7.10	5.81	2.29	0.01
P11H111	D328425	252436	803852	2.12	0.10			0.19	20.1	0.21	7.0	7.72	5.81	2.15	0.01
P11I111	D328379	252406	803849	2.14	0.09			0.18	18.6	0.21	9.8	7.27	4.64	2.56	<0.01
P11I112	D328413	252406	803849	2.15	0.09			0.17	18.3	0.20	9.6	7.05	4.54	2.68	<0.01
P11J111	D328382	252347	803853	2.12	0.08			0.21	16.4	0.22	12.5	6.98	6.47	2.33	0.01
P11J112	D328383	252347	803853	2.13	0.08			0.20	16.2	0.22	12.1	6.73	6.32	2.26	0.01
P11K111	D328357	252320	803846	1.96	0.09			0.19	17.9	0.19	11.4	7.40	6.87	3.03	0.01
P12G111	D328375	252458	803917	2.24	0.09			0.20	20.0	0.25	6.8	6.93	8.67	2.43	0.01
P12I111	D328419	252412	803925	1.93	0.08			0.17	18.6	0.19	10.4	7.52	6.75	2.59	<0.01
P12I112	D328390	252412	803925	1.84	0.08			0.17	18.1	0.19	10.3	7.41	6.56	2.55	<0.01
P12J111	D328378	252345	803921	2.37	0.08			0.15	19.6	0.19	7.3	6.61	8.42	2.17	<0.01
P12J112	D328418	252345	803921	2.37	0.08			0.14	19.2	0.18	7.2	6.40	8.18	2.26	<0.01

Table A4. Element concentrations in pine needles (continued).

				%, dry-weight		µg/g, dry-weight		Percent, ash-weight basis							
Field #	Lab #	Lat	Long	Ash	S	As	Hg	Al	Ca	Fe	K	Mg	Na	P	Ti
P12K111	D328404	252322	803922	1.95	0.08			0.18	19.9	0.21	8.7	7.41	5.49	2.79	0.01
P13G111	D328410	252502	803950	2.38	0.09			0.14	23.3	0.18	5.1	6.15	7.13	2.49	<0.01
P13I111	D328367	252415	803949	2.41	0.10			0.17	22.2	0.18	5.9	5.01	9.66	2.34	<0.01
P13J111	D328398	252342	803939	2.12	0.07			0.15	19.5	0.17	7.2	6.46	8.22	2.38	<0.01
P13K111	D328391	252319	803947	2.18	0.09			0.17	19.2	0.21	8.8	6.11	8.45	2.41	<0.01
P14F111	D328355	252529	804014	2.33	0.08			0.28	19.5	0.24	7.5	6.70	8.48	2.45	0.02
P14G111	D328395	252503	804021	2.32	0.08			0.17	24.1	0.21	5.8	5.55	6.13	2.06	0.01
P14H111	D328412	252433	804016	2.13	0.09			0.16	21.1	0.19	6.6	6.49	7.45	2.89	<0.01
P14I111	D328399	252407	804011	2.15	0.10			0.14	20.8	0.18	6.9	5.68	4.63	2.64	<0.01
P14I211	D328352	252413	804011	2.29	0.10			0.19	19.3	0.20	7.6	6.39	9.20	2.43	0.01
P14J111	D328397	252344	804011	3.20	0.10			0.13	20.1	0.16	4.9	7.29	6.54	1.96	<0.01
P14K111	D328388	252323	804019	1.97	0.09			0.24	18.0	0.25	8.9	6.80	8.49	2.82	0.01
P15E111	D328396	252550	804037	2.29	0.08			0.21	22.5	0.21	6.5	5.92	6.82	2.39	0.01
P15F111	D328392	252519	804036	2.39	0.08			0.23	21.4	0.24	4.8	4.51	11.1	2.16	0.01
P15F121	D328430	252519	804036	2.46	0.08			0.20	22.6	0.19	5.7	5.55	8.09	2.33	<0.01
P15I111	D328434	252413	804041	2.03	0.08			0.16	18.3	0.16	8.1	7.97	7.69	2.36	<0.01
P15J111	D328408	252346	804035	2.20	0.10			0.16	16.6	0.20	6.6	6.37	12.1	2.39	<0.01
P16E111	D328369	252549	804104	2.52	0.09			0.17	22.0	0.23	4.9	4.78	10.0	2.35	0.01
P16F111	D328421	252524	804108	2.01	0.08			0.17	18.6	0.21	7.6	6.04	10.5	2.60	<0.01
P16I111	D328427	252408	804107	1.99	0.08			0.15	17.6	0.15	10.4	6.37	8.49	2.54	<0.01
P16I211	D328356	252411	804104	1.97	0.08			0.21	17.7	0.19	12.2	7.27	7.04	2.49	0.02
P16J111	D328381	252341	804107	2.32	0.08			0.20	19.7	0.23	8.7	6.81	6.46	2.33	0.01
P17E111	D328351	252550	804135	2.57	0.09			0.14	23.7	0.14	4.9	6.30	7.95	1.80	<0.01
P17F111	D328368	252526	804135	1.98	0.08			0.20	20.3	0.21	7.9	6.53	8.19	2.66	0.01
P17F121	D328354	252526	804135	2.11	0.09			0.21	20.9	0.20	7.3	6.47	8.11	2.40	0.01
P17G111	D328422	252501	804131	2.57	0.08			0.14	19.2	0.17	4.7	5.87	11.4	2.03	<0.01
P17H111	D328347	252435	804134	1.90	0.08			0.21	20.7	0.19	6.7	6.35	8.89	2.43	0.02
P17I111	D328384	252410	804137	2.01	0.07			0.16	18.6	0.21	8.9	6.07	8.85	2.43	0.01
P17J111	D328361	252348	804131	2.15	0.08			0.21	18.1	0.20	7.5	8.49	6.65	2.49	0.01
P18E111	D328406	252547	804159	2.05	0.09			0.17	21.7	0.21	7.2	6.12	6.32	2.47	0.01
P18F111	D328420	252528	804202	2.19	0.08			0.19	20.9	0.22	6.7	6.11	8.06	2.74	<0.01
P18G111	D328416	252459	804158	2.54	0.08			0.16	23.6	0.18	4.9	4.37	8.59	2.28	<0.01
P18H111	D328345	252437	804157	2.16	0.08			0.16	21.6	0.16	6.7	6.23	7.62	2.30	<0.01
P18I111	D328348	252412	804157	2.52	0.08			0.19	20.0	0.16	5.4	7.06	9.23	1.68	0.01
P18J111	D328385	252342	804155	2.28	0.08			0.16	18.8	0.16	7.2	7.61	7.61	2.73	<0.01
P19E111	D328235	252552	804228	2.64	0.11	<0.05	0.03	0.18	20.8	0.18	5.9	7.22	7.14	2.48	0.01
P19E211	D328246	252554	804226	2.38	0.10	<0.05	0.03	0.16	22.0	0.16	5.3	6.33	7.51	2.45	0.01
P19E212	D328241	252554	804226	2.38	0.10	<0.05	0.03	0.16	21.8	0.15	5.3	6.33	7.56	2.43	<0.01
P19F111	D328232	252525	804227	2.29	0.12	<0.05	0.05	0.17	19.4	0.18	7.7	6.01	8.94	2.50	0.01
P19F121	D328242	252525	804227	2.26	0.09	<0.05	0.03	0.14	19.5	0.16	7.0	6.60	7.64	2.56	0.01

Table A4. Element concentrations in pine needles (continued).

