

RELATIONSHIP OF TRACE ELEMENTS IN SOILS AND PLANTS
TO PETROLEUM PRODUCTION IN EAGLE SPRINGS OIL FIELD,
RAILROAD VALLEY, NEVADA

BY
Mahyoub A. Saeed

ProQuest Number: 10782972

All rights reserved

INFORMATION TO ALL USERS

The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript and there are missing pages, these will be noted. Also, if material had to be removed, a note will indicate the deletion.



ProQuest 10782972

Published by ProQuest LLC (2018). Copyright of the Dissertation is held by the Author.

All rights reserved.

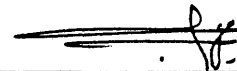
This work is protected against unauthorized copying under Title 17, United States Code
Microform Edition © ProQuest LLC.

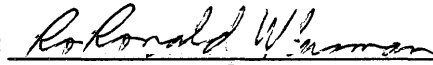
ProQuest LLC.
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106 – 1346

A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Master of Science in Geochemistry.

Golden, Colorado

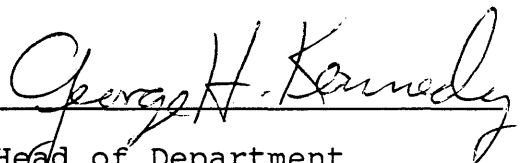
Date 3/18/88

Signed: 
Mahyoub A. Saeed

Approved: 
Ronald W. Klusman
Thesis Advisor

Golden, Colorado

Date 3/18/88


Head of Department
George H. Kennedy

ABSTRACT

Previous studies have shown the presence of hydrocarbons leaking from the Eagle Springs and other fields in Railroad Valley, Nevada. The Eagle Springs oil field is about 1.5 km wide and 3 km long. Atriplex confertifolia (Fourwing saltbush) and surface soils were sampled over an area of 5.5 km by 5.5 km at 500 m intervals. A DTPA (diethylenetriaminepentaacetic acid) extract of the soil samples and nitric acid digestion of the plants were analyzed for Zn, Fe, Mn, Al, Ti, Cr, Sr, B, Ba, P, K, Ca, Mg and Na by inductively coupled plasma atomic emission spectroscopy. Results of the chemical analysis were used to assess the possibility of the effect of hydrocarbon seepage on the near-surface soils and plants in the Eagle springs oil field, Railroad Valley, Nevada. Contour maps of Fe, Mn, Ti, and Cr in Atriplex confertifolia show high concentration over the oil field, while alkaline earth elements to aluminum ratios show the opposite relationship to the redox-sensitive elements. The high values of redox-sensitive elements are considered to reflect their enrichment in the soil solution in the reduced forms (i.e., more available to plants) as a result of the reducing environment, which is produced by the oxidation of the leaking hydrocarbons. The low Sr/Al, Ba/Al, and Ca/Al ratios are considered to reflect the depletion of alkaline-earth elements in the soil solution due to the precipitation of

carbonates during the hydrocarbon oxidation in soils over the oil field and along faults. Both redox-sensitive trace elements and alkaline-earth elements in soils do not show any particular relationship to the Eagle Springs production. The depth of carbonate formation and redox reactions is a function of microseepage rate and climate. This zone is generally too deep to reach with hand tools and needs more costly sampling tools to reach the appropriate depth.

TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	iii
LIST OF FIGURES	vi
LIST OF TABLES	viii
ACKNOWLEDGMENTS	ix
I. INTRODUCTION	1
II. STUDY AREA	12
Geology and Structure	12
Oil Production	14
Previous Studies	17
III. SAMPLING METHODS	19
IV. STATISTICAL ANALYSIS OF DATA	22
Data Distribution	22
Analysis of Variance	24
Correlation Analysis	27
Factor Analysis	28
V. SOIL COMPOSITION RESULTS	30
VI. PLANT COMPOSITION RESULTS AND DISCUSSION	31
Summary Statistics	31
Analysis of Variance	42
VII. R-MODE FACTOR ANALYSIS	54
VIII. CONCLUSIONS	59
IX. RECOMMENDATIONS FOR FURTHER STUDY	61
REFERENCES CITED	62
APPENDIX 1: Analytical Methods	66
APPENDIX 2: Analytical Results	70
APPENDIX 3: Cumulative Frequency plots and Geochemical maps	75

LIST OF FIGURES

<u>Figure</u>	<u>Page</u>
1. Vertical migration model for hydrocarbons at Eagle Springs oil field	2
2. The effect of pH on the carbonate species distribution in solution	9
3. The effect of pH on the activities of carbonate species in equilibrium with 0.0003 atm of CO ₂ (g)	10
4. Index map of Eagle Springs oil field and adjacent areas	13
5. North-South and East-West cross-sections at Eagle Springs area	15
6. Structural map of the Eagle Springs oil field and adjacent area	16
7. Soil gas propane anomalies, Railroad Valley, Nevada	18
8. Location map for the collected samples, Eagle Springs area	20
9. The effect of pH on aluminum species in solution	32
10. Cumulative frequency plot for aluminum in <u>Atriplex confertifolia</u> , Eagle Springs, area	33
11. Cumulative frequency plot for iron in <u>Atriplex confertifolia</u> , Eagle Springs, area	37
12. Cumulative frequency plot for chromium in <u>Atriplex confertifolia</u> , Eagle Springs, area	38
13. Cumulative frequency plot for Ca/Al ratio in <u>Atriplex confertifolia</u> , Eagle Springs area	39
14. Contour map of soil pH, Eagle Springs oil field, Railroad Valley, Nevada	41

LIST OF FIGURES (continued)

<u>Figure</u>		<u>Page</u>
15.	Contour map of (Sr/Al)x100 in the <u>Atriplex confertifolia</u> , Eagle Springs area	46
16.	Contour map of Ca/Al in the <u>Atriplex confertifolia</u> , Eagle Springs area	47
17.	Contour map of (Ba/Al)x100 in the <u>Atriplex confertifolia</u> , Eagle Springs area	48
18.	Contour map of iron in the <u>Atriplex confertifolia</u> , Eagle Springs area	49
19.	Contour map of manganese in <u>Atriplex confertifolia</u> , Eagle Springs area	50
20.	Contour map of chromium in <u>Atriplex confertifolia</u> , Eagle Springs area	51
21.	Contour map of titanium in <u>Atriplex confertifolia</u> , Eagle Springs area	52

LIST OF TABLES

<u>Table</u>		<u>Page</u>
1.	Solubility products of alkaline-earth elements	7
2.	Chi-square statistics for chemical variables of <u>Atriplex confertifolia</u> , Eagle Springs oil field	34
3.	Summary statistics for chemical variables of <u>Atriplex confertifolia</u> , from Eagle Springs area	36
4.	Spearman correlation coefficients for chemical variables of <u>Atriplex confertifolia</u>	40
5.	Total logarithmic variance and variance components as percentage of the total variance	43
6.	Variance ratios for chemical variables of <u>Atriplex confertifolia</u>	45
7.	Communalities and varimax loadings for the two-factor model (X100) from the <u>Atriplex confertifolia</u> samples, Eagle Springs area	56
8.	Communalities and varimax loadings for the three-factor model (X100) from the <u>Atriplex confertifolia</u> samples, Eagle Springs area	57
9.	Positive eigenvalues for three-factor model computed from the <u>atriplex confertifolia</u> samples, Eagle Springs area	58
10.	Detection limits for the ICP-AES for elements in <u>Atriplex confertifolia</u> , Eagle Springs area	69

ACKNOWLEDGMENTS

I would particularly like to express my gratitude to my advisor, Dr. Ronald Klusman, for his teaching, recommendations, and technical guidance in my research efforts. I would like also to thank Dr. Graham Closs and Dr. Thomas Wildeman for serving as thesis committee members and for their suggestions and advice.

I am grateful to my family for their unlimited support and patience during my study. Special thanks are due to the U.S. Agency for International Development for its financial support.

INTRODUCTION

Current methods of exploration for petroleum in the United States and other countries rely heavily on geophysics, particularly seismic methods. Rapid increase in costs of seismic data acquisition during the latter half of the 1970's and the first part of the 1980's are pushing "finding costs" to unacceptable levels, considering the current and recent low prices of petroleum.

There is a need for better integration of exploration methods which use the lower cost techniques to determine the most prospective portions of the basins. One of these techniques is surface geochemistry.

Surface geochemical exploration methods for petroleum are based essentially on the observation that lighter hydrocarbons contained in or associated with oil and gas deposits migrate upward from buried oil reservoirs. The mechanisms for migration include vertical movement along faults or fractures as a result of hydrodynamic changes in pressure and temperature, solution in water and vertical diffusion through shales and clays (Donovan and Dalziel, 1977). Figure 1 represents a vertical migration model for the Eagle Springs oil field.

As the hydrocarbons enter the oxygenated, porous shallow soils, the aerobic bacteria (methane-oxidizing bacteria) selectively oxidize the paraffins (Jobson et. al., 1979), consuming oxygen and producing water and carbon dioxide

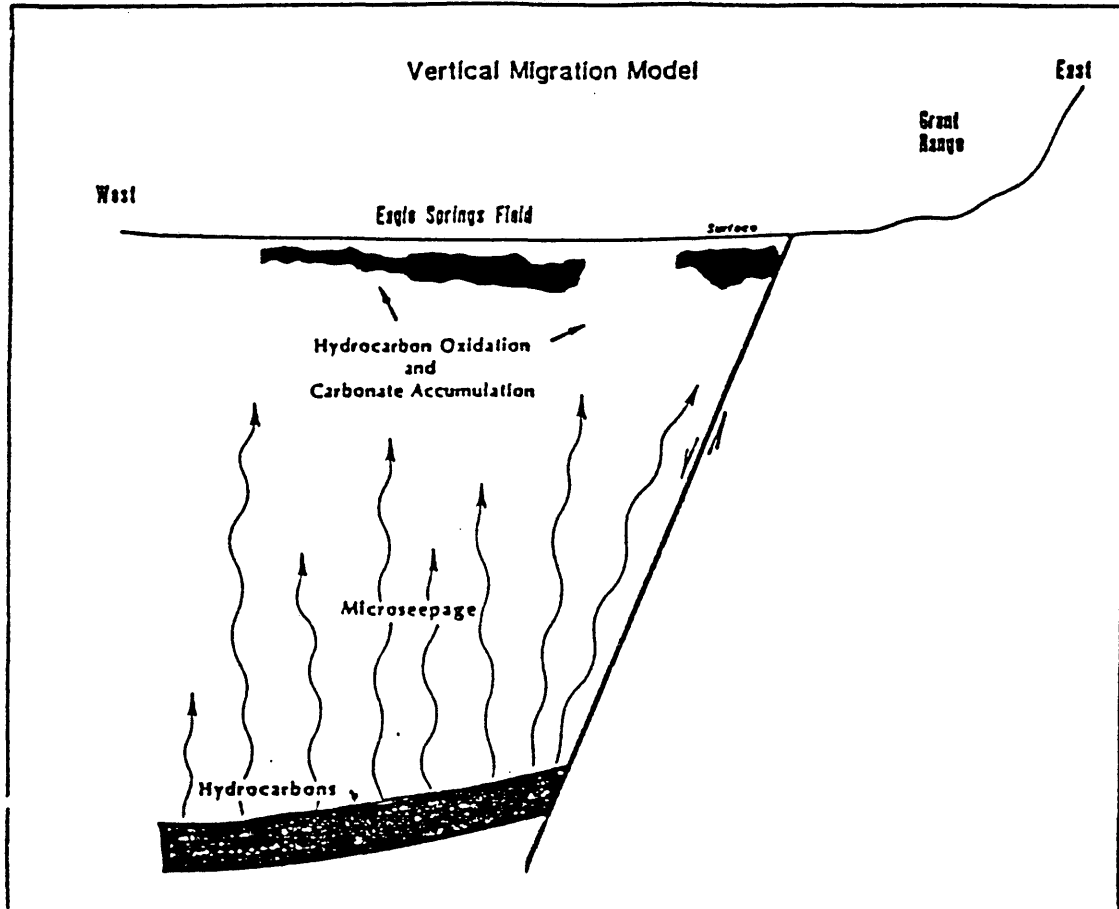
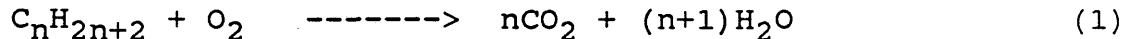
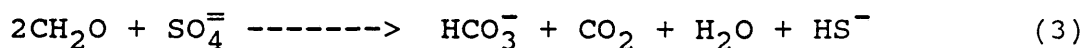
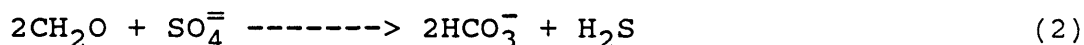


Figure 1. Vertical migration model for hydrocarbons at Eagle Springs oil field, Railroad Valley, Nevada.

which may react to form bicarbonate and carbonate ions.



Intermediate byproducts of bacterial oxidation of hydrocarbons may be oxidized by anaerobic sulfate-reducing bacteria (Jobson et. al., 1979; Oehler et. al., 1984). Anaerobic sulfate reduction produces highly reactive hydrogen sulfides and bicarbonate. Bicarbonate ions may react with calcium in pore water to form calcite, ferroan dolomite or siderite (Oehler et. al., 1984). At low pH's, reaction 2 describes the process, while at higher pH's, reaction 3 is favored.



Methane-oxidizing (aerobic) bacteria and anaerobic bacteria are extremely common in nature.

The hydrocarbon oxidation near the surface creates a slightly reducing zone directly above the oil deposit which may result in reduction, mobilization, and redistribution of redox-sensitive elements from solid mineral phases and adsorbed forms within the near-surface soils. As a result of this process, transition elements will be more soluble over the oil field and in turn more available to be assimilated by plants.

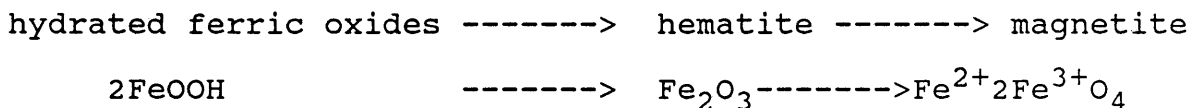
The mobilized trace elements can be held in soil for plant uptake in one or a combination of the following forms (Mitchell, 1972): (1) as hydrated ions in soil solution; (2) as readily exchangeable ions in organic or organic exchange-active complexes; (3) as more firmly bound ions in the exchange complexes; (4) in insoluble organic or organometallic complexes; (5) incorporated in precipitated oxides or other insoluble salts; (6) in secondary clay minerals. The proportion of trace elements present in any particular form depends on the nature and amount of organic matter and clay minerals, and on the pH and Eh of the soil as well as on the properties of the element in consideration. Continual microseepage and subsequent oxidation of hydrocarbons will facilitate the release of reduced forms of transition elements (e.g., Fe^{2+} , Mn^{2+}) from their solid mineral phases and result in immediate complexation, chelation, and adsorption by the soils. These organically-bound and adsorbed forms will be taken up by plants resulting in anomalous high concentration of these elements in plants (Dalziel and Donovan, 1980).

The expected results are a soil depleted in redox-sensitive elements and deep-rooted plants enriched in those elements over the oil fields. The depletion of redox-sensitive elements in soil may be too minor to detect because of their relatively high concentrations in soils, but the

enrichment in plants may be detected due to their relatively low concentrations in plants.

The high manganese-to-iron ratios in pine needles and sage leaves and the low ratios in soils overlying the Recluse Oil Field, Wyoming is suggested to be evidence of the presence of the reducing environment over the oil field due to the hydrocarbon seepage and subsequent oxidation of the hydrocarbons (Dalziel and Donovan, 1980).

The slow and continual leakage of hydrocarbons and the subsequent oxidation of hydrocarbons at Bell Creek oil field, Montana and Cement oil field, Oklahoma resulted in the reduction of hydrated ferric oxides and/or hematite to form magnetite. This can be represented as follows:

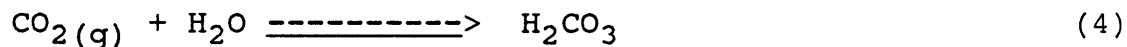


The formation of magnetite over the oil fields resulted in a high-wave number of magnetic anomalies (Donovan et al., 1979; Dalziel and Donovan, 1984). The reduction of hydrated ferric oxides and/or hematite will release the more soluble ferrous iron in solution which could be assimilated by plants.

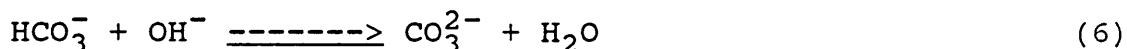
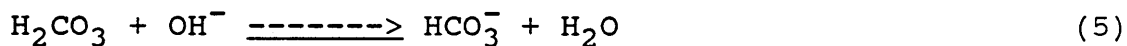
DTPA soil extractions (Romeing and Donovan, 1984) and the total trace element analysis (Duchscherer, 1984) at Bell Creek oil field, Powder River Basin, Montana showed that iron and manganese concentrations are lower over the oil field

than the concentrations away from the oil field as a result of their uptake by plants under the reducing environment.

On the other hand, oxidation of hydrocarbons has a hypothesized effect on the alkaline earth-elements. The carbon dioxide that is produced during the hydrocarbon oxidation will dissolve in water to form both dissolved carbon dioxide and carbonic acid.



Under basic conditions, carbonic acid will dissociate forming bicarbonate and carbonate ions respectively.



Continual microseepage and neutralization of carbonic acid will drive the reaction to the right to form carbonate ion. The limiting reactants in the above reactions are the carbonate species. Under acidic conditions, i.e., low pH, the neutralization of carbonic acid will not be favored because of the low OH^- concentration. Some carbonate ions could be formed and the excess carbon dioxide will evolve to the atmosphere. The bicarbonate ions that may be formed as a result of sulfate-reduction bacteria will also dissociate under

alkaline conditions to form carbonate ions in solution.

The alkaline-earth carbonates will precipitate as their solubility products are exceeded. In this case, the alkaline-earth elements in the soil solution may become the limiting reagents and driven to very low activities. The solubility products of selected alkaline earth carbonates are shown in Table 1.

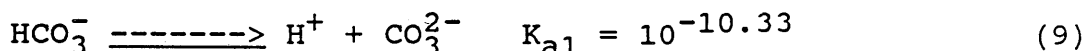
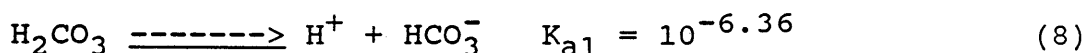
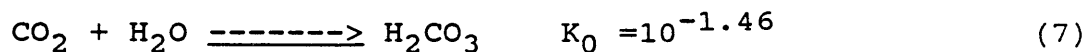
Table 1. Solubility Products of Alkaline-Earth Carbonates at 25°C

	K_{sp}
BaCO ₃	10 ^{-8.3}
CaCO ₃	10 ^{-8.35}
SrCO ₃	10 ^{-9.0}
MgCO ₃	10 ^{-7.5}

Data from R. M. Smith and A. E. Martell, Critical Stability Constants, Vol. 4: Inorganic Complexes, Plenum Press, New York, 1976.