				%, dry-weight		μg/g, dry-weight		Percent, ash-weight basis							
Field #	Lab #	Lat	Long	Ash	S	As	Hg	Al	Ca	Fe	K	Mg	Na	P	Ti
P19G111	D328363	252505	804222	2.45	0.10			0.15	21.6	0.16	7.0	6.06	8.15	2.26	<0.01
P19G121	D328371	252505	804222	2.42	0.09			0.17	23.6	0.22	6.2	5.91	6.77	2.37	0.01
P19H111	D328393	252433	804226	2.26	0.08			0.19	20.5	0.23	6.4	5.76	8.90	2.05	0.01
P19I111	D328415	252414	804231	2.12	0.07			0.18	21.9	0.19	7.0	6.20	7.06	2.27	<0.01
P19J111	D328417	252344	804228	2.68	0.09			0.18	23.0	0.21	5.4	5.99	6.46	2.26	0.01
P20E111	D328350	252553	804259	2.78	0.08			0.15	25.7	0.19	3.6	5.38	8.45	1.56	<0.01
P20F111	D328374	252530	804258	2.40	0.09			0.17	22.1	0.22	5.8	6.18	7.92	2.30	<0.01
P20G111	D328373	252501	804253	2.56	0.08			0.16	23.0	0.20	6.1	5.92	7.84	1.90	<0.01
P20H111	D328243	252436	804251	1.78	0.09	<0.05	0.02	0.17	20.9	0.17	8.3	7.14	5.45	2.68	0.01
P20H121	D328229	252436	804251	2.42	0.09	<0.05	0.03	0.13	21.7	0.14	5.8	6.32	7.28	2.11	0.01
P20H122	D328245	252436	804251	2.40	0.09	<0.05	0.02	0.13	21.3	0.14	5.7	6.21	7.21	2.08	<0.01
P20I111	D328364	252413	804254	2.00	0.09			0.19	21.2	0.20	7.3	6.19	8.13	2.48	0.01
P20I121	D328389	252413	804254	1.98	0.09			0.17	21.3	0.20	7.3	5.59	7.61	2.54	<0.01
P21E111	D328376	252551	804322	2.36	0.10			0.15	23.9	0.19	5.2	6.39	6.86	2.06	0.01
P21G111	D328365	252459	804325	2.28	0.10			0.16	21.9	0.17	6.6	6.83	7.57	2.32	0.01
P21H111	D328228	252436	804328	2.36	0.10	<0.05	0.05	0.14	22.1	0.15	7.2	6.40	6.53	2.82	<0.01
P21H211	D328234	252434	804328	2.51	0.11	<0.05	0.04	0.14	20.0	0.15	6.6	5.91	8.49	2.88	<0.01
P21I111	D328387	252411	804320	2.17	0.07			0.16	22.5	0.18	6.0	5.06	7.33	2.29	0.01
P21I121	D328372	252411	804320	2.24	0.08			0.16	23.5	0.18	6.1	6.42	6.39	2.17	<0.01
P22I111	D328366	252412	804349	1.89	0.09			0.20	22.8	0.24	7.3	5.82	7.53	2.58	0.01
P23H111	D328407	252435	804414	2.44	0.09			0.14	22.1	0.19	8.6	6.25	5.96	2.73	<0.01
P23I111	D328424	252408	804417	2.11	0.10			0.21	20.0	0.18	9.2	7.46	6.23	2.94	0.01
P33R111	D328362	252038	804846	2.21	0.10			0.17	20.0	0.17	7.3	7.90	7.37	2.45	<0.01
P34Q111	D328400	252101	804907	2.74	0.08			0.18	23.4	0.20	4.3	6.14	7.94	2.02	<0.01
P35S111	D328402	252015	804949	2.42	0.08			0.24	13.8	0.22	8.3	8.19	11.4	2.11	0.02

Table A4. Element concentrations in pine needles (continued).

	μg/g, ash-weight basis												
Field #	Ba	Co	Cr	Cu	La	Li	Mn	Nd	Ni	Pb	Sr	V	Zn
P03J111	21	2	13	117	7	6	1820	<8	9	14	2060	6	479
P03K111	29	3	19	92	7	<4	927	<8	5	19	1370	6	243
P04L111	18	3	9	69	5	<4	665	<8	12	12	1340	4	601
P08H111	31	4	12	107	8	5	768	<8	11	19	2330	9	225
P08I111	21	4	11	99	7	<4	349	<8	11	17	1020	6	352
P08J111	19	4	8	109	5	<4	3320	<8	12	11	945	5	299
P08J211	20	4	13	119	5	<4	2790	<8	16	12	829	7	398
P08J221	20	4	10	122	7	<4	3200	<8	13	13	983	7	484
P08J222	19	4	10	119	5	<4	3180	10	11	13	951	7	452
P08K111	23	3	8	121	5	<4	628	<8	8	10	2420	5	387
P09H111	20	3	8	101	6	<4	483	<8	6	18	2760	6	419
P09H121	22	3	7	117	6	<4	440	<8	6	19	1960	6	437
P09H122	19	2	7	114	6	<4	439	<8	8	20	1960	6	423
P09I111	19	3	8	105	5	<4	1770	9	7	12	1410	5	453
P09J111	24	4	17	118	7	6	4470	<8	11	24	1560	8	408
P09J112	23	4	16	111	6	5	4270	<8	10	22	1510	8	394
P09J121	18	3	10	123	6	<4	2080	<8	7	24	1250	7	561
P09K111	21	4	17	111	5	4	4050	<8	11	21	1450	6	619
P09K211	19	5	5	92	6	<4	4000	<8	7	21	1150	5	693
P10G111	34	5	13	129	8	4	1040	<8	15	22	1830	13	329
P10H111	18	3	8	115	5	<4	847	<8	<4	19	2260	5	654
P10H211	21	3	8	116	5	<4	1020	<8	6	19	3270	5	443
P10I111	18	2	8	94	5	<4	830	<8	13	11	2260	<4	461
P10I112	19	3	8	94	6	<4	840	<8	12	12	2270	4	489
P10J111	20	3	5	114	5	<4	954	<8	8	11	1760	7	375
P10J211	17	3	6	96	6	<4	1970	<8	<4	9	1550	<4	479
P10K111	21	3	9	102	5	<4	1300	<8	14	13	2300	6	325
P10K211	20	3	10	105	5	<4	1100	<8	14	11	1570	5	382
P11G111	28	4	11	122	6	5	638	<8	12	15	1620	10	677
P11H111	25	4	9	110	6	<4	893	10	12	13	2370	8	673
P11I111	22	3	10	133	6	<4	1100	<8	13	14	2580	6	642
P11I112	21	2	10	129	5	<4	1070	<8	16	11	2450	6	583
P11J111	20	3	9	112	7	<4	3070	<8	11	13	1610	5	660
P11J112	20	4	12	111	7	<4	2950	<8	8	13	1570	6	691
P11K111	21	3	10	123	7	<4	1200	<8	7	15	1490	6	412
P12G111	26	3	9	113	7	<4	681	9	5	16	1890	7	285
P12I111	19	3	10	114	5	<4	1140	<8	6	12	2440	6	363
P12I112	18	3	7	112	5	<4	1110	<8	6	12	2360	6	352
P12J111	22	3	7	107	6	<4	1440	9	7	12	2150	4	523
P12J112	21	4	7	99	5	<4	1430	<8	5	8	2060	<4	470

Table A4. Element concentrations in pine needles (continued).

	µg/g, ash-weight basis												
Field #	Ba	Co	Cr	Cu	La	Li	Mn	Nd	Ni	Pb	Sr	V	Zn
P12K111	20	4	7	130	6	<4	1330	<8	11	13	1810	6	417
P13G111	26	3	7	103	5	<4	917	<8	5	8	2020	5	335
P13I111	21	3	8	113	7	<4	939	9	8	15	2220	6	259
P13J111	22	4	9	96	5	<4	1500	<8	8	9	2140	5	352
P13K111	23	5	9	98	5	<4	1070	9	12	10	2470	7	347
P14F111	25	3	8	111	8	5	425	<8	12	21	1870	10	706
P14G111	23	4	6	110	5	<4	943	9	10	12	2320	7	266
P14H111	18	3	8	104	4	<4	844	<8	5	10	1950	6	471
P14I111	21	3	5	104	5	<4	966	<8	6	9	2570	5	903
P14I211	21	3	9	111	7	<4	933	<8	6	15	2190	7	685
P14J111	18	4	7	90	6	<4	958	<8	5	8	2320	<4	400
P14K111	23	3	11	127	6	4	828	9	14	13	1730	10	378
P15E111	29	4	9	105	6	<4	510	<8	13	12	1880	8	269
P15F111	24	4	12	101	6	<4	802	<8	13	14	1550	9	169
P15F121	27	4	10	108	6	4	1000	9	11	15	3100	8	250
P15I111	17	3	7	115	5	<4	1230	10	13	13	1580	6	352
P15J111	16	3	9	112	5	<4	1080	<8	11	8	2120	6	610
P16E111	27	5	9	92	7	<4	697	<8	5	12	1970	6	207
P16F111	18	4	8	106	5	<4	1020	<8	6	10	2150	5	258
P16I111	18	4	8	96	5	<4	1110	<8	11	13	2740	<4	441
P16I211	20	3	10	119	7	<4	1860	<8	9	16	1770	7	369
P16J111	21	4	9	117	6	<4	1400	<8	6	15	1620	7	630
P17E111	25	4	7	79	7	<4	981	<8	6	10	2040	<4	319
P17F111	21	4	11	126	7	<4	1130	<8	8	14	2220	7	285
P17F121	21	4	6	122	7	4	1580	<8	8	17	2390	7	298
P17G111	17	5	6	95	5	<4	1120	<8	10	10	2670	5	256
P17H111	20	4	10	111	8	<4	1150	<8	11	15	2450	8	275
P17I111	19	4	9	102	5	<4	1550	<8	12	11	2430	6	393
P17J111	21	4	10	103	6	<4	2040	<8	11	15	2090	7	401
P18E111	20	4	8	112	5	<4	941	<8	7	11	1850	5	489
P18F111	23	4	9	121	5	<4	1650	<8	8	12	2430	6	287
P18G111	17	4	7	89	5	<4	608	9	5	10	1900	5	288
P18H111	18	5	7	96	7	<4	845	10	6	14	2020	5	341
P18I111	23	4	8	75	7	<4	1340	<8	5	13	1460	5	252
P18J111	19	4	7	95	5	<4	1440	<8	8	9	2760	5	338
P19E111	22	3	8	102	6	4	1020	<8	7	16	2520	6	545
P19E211	22	3	7	99	6	<4	1380	<8	6	17	2430	6	303
P19E212	21	4	7	98	6	<4	1340	8	7	16	2410	5	302
P19F111	20	3	7	111	5	<4	1060	<8	6	20	2000	6	534
P19F121	18	4	6	111	5	<4	1140	<8	6	16	2110	4	441

Table A4. Element concentrations in pine needles (continued).

	µg/g, ash-weight basis												
Field #	Ba	Co	Cr	Cu	La	Li	Mn	Nd	Ni	Pb	Sr	V	Zn
P19G111	16	4	5	99	6	<4	783	<8	9	11	2080	5	223
P19G121	17	3	9	106	7	<4	737	<8	7	14	2020	5	234
P19H111	20	3	6	89	5	<4	827	<8	10	12	1950	7	454
P19I111	19	4	8	97	5	<4	1280	<8	8	10	2700	6	396
P19J111	22	4	9	96	6	<4	630	8	10	12	2170	8	318
P20E111	24	4	8	73	7	<4	760	<8	<4	12	1830	5	241
P20F111	20	3	9	93	7	<4	1400	9	6	12	2630	5	328
P20G111	17	4	7	81	7	<4	769	<8	6	13	2940	5	318
P20H111	19	3	8	115	5	<4	1920	9	7	22	3100	6	906
P20H121	17	4	6	87	5	<4	991	<8	<4	18	3090	<4	701
P20H122	17	3	6	85	6	<4	962	<8	5	13	3030	<4	683
P20I111	20	4	8	116	7	<4	1260	<8	50	16	1980	7	434
P20I121	18	4	6	96	5	<4	1170	<8	7	<8	2220	6	376
P21E111	24	4	7	101	7	<4	1150	<8	6	13	2030	5	357
P21G111	19	3	7	100	6	<4	828	<8	7	11	1930	5	166
P21H111	18	3	8	99	6	<4	1380	<8	6	28	2290	<4	447
P21H211	16	4	6	88	6	<4	416	8	<4	14	2190	5	393
P21I111	19	3	8	92	6	<4	1350	9	16	10	2770	6	411
P21I121	19	3	8	92	7	<4	1350	<8	8	12	2600	5	542
P22I111	21	4	10	109	7	<4	1340	10	18	14	2560	8	291
P23H111	16	4	7	99	6	<4	209	10	11	10	1700	5	201
P23I111	19	5	8	95	6	<4	940	8	8	11	1540	6	200
P33R111	19	2	8	102	7	<4	1940	<8	12	9	2110	<4	584
P34Q111	19	2	8	80	5	<4	1890	<8	8	9	1670	5	208
P35S111	19	3	10	77	5	<4	882	<8	4	12	1100	7	189

Table A5. Element concentrations in rockland soils.

					Percent, dry-weight basis					µg/g. dry-wt.		Percent, ash-weight basis			
Field #	Lab #	Lat	Long	pH	Ash	C total	C organic	C crbnt	S	As	Hg	Al	Ca	Fe	K
S03J111	D328337	252350	803518		69.3				<0.05			12.7	9.79	5.98	0.17
S03K111	D328301	252328	803520		69.9				0.06			13.0	6.81	6.90	0.21
S04L111	D328307	252254	803544		41.1				0.08			7.56	18.4	3.27	0.14
S08H111	D328318	252437	803734		62.1				0.15			7.09	23.9	4.36	0.13
S08I111	D328266	252412	803730		72.8				0.05			15.9	2.72	7.82	0.23
S08J111	D328333	252348	803729		75.4				<0.05			14.5	4.03	7.25	0.18
S08J211	D328295	252345	803730		75.5				0.09			15.5	1.59	8.15	0.21
S08J221	D328316	252345	803730		71.7				<0.05			15.0	4.93	7.53	0.17
S08J222	D328269	252345	803730		72.0				<0.05			14.4	4.88	7.41	0.17
S08K111	D328279	252322	803729		78.6				<0.05			14.2	4.49	7.49	0.15
S09H111	D328213	252438	803802	6.9	51.0	22.2	21.6	0.55	0.07	10	0.11	14.4	7.71	7.29	0.16
S09H121	D328211	252438	803802	7.3	50.0	23.8	23.1	0.70	0.08	9.5	0.40	13.7	8.82	6.76	0.18
S09H122	D328207	252438	803802	7.3	49.2	24.2	23.5	0.68	0.08	9.5	0.28	14.1	8.98	6.96	0.19
S09I111	D328284	252412	803801		65.0				<0.05			13.8	7.06	6.97	0.11
S09J111	D328223	252341	803801	7.7	78.4	10.0	9.3	0.70	<0.05	17	0.21	14.4	4.87	6.99	0.13
S09J112	D328217	252341	803801	7.7	78.5	9.95	9.17	0.78	<0.05	16	0.08	14.2	4.91	6.97	0.13
S09J121	D328203	252341	803801	7.7	72.8	12.7	11.6	1.14	<0.05	14	0.11	13.3	7.43	6.40	0.14
S09K111	D328220	252330	803755	6.8	55.9	22.0	20.3	1.69	0.06	7.5	0.20	9.53	13.0	4.34	0.16
S09K211	D328205	252332	803751	6.8	76.6	11.0	10.9	0.12	<0.05	19	0.50	15.3	1.81	8.13	0.17
S10G111	D328252	252450	803825		74.1				0.11			8.13	20.6	4.90	0.12
S10H111	D328212	252434	803820	7.5	44.8	26.6	26.1	0.54	0.10	4.7	0.10	8.77	17.9	4.31	0.18
S10H211	D328209	252431	803821	7.4	69.0	13.8	13.1	0.66	<0.05	14	0.42	15.0	6.09	7.69	0.17
S10I111	D328274	252407	803825		49.5				0.05			10.0	12.4	5.17	0.19
S10I112	D328257	252407	803825		54.1				0.06			10.1	12.8	5.22	0.20
S10J111	D328302	252345	803824		66.3				<0.05			9.03	17.3	3.93	0.13
S10J211	D328280	252343	803823		67.1				<0.05			12.3	9.95	5.72	0.14
S10K111	D328267	252324	803828		75.4				<0.05			10.7	13.6	5.34	0.11
S10K211	D328265	252325	803826		74.9				<0.05			15.5	3.05	8.48	0.20
S11G111	D328332	252452	803857		63.8				0.19			15.7	3.45	7.84	0.18
S11H111	D328253	252436	803852		69.2				0.08			16.3	2.75	9.41	0.13
S11I111	D328261	252406	803849		57.0				0.08			11.4	11.2	6.56	0.23
S11I112	D328334	252406	803849		56.8				0.08			11.7	11.0	6.41	0.23
S11J111	D328250	252347	803853		69.5				<0.05			12.9	7.80	7.00	0.15
S11J112	D328298	252347	803853		69.8				<0.05			13.6	8.11	7.17	0.15
S11K111	D328299	252320	803846		77.0				<0.05			14.3	5.53	7.20	0.22
S12G111	D328304	252458	803917		86.1				<0.05			18.1	2.20	9.67	0.14
S12I111	D328278	252412	803925		72.2				<0.05			11.8	10.2	6.13	0.15
S12I112	D328260	252412	803925		72.1				<0.05			12.1	10.3	6.26	0.15
S12J111	D328275	252345	803921		80.0				<0.05			16.8	1.74	9.37	0.17
S12J112	D328297	252345	803921		80.4				0.05			16.4	1.63	8.97	0.17

Table A5. Element concentrations in rockland soils (continued).