Carbon-isotope values of the pore-filling carbonate cement at Recluse Oil Field, Wyoming showed that they are characterized by C¹² enrichment which is a result of hydrocarbon oxidation and subsequent precipitation of carbonates (Dalziel and Donovan, 1980).

The distribution of carbonate species as a function of pH can be obtained from the equilibrium relationships of the different species in solution at 25°C using the following equations from Lindsay and Norvell (1979). These can be represented graphically in Figure 2.



By combining these equations, we can obtain the following relationships between the partial pressure of carbon dioxide, pH and carbonate species.

$$\log \text{H}_2\text{CO}_3 = -1.46 + \log \text{CO}_2 \quad (10)$$

$$\log \text{HCO}_3^- = -7.82 + \text{pH} + \log \text{CO}_2 \quad (11)$$

$$\log \text{CO}_3^{2-} = -18.15 + 2\text{pH} + \log \text{CO}_2 \quad (12)$$

A Plot of these relationships as a function of pH is represented in Figure 3.

It is clear that the activity of CO_3^{2-} in acidic soils is low, so very few metal carbonates can form. In alkaline soils, CO_3^{2-} reaches activities in which many metal carbonates can form. From the previous discussion we can conclude that in swamps and some forest soils with $\text{pH} < 5.5$, the amount of CO_3^{2-} is too low to form carbonates. In soils with pH near neutral the amount of CO_3^{2-} may also be insignificant to form carbonates. In alkaline soils the activity of CO_3^{2-} in soil solution will be high enough to form alkaline carbonates.

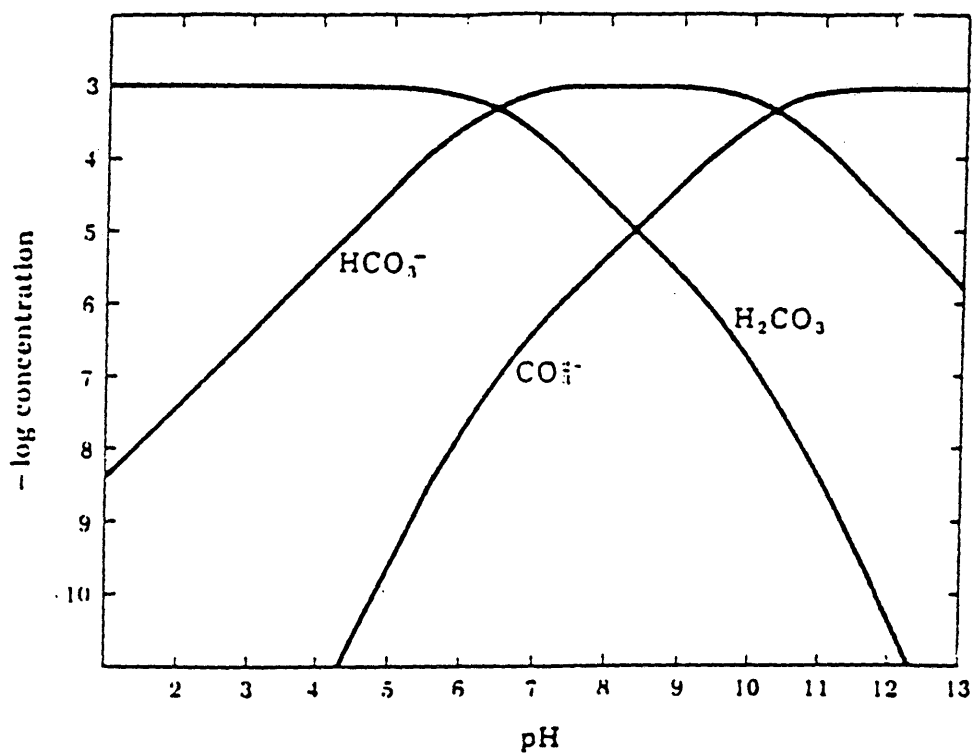


Figure 2. The effect of pH on the distribution of carbonate species in solution at 25°C (from Krauskopf, 1979).

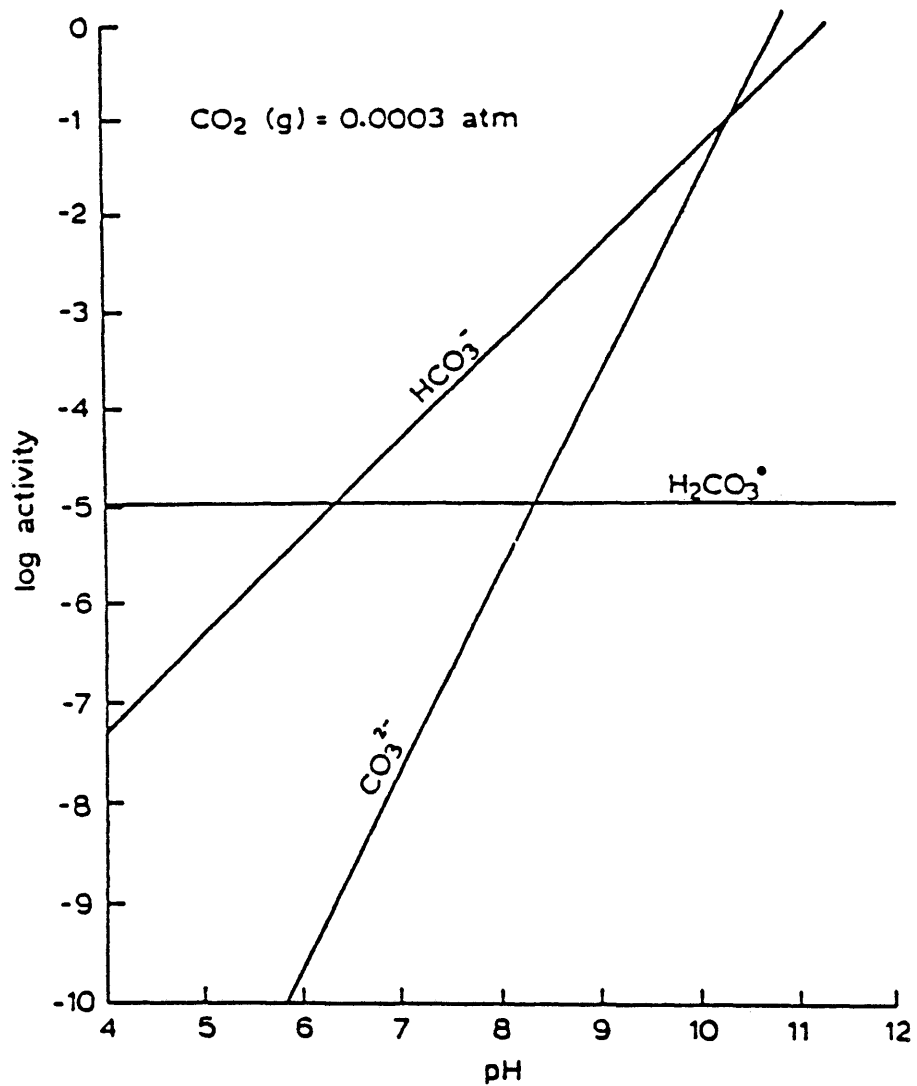


Figure 3. The effect of pH on the activities of carbonate species in equilibrium with .0003 atm. of $\text{CO}_2(\text{g})$ (Lindsay, 1979).

The precipitation of alkaline-earth carbonates will result in the depletion of alkaline-earth elements in the soil solution and in turn the plants will be depleted in these elements. This hypothesis could be tested in an area characterized by a relatively arid environment and alkaline soils.

The objective of this study was to investigate the potential of using biogeochemistry to aid in hydrocarbon exploration in an arid environment. The investigation was conducted at Eagle Springs oil field, Railroad Valley, Nevada located approximately 70 miles southwest of the town of Ely, Nevada.

Eagle Springs oil field was selected because it is one of the few areas in Nevada currently producing oil, has alkaline soils, and because previous studies demonstrated the existence of hydrocarbon microseepage.

In this study, selected trace elements and alkaline-earth elements in soils and plants (Fourwing saltbush, Atriplex confertifolia) were measured. The distribution of these elements in soils and plants were used to test the proposed hypothesis. The purpose was to evaluate the potential and utility of this approach in petroleum exploration.

STUDY AREA

Eagle Springs oil field, Nevada's first oil field, was discovered by Shell Oil Company in 1954. It is located on the east side of the Railroad Valley, 70 miles southwest of Ely, Nevada (Figure 4). The field is about 1.5 km wide and 3 km long, located primarily in S35, T9N, R57E. Railroad Valley is a large north-south trending graben bounded by the Grant Range on the east and the Pancake Range on the west. The valley floor has an elevation of 1435 to 1465 meters above sea level.

Geology and Structure

The youngest rocks at Eagle Springs oil field are those of Miocene to Recent age, the Horse Camp Formation, which comprise the valley fill sequence. This formation consists of alluvial clastic rocks and lacustrine or playa clay deposits. Adjacent to the Grant Range, sandstones and conglomerates are the predominant rock types. These sediments are separated from underlying strata by an angular unconformity "A" (Bortz and Murray, 1979).

The coarse facies of the valley fill overlying unconformity "A" is relatively impermeable because of poor depositional sorting and subsequent diagenesis and so it forms the top seal for the reservoirs in the Eagle Springs field. The thickness of the Horse Camp Formation ranges from less than

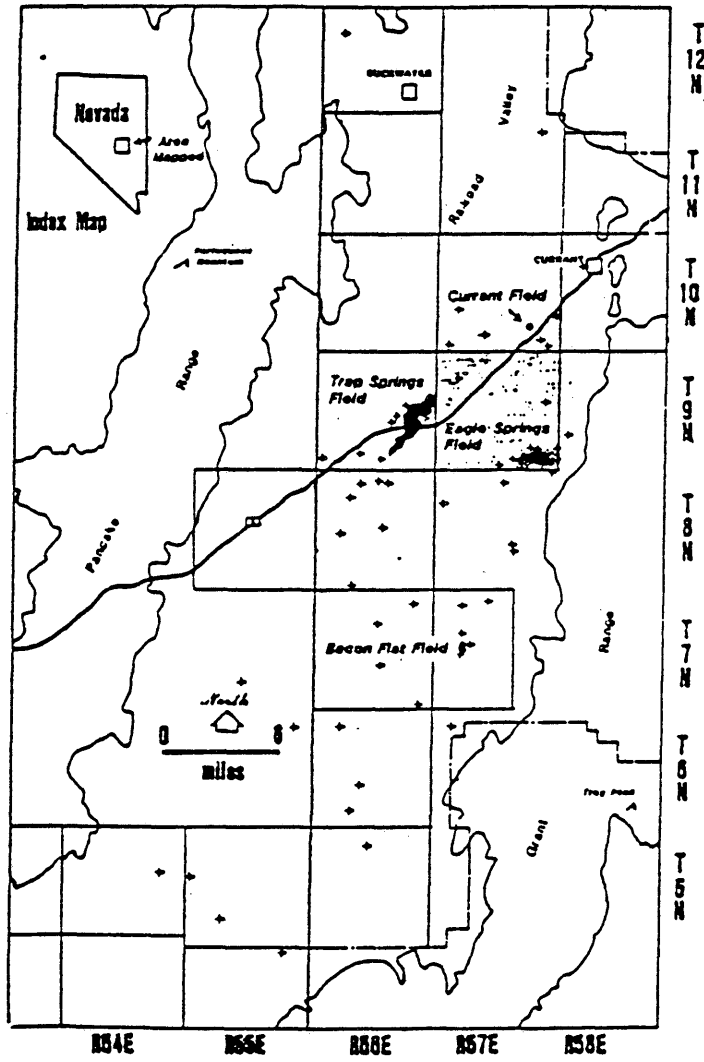


Figure 4. Index map of Eagle Springs oil field and adjacent area.

300 meters to 3,000 meters in the deeper parts of Railroad Valley (Dolly, 1979).

The unconformity "A" is underlain by Oligocene volcanic rocks. They consist of light-colored tuff, crystal tuff, andesitic lava flows, and ignimbrite flows of as much as 900 meters in thickness. The volcanic rocks are underlain by the Cretaceous-Eocene Sheep Pass Formation, which consists of lacustrine limestone and shale, with subordinate sandstone, mudstone, and conglomerate. The maximum thickness of this formation is 267 meters (Bortz and Murray, 1979).

Paleozoic rocks unconformably underlie the Sheep Pass formation. The Paleozoic rocks consist of marine carbonates (Ely Limestone), dark shale (Chainman Shales) and some sandstone. The maximum total thickness is found to be 777 meters. Figure 5 portrays east-west and north-south cross sections of the Eagle Springs oil field.

Structure in the basin is complex, composed of north-south trending normal faults and a number of oblique normal and left lateral strike slip faults (Figure 6). A plunging anticline nose on the most down-thrown fault block at the basin margin is also recognized.

Oil Production

The trapping mechanism at Eagle Springs Oil Field consists of a truncated wedge of Tertiary rocks that has a top seal of Miocene valley fill sediments, an east-side seal

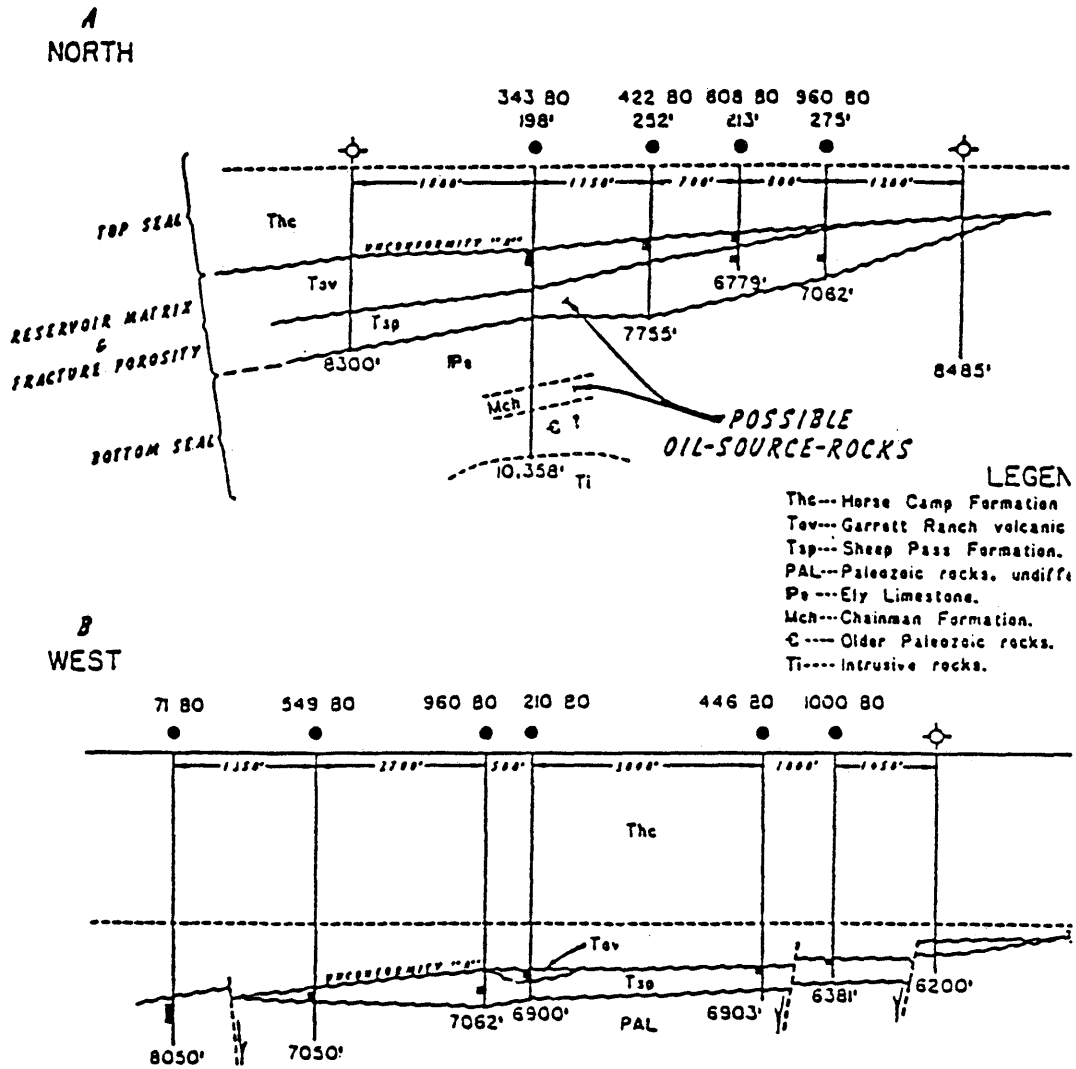


Figure 5. North-South and East-West cross sections at Eagle Springs oil field (from Dolly, 1979).