					Percent, dry-weight basis					µg/g, dry-wt.		Percent, ash-weight basis			
Field #	Lab #	Lat	Long	pH	Ash	C total	C organic	C crbnt	S	As	Hg	Al	Ca	Fe	K
S12K111	D328306	252322	803922		76.8				<0.05			14.3	6.22	6.81	0.20
S13G111	D328315	252502	803950		66.5				0.11			4.51	30.1	2.35	0.07
S13I111	D328308	252415	803949		79.7				0.05			15.3	6.64	9.69	0.16
S13J111	D328335	252342	803939		78.5				<0.05			18.0	1.24	9.00	0.17
S13K111	D328264	252319	803947		76.5				0.06			16.6	1.80	9.03	0.17
S14F111	D328312	252529	804014		56.4				0.08			15.3	5.75	7.24	0.19
S14G111	D328303	252503	804021		73.2				0.10			7.41	24.9	3.49	0.08
S14H111	D328291	252433	804016		78.9				0.06			16.7	1.75	9.49	0.14
S14I111	D328283	252407	804011		70.0				0.06			16.6	2.40	9.40	0.16
S14I211	D328248	252413	804011		57.3				0.08			15.2	5.54	8.05	0.15
S14J111	D328310	252344	804011		60.5				0.09			16.3	3.76	8.94	0.22
S14K111	D328320	252323	804019		82.1				0.05			11.6	13.7	6.05	0.14
S15E111	D328271	252550	804037		58.9				0.17			14.1	7.80	7.43	0.17
S15F111	D328317	252519	804036		76.1				0.09			3.85	31.3	2.56	0.07
S15F121	D328281	252519	804036		71.2				0.11			7.04	24.0	4.53	0.09
S15I111	D328319	252413	804041		67.6				<0.05			16.5	3.27	8.61	0.18
S15J111	D328292	252346	804035		46.7				0.10			13.9	7.68	7.20	0.22
S16E111	D328331	252549	804104		56.4				0.12			14.8	9.60	7.88	0.14
S16F111	D328276	252524	804108		61.3				0.09			15.2	6.33	8.11	0.14
S16I111	D328294	252408	804107		74.1				0.05			15.9	3.22	8.64	0.17
S16I211	D328249	252411	804104		73.2				<0.05			14.5	4.26	6.97	0.14
S16J111	D328255	252341	804107		71.2				<0.05			16.3	2.32	8.25	0.11
S17E111	D328296	252550	804135		75.4				0.09			15.8	3.92	8.28	0.17
S17F111	D328305	252526	804135		72.2				0.06			18.1	3.32	9.28	0.15
S17F121	D328258	252526	804135		59.5				0.07			16.3	5.81	8.56	0.16
S17G111	D328288	252501	804131		44.8				0.08			17.2	5.22	8.42	0.17
S17H111	D328309	252435	804134		70.3				0.05			16.4	4.11	8.23	0.14
S17I111	D328285	252410	804137		76.9				<0.05			16.3	2.17	8.48	0.17
S17J111	D328263	252348	804131		74.0				<0.05			15.8	2.64	8.48	0.16
S18E111	D328314	252547	804159		59.4				0.07			14.3	8.50	6.22	0.16
S18F111	D328259	252528	804202		72.8				<0.05			16.5	2.35	8.63	0.12
S18G111	D328293	252459	804158		74.2				0.07			18.6	1.76	10.00	0.13
S18H111	D328323	252437	804157		53.2				0.10			16.1	4.75	8.05	0.13
S18I111	D328326	252412	804157		68.6				0.05			16.8	2.28	9.18	0.12
S18J111	D328273	252342	804155		56.4				0.11			14.7	5.07	7.96	0.16
S19E111	D328215	252552	804228	7.5	75.1	10.4	10.0	0.43	0.08	18	0.10	16.4	3.84	8.15	0.17
S19E211	D328204	252554	804226	7.5	57.3	20.7	18.2	2.46	0.21	6.4	0.48	10.3	16.7	4.57	0.13
S19E212	D328216	252554	804226	7.7	57.5	20.0	17.6	2.38	0.19	6.2	0.50	10.4	16.5	4.55	0.13
S19F111	D328219	252525	804227	7.5	74.9	10.8	10.7	0.11	0.05	20	0.10	16.9	2.21	8.46	0.12
S19F121	D328214	252525	804227	7.4	70.0	12.1	11.7	0.42	0.05	17	0.14	16.4	4.36	7.94	0.14

Table A5. Element concentrations in rockland soils (continued).

					Percent, dry-weight basis					µg/g, dry-wt.		Percent, ash-weight basis			
Field #	Lab #	Lat	Long	pH	Ash	C total	C organic	C crbnt	S	As	Hg	Al	Ca	Fe	K
S19G111	D328324	252505	804222		45.2				0.13			16.8	6.27	9.21	0.17
S19G121	D328247	252505	804222		48.2				0.11			14.3	9.35	7.55	0.18
S19H111	D328286	252433	804226		51.3				0.06			13.0	8.04	6.57	0.15
S19I111	D328336	252414	804231		59.4				0.06			12.6	8.95	5.98	0.18
S19J111	D328254	252344	804228		41.0				0.35			12.3	14.1	6.58	0.19
S20E111	D328327	252553	804259		73.0				0.11			11.4	16.6	5.02	0.09
S20F111	D328289	252530	804258		67.0				0.05			17.0	2.66	8.82	0.11
S20G111	D328300	252501	804253		30.4				0.08			11.1	13.8	5.40	0.23
S20H111	D328206	252436	804251	7.0	55.2	19.7	19.4	0.31	0.07	12	0.40	16.0	5.61	8.70	0.22
S20H121	D328222	252436	804251	7.4	57.2	19.8	19.4	0.37	0.08	10	0.13	12.6	11.9	6.26	0.15
S20H122	D328221	252436	804251	7.4	57.4	19.7	19.3	0.38	0.08	10	0.20	12.7	12.0	6.29	0.16
S20I111	D328272	252413	804254		65.6				0.08			16.0	3.99	8.28	0.15
S20I121	D328321	252413	804254		54.8				0.06			16.7	5.31	8.22	0.15
S21E111	D328262	252551	804322		73.0				0.09			10.9	16.0	5.22	0.15
S21G111	D328290	252459	804325		79.1				0.08			4.04	31.2	1.93	<0.05
S21H111	D328208	252436	804328	7.1	65.4	13.5	13.2	0.26	0.08	16	0.46	16.3	3.64	8.03	0.15
S21H211	D328224	252434	804328	6.9	25.6	35.1	34.9	0.19	0.13	5.7	0.11	7.95	20.1	4.86	0.19
S21I111	D328313	252411	804320		50.2				0.07			16.1	6.12	7.25	0.16
S21I121	D328287	252411	804320		72.0				<0.05			16.0	5.18	7.57	0.15
S22I111	D328322	252412	804349		66.7				0.07			16.5	2.66	8.14	0.13
S23H111	D328268	252435	804414		61.6				0.21			17.5	3.64	7.86	0.15
S23I111	D328270	252408	804417		76.0				0.08			17.5	2.05	9.21	0.17
S33R111	D328330	252038	804846		64.0				0.10			17.4	5.26	8.69	0.17
S34Q111	D328282	252101	804907		72.2				0.11			17.3	4.55	9.90	0.10
S35S111	D328277	252015	804949		40.7				0.12			6.71	22.0	3.40	0.18

Table A5. Element concentrations in rockland soils (continued).