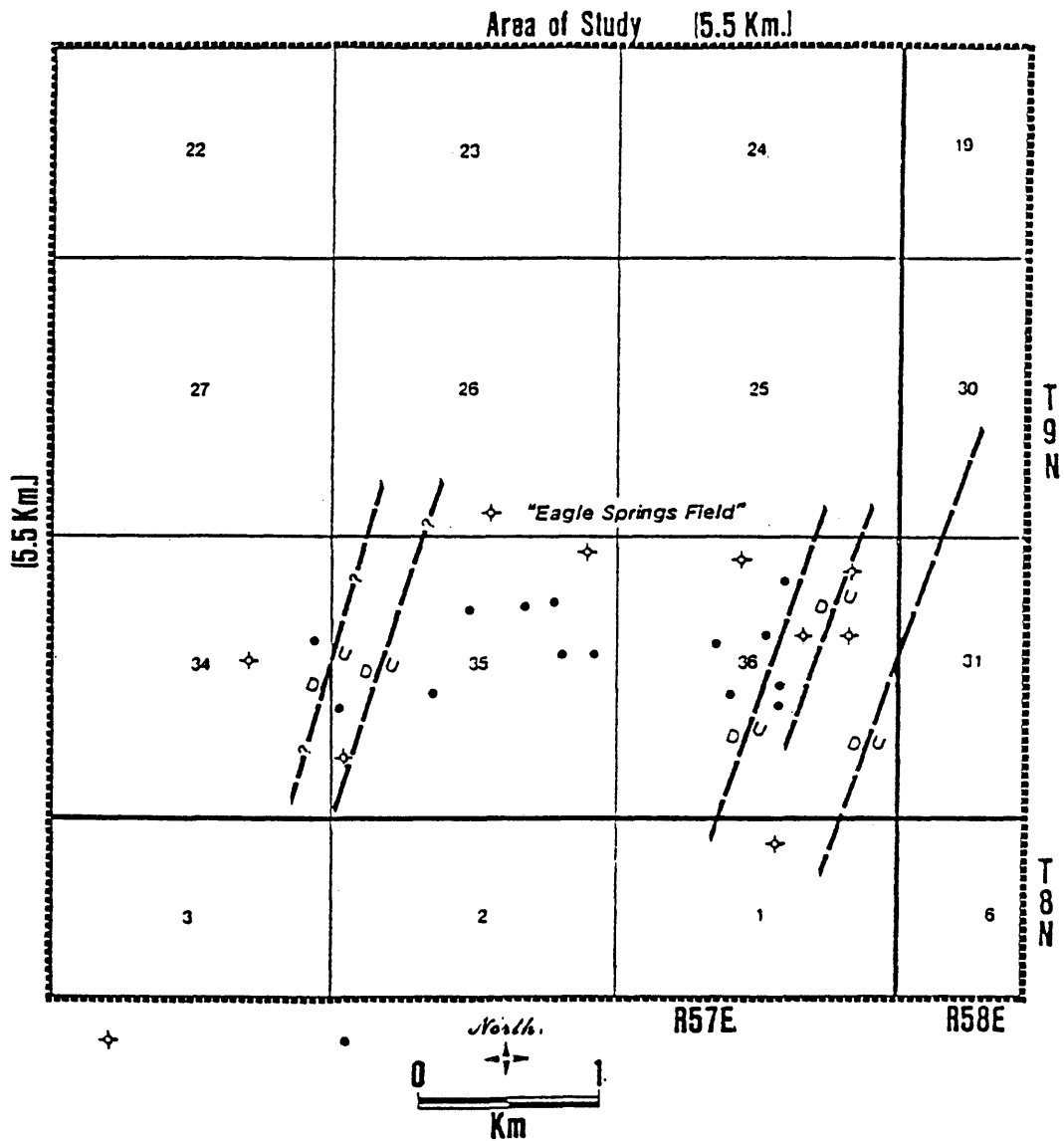


Figure 6. Structural map of the Eagle Springs oil field (modified from Bortz and Murray, 1979).

provided by the basin-margin boundary fault system, and a bottom seal of Paleozoic rocks. The reservoir formations in the field are Oligocene volcanic rocks, the Cretaceous-Eocene Sheep Pass Formation, and the Pennsylvanian Ely Formation.

Previous Studies

Foster (1979) demonstrated the existence of hydrocarbon seepage in the vicinity of Eagle Springs and Trap Springs oil fields (Figure 7). Jones et al. (1985) confirmed hydrocarbon microseepage along basin and range boundary faults and associated it with petroleum production throughout Railroad Valley. Roberts (1985) described a vegetation anomaly associated with Eagle Springs oil field. Bortz and Murray (1974, 1979) and Duey (1979) described the geology of Eagle Springs and Trap Springs oil fields, respectively. Dolly (1979) described the geological techniques utilized in the Trap Spring oil field discovery.

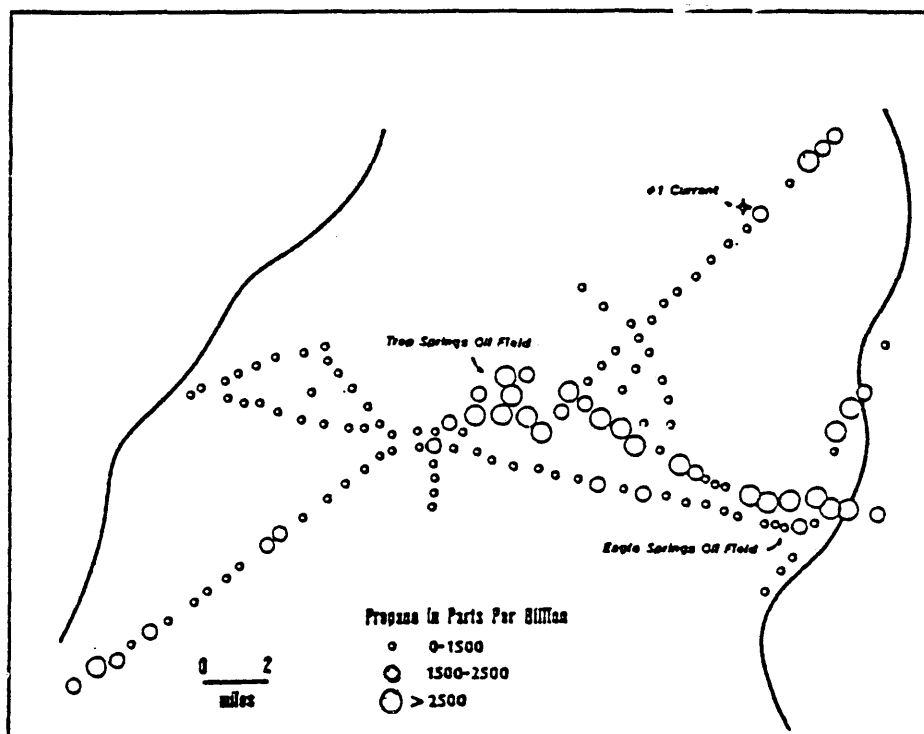


Figure 7. Soil gas propane anomalies, Railroad Valley, Nevada (after Foster, 1979).

SAMPLING METHODS

Soil and plant samples (Atriplex confertifolia) were collected on a grid over the Eagle Springs field, Railroad Valley, Nevada. The grid was 5.5 x 5.5 km, and samples were collected at 500 meter intervals. A total of 150 soil samples and 132 plant samples were collected with six duplicates from over the Eagle Springs and the surrounding area as shown in Figure 6. Sampling was conducted from August 8, 1986 to August 16, 1986.

Soils were taken from a depth of 5-6 inches ("B-horizon") using a teflon scoop and sieved to -80 mesh in the field. The -80 mesh soil samples were stored in paper soil bags to air dry.

Fourwing saltbush (Atriplex confertifolia) was collected with pruning shears from all sides of the plant and taken from as high on the plant as possible to eliminate possible rainsplash. The samples were allowed to air dry in stapled bags prior to analysis. The sample locations are shown in Figure 8. Blank areas are locations where plant material was unavailable. The analysis of both soil and plant samples was performed at the Colorado State University Soil Testing Lab. in Fort Collins, Colorado. The collected soil samples were extracted with "DTPA" and then analyzed for Zn, Fe, Mn,

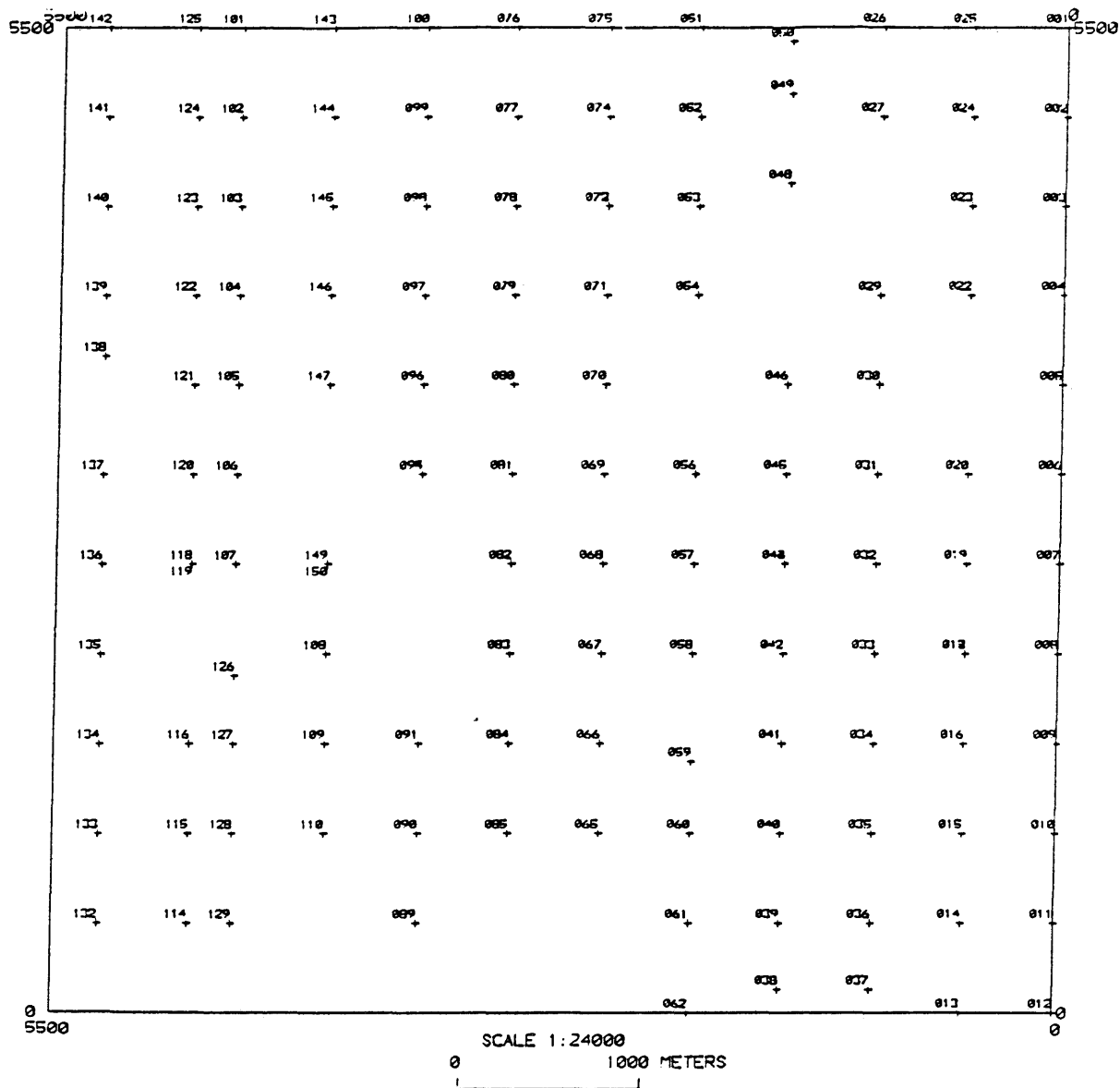


Figure 8. Map showing locations and sampled sections Eagle Springs oil field, Railroad Valley, Nevada.

Cu, Al, Mo, Ni, Se, Cr, Sr, B, Ba, Ti, P, K, and Mg using an inductively coupled plasma (ICP-AES) method. The DTPA (Lindsay and Norvell, 1978) extraction dissolves only the adsorbed trace elements, which have been redistributed by weathering and the hydrocarbon migration processes. This is considered superior to total digestion that includes elements contained in the silicate matrix which are not of interest. The nitric acid digestion method that is described by Havlin and Soltanpour (1980) was used to determine the same trace elements in plant samples. Analysis of soil pH (Peech, 1956) was performed at CSM by the author. The procedures for those analyses are described in Appendix 1. The results of the chemical analysis of the Atriplex confertifolia samples as well as the soil pH are listed Appendix 2. The analytical precision of the different parameters in plants was estimated to be better than \pm 15-20 percent at 90% C. L. . This was obtained by plotting the original determinations vs the duplicate determinations.

STATISTICAL ANALYSIS OF DATA

Due to the large number of samples and the 16 chemical elements for which each sample was analyzed, statistical techniques were used to reduce the data to a more manageable and simpler form.

Data Distribution

The first step in data analysis involved the substitution of data values for samples below the detection limits. Miesch (1967) states that when values below the detection limit comprise less than 20% of the total data set, their values may be approximated by multiplying the detection limit by 0.7 because 20% or less replacement values will not significantly affect geochemical interpretation.

The second step of data analysis involved the determination of whether population distributions are normal or skewed. Statistical estimates are more reliable when the data are distributed symmetrically around their means (Crow and Davis, 1960). Geochemical data, however, commonly exhibit a positively-skewed distribution (Crow and Davis, 1960), so the most appropriate transformation of the data of this type is frequently a logarithmic one (Bartlett, 1947).

The appropriateness of normal or lognormal distribution was determined by calculating the chi-square statistics of both

the raw data and log-transformed data using a statistical program (CUMFREQ.FOR) written by Klusman (1986).

The arithmetic mean value \bar{X} was calculated by:

$$\bar{X} = \frac{\sum X_i}{n} \quad (13)$$

where x_i 's are individual measurements on n samples.

Because most geochemical data are more symmetrical on a logarithmic scale than an arithmetic one, a more appropriate method of estimating the average value is the geometric mean.

The geometric mean (GM) was calculated by:

$$GM = 10^{\log \bar{X}} \quad (14)$$

where $\log \bar{X}$ is the arithmetic mean of the log 10 transformed data.

The standard deviation (S) and geometric deviation (GD) are measured by the variability about the arithmetic mean and geometric mean, respectively. The standard deviation is given by:

$$S = \left[\frac{\sum (X_i - \bar{X})^2}{n-1} \right]^{1/2} \quad (15)$$

The geometric deviation is given by:

$$GD = 10^{\log S} \quad (16)$$

where $\log S$ is the standard deviation of the log 10 transformed data.

The calculation of the arithmetic means, standard deviations, ranges, skewness and kurtosis of the data

(untransformed and log 10 transformed) were calculated with the use of SPSSX statistical package written for the VAX 8600 computer. The geometric means, geometric deviations chi-squares and cumulative frequency diagrams were plotted with the use of a computer program, CUMFREQ.FOR (Klusman, 1986).

As a graphical guide to distinguish background and anomalous populations in the data, cumulative frequency plots as described by Levinson (1980) and Lepeltier (1969) were used. By plotting the cumulative percent on a log scale against the concentration, different populations can be distinguished from the breaks in slope.

Analysis of Variance

Prior to calculation of the analysis of variance, all data were logarithmically transformed. This was carried out to eliminate or at least minimize the relationship between the means and variance in the data (Garrett and Thomas 1978).

The total elemental variation in any variable can be considered to be made up of three components: analytical, sampling (within-site), and regional (between-site). The regional variance is the most important component in mapping geochemical data. It is necessary to investigate the relative magnitude of the three components prior to the geochemical data interpretation in order to identify the variables that

provide the most reliable data for geochemical mapping. Partitioning of the total geochemical data variability of the Eagle Springs Plants into their three components can be done using a three-stage nested analysis of variance model

$$x = \mu + V_r + V_s + V_a \quad (17)$$

where:

x is the metal concentration reported by the laboratory;

μ is the mean metal concentration for all samples;

V_r is the regional (between-site) metal variability;

V_s is the sampling (within-site) metal variability;

V_a is the analytical (laboratory) metal variability.

If a log₁₀ transformation is performed on the data, the model remains unchanged. The model partitions the total variance of the observed values into variance components associated with each level in the design (Miesch, 1976):

$$s_x^2 = s_r^2 + s_s^2 + s_a^2 \quad (18)$$

where:

s_x^2 is the total variance;

s_r^2 is the regional (between-site) variance;

s_s^2 is the sampling (within-site) variance;

s_a^2 is the analytical (between duplicates) variance.

The variance components were calculated using a computer program written by Garrett and Goss (1980) and

modified for the VAX 8600 by Klusman (1986). The F-ratio test was used to determine if there is a significant difference between the regional and the sampling components. It is intuitive that those elements with high regional variance will be most useful for mapping.

Map stability (i.e. reproducibility) is important for data interpretation. Miesch (1976) suggests the variance ratio, V_R , as one method of estimating the reproducibility. It can be calculated as follows:

$$V_R = s_r^2 / (s_s^2 + s_a^2) \quad (19)$$

where s_r^2 , s_s^2 , and s_a^2 have been previously defined. Equation (19) describes V_R as the ratio of the variance between the sample sites divided by the sum of the variance at the sample site and analytical replication levels. If V_R is greater than or equal to 1.0, the variance between sample sites is greater than the variance within the sample sites, then the sampling density was sufficient to reproduce the maps.

To complement the calculation of variance component estimates, appropriate F-tests may be constructed to determine if the estimates differ significantly from zero. Of the methods possible, synthesizing the mean squares of the denominator of the F-tests seems the most appropriate (Tietjen and Moore, 1968). The degrees of freedom are then obtained by applying Satterthwaite's approximation

(Satterthwaite, 1946).

Correlation Analysis

The interrelationships between the different elements in plants (Atriplex confertifolia) can be expressed by Spearman's rank correlation coefficient (r_s).

The Spearman's correlation coefficient is obtained as follows:

$$r_s = 1 - \frac{6\sum d^2}{n^3 - n} \quad (20)$$

where n is the number of pairs of values, and d is the difference of rank of each horizontal pair in the two columns.

When there are tied values in either column, the r_s can be calculated as follows:

$$r_s = \frac{A+B-\sum d^2}{2(AB)^{1/2}} \quad (21)$$

where $A = n^3 - n/12 - T_a$, and $B = n^3 - n/12 - T_b$, where T_a and T_b are corrections for the presence of ties and have the value $(t^3 - t)/12$ and t is the number of observed ties in column a or column b.

Howarth (1973) and Chapman (1976) pointed out that the Pearson correlation matrix may be affected by the presence of outlying data values, and the presence of more than one geochemical population in the data set; for these reasons the

Spearman rank correlation was used. Spearman rank correlation coefficients were calculated using the SPSSX package available for the VAX 8600 at CSM.

Factor Analysis

Factor analysis is a method for reducing the complexity of a given set of intercorrelated data by accounting for the observed correlations among the variables in terms of the fewest possible number of underlying factors (Levinson, 1980). It is a method by which the processes affecting the distribution of the elements may be separated and interpreted based on the geochemistry/geology of the area.

The specific R-mode factor analysis with varimax rotation was used to simplify the element data set into a set of fewer variables. This method of factor analysis first derives principal components which measure the amount of variance-covariance of the data in n-dimensional space. The eigenvalues and eigenvectors are computed from the correlation matrix and represent the lengths of the axes. The eigenvalues represent the proportion of the total variance of the eigenvectors. Therefore, eigenvalues greater than unity are usually a good starting point for a factor model, in order to account for a large amount of the variance with a relatively small number of elemental groupings.

In addition to eigenvalues, the communalities are

important when determining the number of factors to use in the factor model. They refer to the amount of variance retained from the original matrix when less than n factors are used to account for an $m \times m$ matrix (Davis, 1973).

The coefficients of the linear equation which the eigenvectors define are known as loadings and may be interpreted as a measure of the variance for each variable explained.

SOIL COMPOSITION RESULTS

Preliminary contour maps of the soil data show that both redox-sensitive trace elements and alkaline-earth elements in soils do not have any particular spatial relationship to the Eagle Springs oil field production.

The depth of carbonate formation and redox reactions are a function of microseepage rate and climate. This zone is generally too deep to reach with hand tools in an arid climate and needs more costly sampling tools to reach (e.g., truck-mounted auger). The soil data will not be discussed further.

PLANT COMPOSITION RESULTS AND DISCUSSION

Since plant compositional data tend to be noisy, elemental data were ratioed to an "invariant" component such as aluminum. The selection of aluminum is based on trace element speciation, which is calculated from thermodynamic data (Figure 9). The Eagle Spring soils have a pH range of 8.2-10.8 indicating aluminum in the soil exists predominantly as one species and is suitable for ratioing. This is supported by the cumulative frequency plot for aluminum which indicates that aluminum is represented by only one population (Figure 10).

Those elements with more than 20% of their values below the detection limit of the analytical method used were eliminated from further analysis. Those elements are Cu, Ni, and Mo.

Summary Statistics

Chi-square statistics (Table 2) show that Zn, Fe, Ti, Sr/Al, Ba/Al, Ca/Al and Mg/Al are more normally distributed when transformed by using the base 10 logarithm. Manganese and chromium are more normally distributed using the raw data.