	Percent, ash-weight basis				μg/g, ash-weight basis									
Field #	Mg	Na	P	Ti	As	Ba	Be	Ce	Co	Cr	Cu	Eu	Ga	La
S03J111	0.74	0.08	0.04	0.80	20	90	4	150	8	256	11	3	20	72
S03K111	0.70	0.09	0.05	0.80	30	124	4	153	8	260	9	4	21	81
S04L111	0.76	0.11	0.04	0.31	10	89	2	94	8	169	14	<2	11	47
S08H111	0.59	0.07	0.08	0.35	20	72	2	64	6	147	9	<2	11	37
S08I111	0.91	0.07	0.05	0.98	30	154	5	179	11	295	13	4	24	92
S08J111	0.83	0.07	0.04	0.97	30	102	4	243	10	317	10	4	25	103
S08J211	0.85	0.07	0.04	1.09	30	111	5	255	12	325	11	5	26	111
S08J221	0.87	0.09	0.04	0.91	30	126	4	200	12	336	15	4	24	95
S08J222	0.85	0.09	0.04	0.96	30	127	4	216	12	292	18	4	23	94
S08K111	0.97	0.07	0.04	0.92	40	73	4	174	11	280	9	3	22	80
S09H111	1.03	0.11	0.07	0.88	30	75	4	155	9	280	13	3	23	77
S09H121	1.02	0.10	0.09	0.82	30	96	4	147	8	249	14	3	22	72
S09H122	1.05	0.10	0.09	0.82	20	98	4	149	9	275	17	3	22	74
S09I111	0.96	0.08	0.04	0.86	30	117	4	195	10	263	11	3	21	88
S09J111	0.98	0.06	0.04	0.86	30	96	4	182	11	264	7	3	24	83
S09J112	0.97	0.06	0.04	0.87	30	97	4	181	10	283	9	3	24	82
S09J121	0.89	0.07	0.04	0.82	20	94	4	174	10	272	10	3	22	81
S09K111	0.79	0.08	0.05	0.61	20	89	3	151	8	189	14	3	17	64
S09K211	0.83	0.06	0.04	1.07	30	106	5	264	11	320	14	4	26	103
S10G111	0.64	0.06	0.06	0.47	20	70	2	88	8	171	10	<2	14	45
S10H111	0.74	0.19	0.08	0.53	20	136	2	88	6	163	18	<2	13	46
S10H211	1.00	0.07	0.05	0.89	30	77	4	166	11	286	9	4	25	82
S10I111	0.90	0.13	0.06	0.65	20	100	3	127	8	205	13	2	16	61
S10I112	0.91	0.14	0.06	0.65	20	103	3	127	8	210	12	2	17	61
S10J111	0.84	0.09	0.04	0.49	10	67	2	106	8	210	9	2	13	54
S10J211	0.95	0.08	0.04	0.75	20	84	3	168	9	251	11	3	18	76
S10K111	0.79	0.07	0.03	0.67	20	97	3	144	8	227	8	3	16	66
S10K211	0.94	0.08	0.04	1.00	30	142	5	219	12	294	12	4	24	100
S11G111	1.06	0.06	0.06	0.90	30	98	4	157	13	290	10	4	27	77
S11H111	1.06	0.08	0.04	1.00	30	81	5	184	12	291	10	4	27	90
S11I111	0.84	0.13	0.08	0.71	20	123	3	132	8	221	14	3	19	73
S11I112	0.82	0.13	0.08	0.66	20	122	3	122	8	202	12	3	19	71
S11J111	0.90	0.08	0.04	0.85	20	95	4	189	11	270	13	4	21	91
S11J112	0.93	0.08	0.04	0.82	30	93	4	177	11	284	10	4	22	91
S11K111	0.83	0.08	0.04	0.85	30	105	4	180	10	302	11	4	22	87
S12G111	1.07	0.05	0.04	1.00	30	87	5	181	15	339	6	4	31	92
S12I111	0.76	0.08	0.04	0.74	30	80	3	154	9	242	8	3	18	66
S12I112	0.77	0.08	0.04	0.78	20	82	4	159	8	238	9	3	20	68
S12J111	0.88	0.08	0.05	1.04	30	146	5	214	14	345	12	4	26	98
S12J112	0.85	0.07	0.04	0.95	30	139	5	186	14	316	10	4	26	94

Table A5. Element concentrations in rockland soils (continued).

	Percent, ash-weight basis				µg/g, ash-weight basis									
Field #	Mg	Na	P	Ti	As	Ba	Be	Ce	Co	Cr	Cu	Eu	Ga	La
S12K111	0.84	0.08	0.04	0.89	30	98	4	165	12	267	23	4	22	87
S13G111	0.41	0.06	0.07	0.23	< 10	45	1	47	4	91	7	<2	8	29
S13I111	0.96	0.06	0.04	0.83	40	96	4	162	14	298	7	4	27	83
S13J111	0.96	0.08	0.04	0.94	30	134	5	222	13	318	5	4	27	111
S13K111	0.89	0.09	0.05	1.02	30	121	5	211	15	308	12	4	26	100
S14F111	1.07	0.12	0.08	0.88	30	114	4	155	10	302	13	3	25	80
S14G111	0.48	0.06	0.07	0.39	20	42	2	69	6	149	7	<2	13	40
S14H111	0.99	0.06	0.04	0.93	40	74	5	168	15	348	6	4	30	89
S14I111	0.98	0.08	0.05	1.01	30	93	5	192	15	332	9	4	27	92
S14I211	0.89	0.10	0.07	0.96	20	121	4	166	10	268	11	3	24	80
S14J111	1.08	0.11	0.07	0.99	30	106	4	168	12	320	14	4	27	87
S14K111	0.67	0.06	0.04	0.62	20	92	3	111	10	245	10	3	18	61
S15E111	0.94	0.07	0.10	0.82	30	99	4	149	12	293	16	3	24	78
S15F111	0.32	0.05	0.08	0.20	10	37	1	41	3	80	6	<2	7	25
S15F121	0.45	0.06	0.09	0.40	20	63	2	75	6	162	9	<2	13	41
S15I111	1.00	0.09	0.05	0.99	30	105	5	197	13	312	12	4	26	98
S15J111	1.05	0.15	0.10	0.86	20	98	4	156	9	280	15	3	23	86
S16E111	0.92	0.08	0.10	0.79	30	103	4	149	12	275	9	3	26	78
S16F111	0.92	0.08	0.08	0.92	30	79	4	171	11	324	12	3	25	86
S16I111	1.07	0.07	0.05	0.99	40	83	5	217	14	330	9	4	29	105
S16I211	1.10	0.08	0.05	0.94	30	74	4	237	9	251	12	4	25	96
S16J111	1.05	0.08	0.05	1.06	30	71	5	212	11	311	12	4	27	100
S17E111	0.89	0.06	0.06	0.87	40	96	4	151	15	335	9	3	29	79
S17F111	1.06	0.08	0.06	1.03	30	86	5	189	14	370	8	4	32	98
S17F121	0.94	0.11	0.08	0.99	30	70	5	185	12	329	13	4	26	89
S17G111	0.83	0.13	0.07	0.98	20	88	5	161	11	358	13	4	31	88
S17H111	1.04	0.07	0.05	0.96	30	64	4	183	10	340	9	4	28	87
S17I111	1.00	0.07	0.05	1.01	40	90	5	224	12	322	11	4	27	91
S17J111	1.08	0.07	0.04	1.04	30	56	5	210	13	302	11	4	27	95
S18E111	0.91	0.11	0.06	0.86	20	78	4	155	9	283	10	4	25	84
S18F111	1.02	0.08	0.05	1.00	30	80	5	186	12	324	9	4	29	84
S18G111	0.88	0.07	0.05	1.06	40	63	5	179	15	370	7	4	31	94
S18H111	0.98	0.09	0.07	0.87	30	75	4	146	15	306	12	3	29	77
S18I111	0.96	0.08	0.05	0.95	40	100	5	171	12	327	8	4	29	89
S18J111	1.04	0.09	0.07	0.96	30	52	4	186	10	289	16	3	25	82
S19E111	0.91	0.07	0.07	0.91	30	98	5	160	15	315	10	4	30	80
S19E211	0.60	0.08	0.12	0.54	20	64	3	106	8	201	13	2	18	58
S19E212	0.60	0.08	0.11	0.55	20	65	3	106	8	214	15	2	19	58
S19F111	1.10	0.08	0.05	0.98	40	77	5	194	10	311	4	4	30	92
S19F121	0.95	0.09	0.06	0.94	30	81	4	176	11	325	9	4	30	89

Table A5. Element concentrations in rockland soils (continued).

	Percent, ash-weight basis				μg/g, ash-weight basis									
Field #	Mg	Na	P	Ti	As	Ba	Be	Ce	Co	Cr	Cu	Eu	Ga	La
S19G111	0.64	0.15	0.10	0.99	30	132	5	137	10	306	15	3	30	80
S19G121	0.66	0.12	0.10	0.87	30	86	4	154	10	262	14	3	25	79
S19H111	0.97	0.09	0.06	0.84	20	76	4	181	9	263	13	3	22	81
S19I111	0.89	0.12	0.06	0.78	30	78	3	170	8	244	10	3	22	73
S19J111	0.60	0.11	0.35	0.70	30	106	4	168	12	250	37	4	23	89
S20E111	0.55	0.06	0.06	0.59	20	55	3	113	9	217	6	3	22	60
S20F111	1.02	0.07	0.05	0.95	40	71	5	172	11	333	8	4	30	86
S20G111	0.83	0.16	0.11	0.66	20	94	3	103	9	208	25	2	20	56
S20H111	0.86	0.12	0.07	0.97	30	106	4	176	12	304	13	4	31	89
S20H121	0.75	0.10	0.06	0.76	20	67	3	138	7	219	7	3	22	68
S20H122	0.76	0.10	0.06	0.77	30	68	3	140	7	210	8	3	21	69
S20I111	1.03	0.10	0.08	1.06	30	73	5	217	10	288	12	4	29	92
S20I121	1.04	0.11	0.07	0.95	30	104	5	186	12	332	22	4	29	93
S21E111	0.65	0.07	0.06	0.61	20	82	3	123	10	219	6	3	20	67
S21G111	0.33	0.05	0.05	0.19	10	27	1	38	4	97	4	<2	8	24
S21H111	0.88	0.08	0.06	0.89	30	84	5	174	11	312	5	4	29	87
S21H211	0.63	0.15	0.13	0.38	20	85	2	82	7	160	25	<2	15	44
S21I111	1.05	0.12	0.08	0.88	30	85	4	160	10	337	17	3	30	76
S21I121	1.09	0.09	0.05	0.94	30	73	4	180	11	327	8	4	26	90
S22I111	1.00	0.08	0.06	0.96	30	65	5	174	11	325	8	4	30	88
S23H111	0.83	0.08	0.11	1.03	40	87	5	183	16	332	14	4	33	99
S23I111	0.89	0.07	0.06	1.03	40	86	5	214	14	334	10	4	31	105
S33R111	0.90	0.15	0.10	1.01	40	91	5	169	8	293	5	3	30	77
S34Q111	0.73	0.10	0.08	1.02	40	122	5	185	12	310	8	4	30	95
S35S111	1.11	0.32	0.12	0.40	30	101	2	70	5	143	12	<2	11	34

Table A5. Element concentrations in rockland soils (continued).

	μg/g, ash-weight basis												
Field #	Li	Mn	Nb	Nd	Ni	Pb	Sc	Sr	Th	V	Y	Yb	Zn
S03J111	138	426	28	71	70	65	23	662	22	131	81	6	12
S03K111	146	279	26	78	70	67	24	331	22	129	90	6	14
S04L111	74	384	<4	47	45	85	12	781	10	55	40	3	15
S08H111	85	224	11	38	40	51	12	914	9	69	39	3	33
S08I111	201	250	38	85	93	76	29	254	29	182	114	9	16
S08J111	153	1780	33	99	83	64	28	199	28	168	102	8	13
S08J211	163	1780	37	102	94	69	31	123	30	185	114	9	15
S08J221	154	1920	32	87	90	62	28	295	25	164	95	7	13
S08J222	147	1900	39	86	87	72	27	281	28	164	103	9	11
S08K111	157	301	37	73	84	62	25	292	25	147	87	8	12
S09H111	160	473	28	76	80	81	26	578	24	130	86	7	20
S09H121	155	621	28	69	76	88	24	679	22	123	79	6	24
S09H122	159	645	28	71	77	91	24	697	22	126	81	6	25
S09I111	143	1520	34	79	77	73	25	530	25	113	93	8	10
S09J111	148	1270	29	79	83	57	26	275	24	155	80	6	12
S09J112	147	1270	30	80	83	61	26	277	24	155	80	6	11
S09J121	140	1380	29	76	75	63	24	456	23	142	76	6	11
S09K111	102	1000	19	61	56	83	18	901	17	99	56	5	13
S09K211	158	1560	37	99	93	71	30	160	30	190	96	8	14
S10G111	96	337	19	44	44	46	15	481	15	87	55	5	21
S10H111	110	333	16	45	49	117	13	1800	12	77	43	3	24
S10H211	168	513	31	81	85	75	27	419	24	148	95	7	18
S10I111	112	808	24	54	57	87	18	791	17	106	61	5	21
S10I112	114	819	25	56	57	87	18	819	17	109	61	5	21
S10J111	101	325	16	50	51	47	15	896	13	73	50	4	12
S10J211	126	976	29	70	72	76	22	490	19	122	76	7	12
S10K111	112	561	25	62	59	55	19	665	20	111	69	6	6
S10K211	164	671	40	93	95	77	29	242	30	180	115	9	13
S11G111	193	351	30	76	93	62	28	323	25	168	96	7	23
S11H111	188	436	40	83	94	84	30	291	28	179	115	9	23
S11I111	133	576	28	65	60	104	19	722	18	119	75	6	19
S11I112	136	577	21	65	60	96	20	741	16	116	70	5	19
S11J111	132	1540	31	83	76	69	24	413	23	158	97	8	9
S11J112	140	1570	27	84	79	62	25	441	23	159	90	7	10
S11K111	149	534	29	80	82	57	26	322	24	151	84	7	13
S12G111	194	493	35	90	101	60	33	138	30	200	109	8	21
S12I111	129	604	29	64	67	55	22	853	21	127	79	7	11
S12I112	131	630	31	64	68	56	22	862	22	130	81	7	11
S12J111	179	663	41	92	104	69	31	143	30	199	121	10	12
S12J112	174	624	32	89	101	54	31	140	28	189	110	8	9

Table A5. Element concentrations in rockland soils (continued).