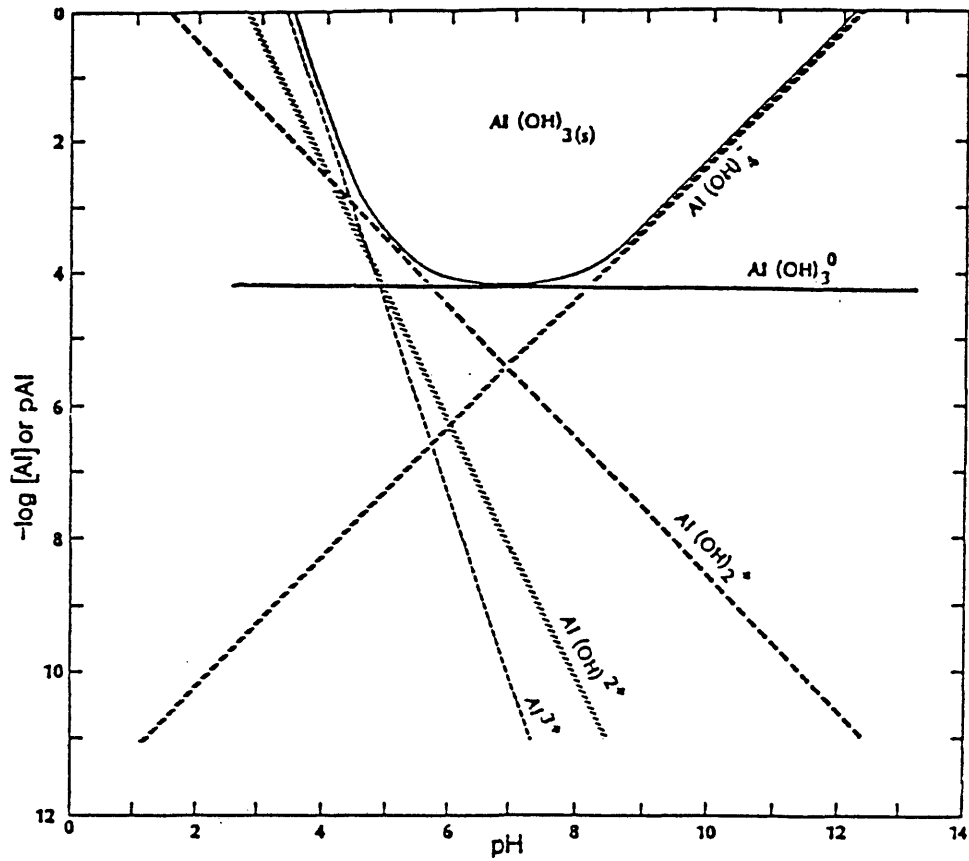


Figure 9. The effect of pH on the aluminum species in solution at 25°C. Figure calculated from thermodynamic data from Stumm and Morgan (1981).

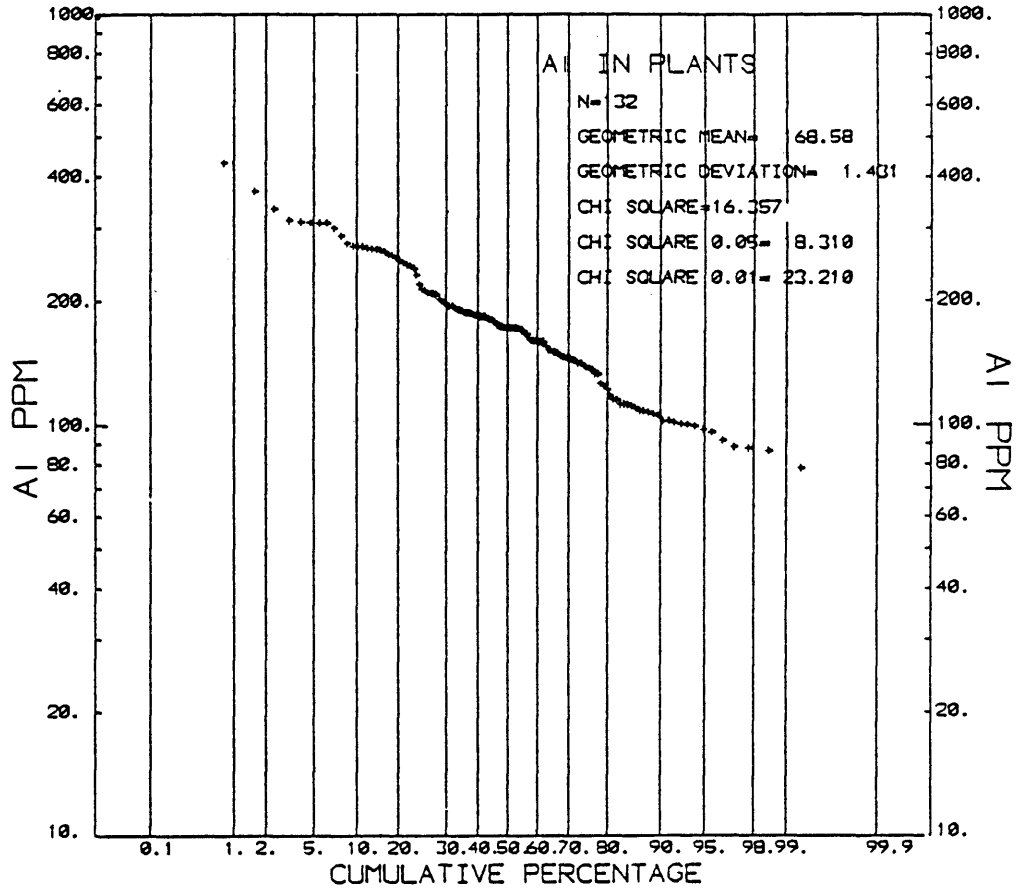


Figure 10. Cumulative frequency plot for aluminum in Atriplex confertifolia, Eagle Springs area.

Table 2

Chi-square Statistics for Chemical Variables of
Atriplex confertifolia. From Eagle Springs area,
Railroad Valley, Nevada

<u>Variable</u>	<u>Untransformed data (X)</u>	<u>Transformed data (log10X)</u>
Zn	58.977	43.002
Fe	76.278	33.340
Mn	10.813	22.900
Ti	57.828	26.153
Cr	16.210	40.471
Ca/Al	133.747	26.407
Sr/Al	45.073	16.384
Ba/Al	72.327	12.733
Sr	19.248	54.500
Ba	15.100	11.286
P	28.715	12.189
K	13.779	22.896
B	45.125	39.425
Ca	105.174	35.558
Mg	130.451	38.955

$\chi^2 = 18.31$ at 95% confidence level

Table 3 lists the summary statistics for each variable. All values except chromium had 100% of their values above the detection limits of the analytical method used. Chromium has two values below the detection limit.

Cumulative frequency plots show that the data set represents at least two populations, i.e., background and anomalous populations. The cumulative frequency plots for iron and chromium as well as for Ca/Al ratio are represented in Figures 11, 12 and 13, respectively, as examples. Two distinctive populations can be seen. Cumulative frequency plots for the elements are shown in Appendix 3.

Table 4 gives the correlation matrix between plant parameters as well as the pH of the soil. It can be seen that there are no strong linear relationships between soil pH and Zn, Fe, Mn, Ti, Cr, Sr/Al, Ba/Al, Al, and Ca/Al, but a relatively strong linear relationship between the soil pH and B, Mg/Al, and Na in plants is observed. This absence of a strong relationship between the soil pH and the transition elements suggests that at this soil pH range most of the elements will be present in the soil in the forms that can not assimilated by plants. On the other hand at this pH range most of the alkaline-earth elements will precipitate as carbonates depleting the soil solution, and in turn they will be less available for plants. The ratioing of Sr, Ca and Ba to aluminum minimizes to some extent the effect of pH. Also the

Table 3

Summary Statistics for Chemical Variables of
Atriplex confertifolia from Eagle Springs area,
 Railroad Valley, Nevada.

<u>Variable</u>	<u>Range</u>	<u>X</u>	<u>S</u>	<u>Gm</u>	<u>GD</u>
Zn	3.01-16.3	5.967	2.875	5.66	1.502
Fe	91.30- 461	217.648	79.856	204.77	1.378
Mn	9.97-55.9	31.691	9.254	30.2	1.378
Al	69.7-433	179.663	65.834	168.58	1.430
Ti	3.34-18.2	8.464	3.285	7.90	1.450
Cr	0.7-4.43	2.161	0.628	2.07	1.355
Sr	16.1-182	81.982	30.315	75.6	1.545
B	31.1-412	99.714	70.961	80.83	1.883
Ba	4.34-39.9	14.582	5.395	13.65	1.445
P	0.044-0.165	0.074	0.020	0.07	1.285
K	0.445-3.74	1.506	0.487	1.43	1.397
Ca	0.626-2.64	1.236	0.389	1.18	1.331
Mg	0.103-1.0	0.342	0.175	0.30	1.607
Na	0.203-9.21	5.176	1.951	4.69	1.607
Ca/Al	23.09-242.46	78.829	42.821	70.27	1.592
Ba/Al	0.017-0.262	0.0924	0.050	0.081	1.675
Sr/Al	0.060-1.820	0.536	0.325	0.45	1.875
Mg/Al	5.012-118.6	22.583	19.312	18.03	1.864
pH (soil)	8.200- 10.8	8.773	0.705	9.29	1.074

Values in ppm except K, P, Ca, Mg and Na which are in percent.