	μg/g, ash-weight basis												
Field #	Li	Mn	Nb	Nd	Ni	Pb	Sc	Sr	Th	V	Y	Yb	Zn
S12K111	150	388	30	81	83	62	26	348	24	140	84	6	12
S13G111	48	226	7	34	24	39	8	805	7	46	27	2	15
S13I111	166	735	26	79	85	52	28	288	24	166	96	8	21
S13J111	178	732	37	103	102	65	33	140	35	187	126	9	12
S13K111	168	594	40	93	100	71	30	208	31	187	107	9	16
S14F111	180	293	31	72	87	83	24	490	22	153	76	6	35
S14G111	76	267	13	43	38	36	13	669	11	70	40	3	17
S14H111	183	442	32	80	102	60	31	188	27	184	104	8	26
S14I111	186	557	40	86	96	80	30	276	28	210	114	10	21
S14I211	171	288	37	72	83	80	25	528	25	155	89	8	30
S14J111	186	445	35	80	92	90	28	408	26	168	84	7	28
S14K111	116	457	21	57	63	38	21	364	18	129	61	5	12
S15E111	187	256	32	72	77	93	25	465	23	160	85	7	33
S15F111	38	368	<4	30	17	20	7	783	6	45	24	2	9
S15F121	75	468	15	44	36	50	12	570	13	81	43	4	17
S15I111	180	454	35	90	96	80	29	279	27	182	102	8	19
S15J111	161	396	28	75	71	103	22	707	17	135	74	6	31
S16E111	158	528	29	78	84	92	27	416	23	153	84	6	37
S16F111	161	1080	37	79	81	87	27	333	27	156	91	8	24
S16I111	168	1390	35	94	91	69	31	220	28	196	103	8	22
S16I211	160	1070	36	89	88	82	27	278	26	166	96	8	18
S16J111	173	465	42	93	101	80	31	203	31	195	115	10	16
S17E111	169	418	30	75	90	64	29	248	27	185	80	7	29
S17F111	194	719	35	91	103	67	32	250	30	185	100	8	26
S17F121	177	725	41	84	95	91	29	385	29	176	104	9	26
S17G111	188	507	33	78	92	102	27	563	23	177	85	7	28
S17H111	180	823	31	82	87	70	29	316	27	184	88	7	22
S17I111	166	1290	39	87	93	79	30	173	31	202	103	9	20
S17J111	172	536	41	88	96	75	30	217	31	191	110	9	16
S18E111	160	297	28	79	82	81	24	539	22	136	79	6	25
S18F111	171	568	39	82	94	76	29	201	30	189	92	8	23
S18G111	198	469	37	87	98	68	33	194	30	199	105	8	24
S18H111	165	454	31	71	90	86	28	423	25	184	77	7	31
S18I111	181	436	33	81	98	72	30	258	27	195	92	7	22
S18J111	168	455	39	75	80	76	27	468	26	167	90	8	20
S19E111	169	483	32	79	95	65	29	261	27	181	85	7	35
S19E211	109	385	19	57	53	81	19	686	16	110	58	5	27
S19E212	109	376	19	59	53	79	19	677	17	110	58	5	27
S19F111	176	596	34	87	96	74	31	200	29	181	89	7	24
S19F121	168	644	35	84	89	71	29	299	28	169	84	7	25

Table A5. Element concentrations in rockland soils (continued).

	μg/g, ash-weight basis												
Field #	Li	Mn	Nb	Nd	Ni	Pb	Sc	Sr	Th	V	Y	Yb	Zn
S19G111	180	348	35	73	83	116	23	654	23	183	74	6	44
S19G121	148	345	35	73	74	112	23	642	22	166	87	7	27
S19H111	141	781	33	74	75	107	24	499	24	148	81	7	21
S19I111	146	1040	25	70	72	98	23	618	22	134	69	6	22
S19J111	126	218	28	84	66	104	24	925	22	165	110	8	46
S20E111	118	252	22	61	58	54	20	416	17	119	60	5	22
S20F111	180	462	33	83	95	70	30	269	29	190	84	7	20
S20G111	124	553	22	54	65	166	17	1250	14	127	48	4	36
S20H111	176	2140	34	83	81	147	26	504	26	179	86	7	33
S20H121	143	795	25	66	61	97	21	818	19	130	66	5	24
S20H122	144	795	27	66	60	99	21	832	19	130	67	6	24
S20I111	181	1070	42	84	88	91	28	356	28	184	92	8	26
S20I121	177	1300	32	85	91	90	29	487	25	173	88	7	44
S21E111	120	252	24	65	57	57	19	521	19	126	71	6	24
S21G111	41	241	6	32	21	19	7	818	6	40	20	2	8
S21H111	172	557	33	84	86	72	29	323	29	171	95	7	22
S21H211	84	284	9	46	42	123	13	1680	11	97	39	3	26
S21I111	174	708	29	69	93	110	26	577	23	168	70	6	26
S21I121	175	859	32	82	90	78	29	340	26	166	90	7	24
S22I111	174	548	31	83	88	67	29	268	27	175	88	7	22
S23H111	188	211	41	94	95	82	30	357	31	219	112	9	34
S23I111	177	339	43	96	96	76	32	237	31	209	117	10	22
S33R111	195	1020	35	74	78	87	24	531	26	180	65	6	32
S34Q111	188	558	41	89	88	74	29	328	31	189	100	9	24
S35S111	78	596	14	34	38	102	10	1360	11	73	28	3	25

Table A6. Stable sulfur isotope ratios.

	$\delta^{34}S$, pine needles			$\delta^{34}S$, soil	
Field #	per mil (‰)	replicate	Field #	per mil (‰)	replicate
P04L111	+1.1		S04L111	+7.8	+8.0
P08J111	-*		S08J111	+2.9	
P09H121	+1.9		S09H121	+7.8	
P09J111	+4.0		S09J111	-*	
P09K111	+2.8		S09K111	+6.2	
P10H111	+1.8		S10H111	+9.8	
P19E211	+4.1		S19E211	+8.7	
P19F111	+2.3		S19F111	+6.5	
P20H121	+3.3		S20H121	+5.0	+5.2
P21H211	+1.8	+1.1	S21H211	+8.6	
P33R111	+3.8		S33R111	-*	
Big Pine Key	+3.9	+4.0			

* Not determined.

QUALITY CONTROL

Each section of the Branch of Geochemistry laboratories has quality control (QC) methods tailored to the specific analyses. The QC methods generally require the analysis of appropriate reference materials and duplicate analyses of the submitted samples. The data from this part of the laboratory QC program are not reported here. As part of the field study QC program NIST and CCRMP standard reference materials (SRMs) were submitted to the laboratories with each suite of plant and soil samples. Samples were submitted in suites with a maximum of 40 samples. In each suite of samples, two SRMs were included. All suites of plant samples included NIST SRMs: 1572, Citrus Leaves; and 1575, Pine Needles. All suites of soil samples included CCRMP SRMs: SO-3, Calcareous C horizon soil; and SO-4, Chernozemic A horizon soil. The results of all analyses of these SRMs are summarized in Tables A7 and A8. Results are compared to NIST certified and CCRMP recommended and non-certified concentration values and other published concentration values[1]. In addition to the analysis of SRMs, samples of the plants and soils were split in the laboratory and submitted randomized within each suite of samples. The duplicate analysis results were examined as part of the hierarchical analysis of variance. The ANOVA results are discussed in earlier sections of this report.

No reference materials were submitted to Coastal Science Laboratories (CSL) as part of the sample suite for stable sulfur isotope ratio determinations. There are no certified botanical or soil reference materials for stable sulfur isotope ratios. However, CSL has its own QA/QC program that uses other types of reference materials. The sulfur isotope ratios are reported relative to the Canyon Diablo troilite standard and are believed accurate to 0.5 per mil or better (K. Winters, CSL, personal communication).

In reviewing our analysis results of the SRMs, several factors must be considered. First, the ICP instrumental determination limits are usually a few μg/g. The concentration of several elements that are given in this report could be determined with lower determination limits by individual element analysis techniques instead of by the multielement ICP technique. Arsenic is an example where another technique, HGAAS, was employed because of its lower determination limit for the analysis of selected samples, including the SRMs. In general, for those elements that do not exceed the determination limit by an order of magnitude, the accuracy and precision of the results are poorer, but are still useful for screening purposes. Secondly, the certified and recommended concentration values have error ranges associated with them that are listed in the Certificates of Analysis. The consensus values (Gladney and others, 1987; Gladney and Roelandts, 1989) are simply arithmetic averages of published values using an iterative mean approach to eliminate extreme outliers when sufficient data were available. In general there is a paucity of published data for these SRMs, especially for many trace elements. In numerous cases, the number of analyses compiled may only be one or two for an individual element and the consensus value is the mean of the limited available data. Despite the caveats associated with the consensus values, they are very useful for comparison. Lastly, the results

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[1] The NIST certified values and CCRMP recommended values are established on a dried at 110°C basis. The SRMs analyzed were on an as-received basis from the original container. No moisture corrections were made to the data.

for the SRMs are only indicative of the quality of the results for the samples studied at EVER. Because of differences in the nature of the samples and their elemental content, only inferences to the quality of chemical analysis results can be made.

The data in Tables A7 and A8 for the botanical and soil SRMs indicate that the among-sample suite precision of the various determination methods was excellent. In regards to accuracy, for the botanical standards the result for Na in SRM 1572 was outside the NIST 95% confidence interval. The Na concentration was too high by 30% (relative) compared to the NIST certified value for this SRM, however, the Na result for SRM 1575 was satisfactory when compared to literature values. Lanthanum was also high in SRM 1572, but not in SRM 1575. In SRM 1575, lead was 11% (relative) low compared to the certified value and was outside NIST's 95% confidence level. However, when taking into account the error about our measurement, there is no statistical difference between the two values and the absolute difference is only 1 μg/g. In general, the results for the botanical SRMs indicate that excellent precision and accuracy have been attained for most elements.

For the soil SRMs, the total carbon content was high by about 15% (relative) compared to other published values. Because organic C is determined from the difference of total and carbonate C measurements, this bias in total C measurements also biases the organic C results. Total C was determined in the SRMs and five of the samples whose C content was below about 11% by using a NIST dolomitic limestone SRM for instrument calibration. The remaining 15 soil samples with higher C contents were analyzed by using a USGS organic-rich shale reference material for instrument calibration. The potential bias in the total and organic C results for these latter samples is believed to be much smaller. For the SO-3 soil reference material, results for other major and minor elements (Al,Ca,Fe,K,Mg,Na,Mn) were also biased high by 4-12% (relative). Measurements of these major and minor elements were acceptable for the other soil SRM, although they generally were slightly low compared to the recommended values. The results for most trace metals for both soil SRMs were within acceptable concentration ranges. However, both Ni and Zn in SO-3 were low and outside the 95% confidence interval compared to the recommended values. Copper in SO-4 also was low and outside the 95% confidence limit of the recommended value, however, the difference was only 2 μg/g. These results indicate that analyses for most elements were within 5-10% relative of both the recommended and other published values. For the purposes of this report, these results were deemed acceptable.

Although the results for Na and La in botanical samples and total/organic C, Ni, and Zn in soil samples should be viewed with some caution, these elements have not been deleted from consideration in the interpretation sections of this report. The apparent biases in these elements do not significantly affect any interpretations presented in this report. However, comparisons with this data in the future must take these apparent biases into account.

Table A7. Summary of analysis results on a dry-weight basis for botanical standard reference materials.

Element	NIST SRM 1572, Citrus Leaves				NIST SRM 1575, Pine Needles			
	This work				This work			
	Mean[1]	Std. Dev.[2]	NIST value[3]	Consensus value[4]	Mean[1]	Std. Dev.[2]	NIST value[3]	Consensus value[4]
S%	0.41	0.02	0.407	0.408	0.13	0.005		0.13
Ash %	13.1	0.1			2.67	0.049		
As µg/g[5]	3.0	-	3.1	3.0	0.15		0.21	0.21
Hg µg/g[5]	0.11	-	0.08		0.14		0.15	
Al µg/g	80	0.6	92	76	561	10	545	510
Ca%	3.05	0.04	3.15	3.13	0.40	0.009	0.41	0.42
Fe µg/g	90	0.7	90	101	190	8	200	185
K%	1.79	0.02	1.82	1.83	0.36	0.01	0.37	0.37
Mg µg/g	5610	40	5800	5600	1110	30		1200
Na µg/g	210	10	160	163	47	2		50
P µg/g	1540	60	1300	1310	1340	70	1200	1200
Ti µg/g	< 13	-		22	10	2		14
Mn µg/g	21	0.2	23	23	630	13	675	650
Ba µg/g	20	0.2	21	24	7.1	0.1		7.2
Cd µg/g	< 0.5	-	0.03	0.046	0.2	0.02	(<0.5)	0.22
Ce µg/g	< 1	-	(0.28)	0.45	0.1	0.1	(0.4)	0.21
Co µg/g	< 0.3	-	(0.02)	0.016	0.2	0.02	(0.1)	0.12
Cr µg/g	1	0.2	0.8	1	2.7	0.5	2.6	2.6
Cu µg/g	16	0.5	16.5	16	2.9	0.08	3	3
Ga µg/g	< 1	-			0.38	0.04		
La µg/g	0.8	0.1	(0.19)	0.2	0.2	0.03	(0.2)	0.16
Li µg/g	< 0.5	-		0.23	0.2	0.02		0.34
Mo µg/g	< 0.5	-	0.17	0.15	< 0.1	-		0.15
Nd µg/g	0.9	0.6			0.1	0.1		
Ni µg/g	< 0.5	-	0.6	0.72	2.3	0.04	(3.5)	2.5
Pb µg/g	12	1	13.3	13.4	9.6	0.9	10.8	10.7
Sr µg/g	103	3	100	98	4.9	0.2	4.8	5
V µg/g	< 0.5	-		0.24	0.29	0.02		0.39
Y µg/g	< 0.5	-			0.08	0.01		
Zn µg/g	28	1	29	30	68	4		67

[1] Arithmetic average of four analyses. [2] Sample standard deviation. [3] NIST values from Certificate of Analysis for each reference material; values in parentheses are non-certified values. [4] Arithmetic average of all published values as of 3/86, frequently n equals only 1 or 2 (Gladney and others, 1987). [5] Mean represents only one analysis.

Table A8. Summary of analysis results for soil standard reference materials.

	CCRMP SO-3, Calcareous C horizon soil				CCRMP SO-4, Chernozemic A horizon soil			
	This work				This work			
Element	Mean[1]	Std. Dev.[2]	Recommended value[3]	Consensus value[4]	Mean[1]	Std. Dev.[2]	Recommended value[3]	Consensus value[4]
Ash %	99.1	0.08			90.0	0.05		
C total %	7.77	-		6.73[6]	5.13	-		4.42[6]
C organic %	1.08	-		0.10[6]	5.13	-		4.41[6]
C carbonate %	6.69	-		6.63[6]	< 0.01	-		0.013[6]
S%	< 0.05	-		0.013	< 0.05	-		0.05
As μg/g[5]	2.5	-		2.51	5.8	-		7.4
Hg μg/g[5]	0.01	-	0.017	0.017	0.03	-	0.030	0.032
Al%	3.36	0.07	3.06	3.07	5.33	0.12	5.46	5.41
Ca%	15.2	0.3	14.63	14.8	1.12	0.02	1.11	1.11
Fe%	1.58	0.03	1.51	1.55	2.32	0.03	2.37	2.36
K%	1.29	0.2	1.16	1.16	1.62	0.03	1.73	1.72
Mg%	5.2	0.1	4.98	5.08	0.55	0.008	0.56	0.54
Na%	0.83	0.01	0.74	0.75	0.96	0.02	1	0.99
P%	0.05	0.005	0.048	0.048	0.10	0	0.09	0.088
Ti%	0.18	0.008	0.2	0.20	0.28	0.008	0.34	0.334
Mn μg/g	550	6	520	540	583	10	600	600
Ba μg/g	300	3	296	290	717	8		700
Be μg/g	< 1	-		0.81	0.9	0		1.26
Ce μg/g	33	1		34	49	3		54
Co μg/g	7	0	8	5.5	12	0.4	11	10.4
Cr μg/g	28	0.9	26	27	54	3	61	64
Cu μg/g	15	1	17	17	20	0.5	22	21
Ga μg/g	9	1		6.4	12	0.4		10.7
La μg/g	19	0.8		16.9	25	0.7		28.2
Li μg/g	14	0		9	22	0.7		17
Nb μg/g	< 4	-		6.4	7	1		10
Nd μg/g	23	1		17.2	23	2		25
Ni μg/g	12	0.5	16	14	24	1	26	24
Pb μg/g	14	1	14	13	16	0.4	16	14
Sc μg/g	5	0.5		5.2	8	0		8.4
Sr μg/g	250	6	217	222	168	5	170	168
Th μg/g	< 4	-		3.88	6	0.7		8.6
V μg/g	34	0.8	38	36	81	0.4	90	85
Y μg/g	14	0.5		16.4	16	0.9		22
Yb μg/g	1	0.5		1.67	2	0		2.1
Zn μg/g	41	2	52	48.3	92	3	94	94

[1] Average of four analyses. [2] Sample standard deviation. [3] CCRMP values from Certificate of Analysis for each reference material (Bowman and others, 1979; Steger and others, 1985). [4] Arithmetic average of published values (Gladney and Roelandts, 1989). [5] Mean represents only one analysis. [6] Jackson and Roof, 1992.