n = 132

X⁻ = Arithmetic mean

S = Standard Deviation

Gm = Geometric mean

GD = Geometric deviation

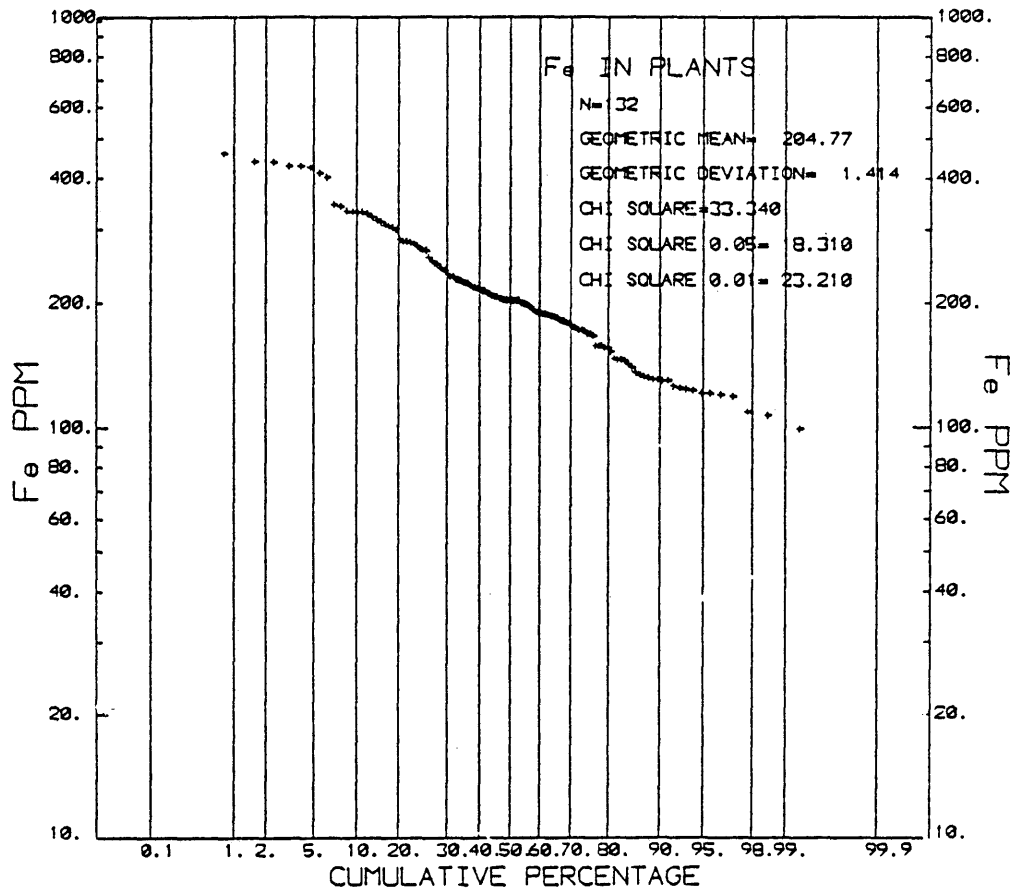


Figure 11. Cumulative frequency plot for iron in Atriplex confertifolia, Eagle Springs area.

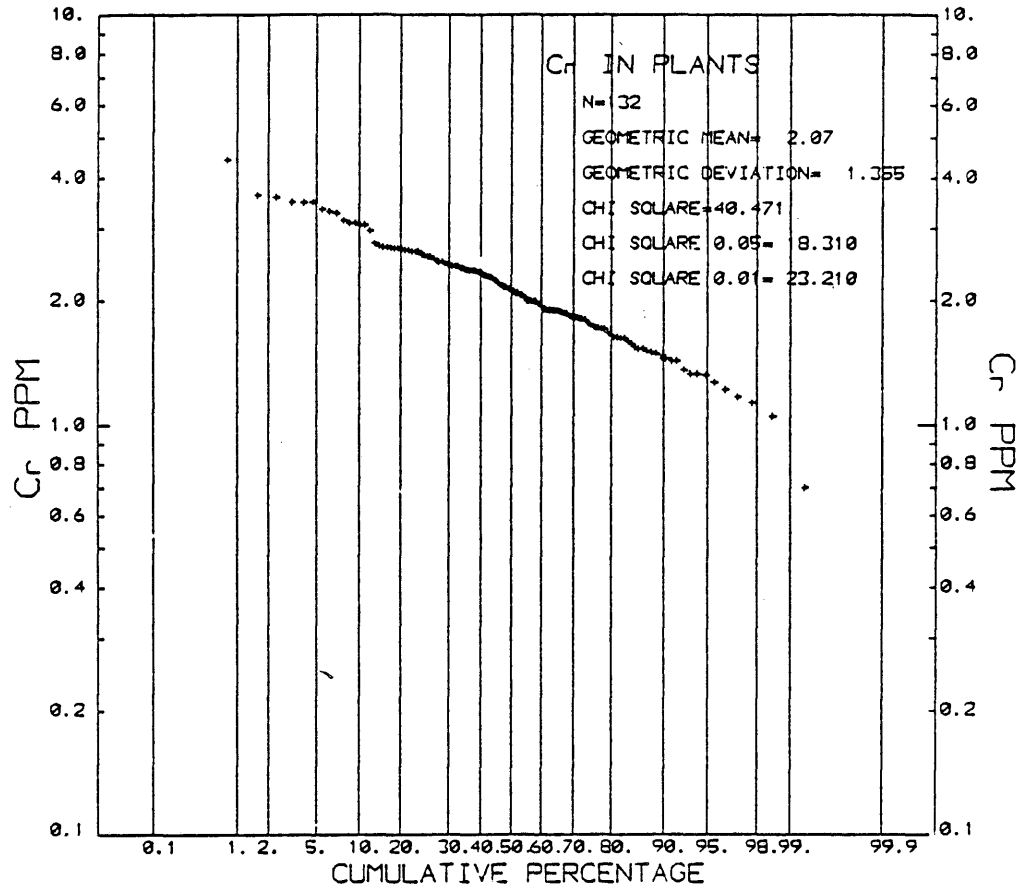


Figure 12. Cumulative frequency plot for chromium in Atriplex confertifolia, Eagle Springs area.

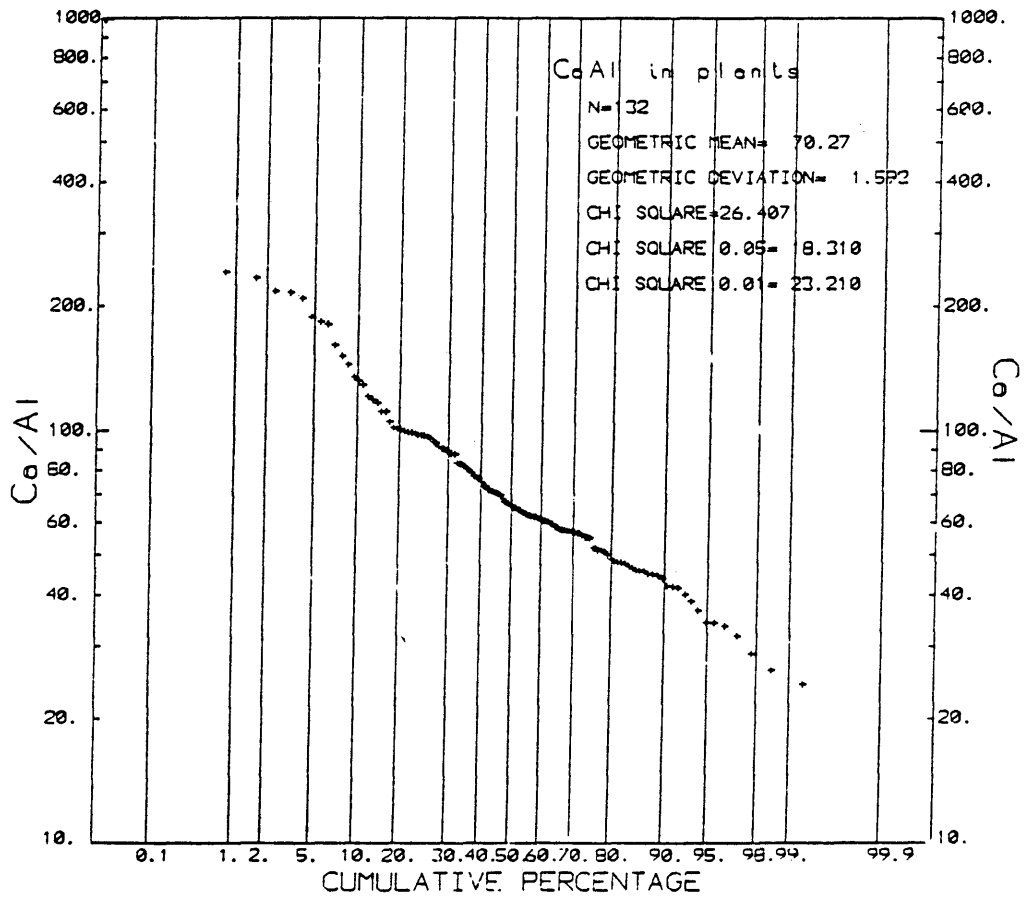


Figure 13. Cumulative frequency plot for Ca/Al in Atriplex confertifolia, Eagle Springs area.

Table 4. Spearman Correlation Coefficients
Significant $r_s = .23$ at 99% C.L

Fe	.26										
Mn	.55	.24									
Al	.31	.93	.25								
Ti	.29	.92	.22	.95							
Cr	.28	.25	.26	.27	.23						
Sr/Al	-.45	-.72	-.35	-.76	-.73	-.20					
B	-.56	.04	-.54	-.07	-.03	-.28	.15				
Ba/Al	-.05	-.66	.05	-.70	-.68	.03	.63	-.16			
P	.51	.12	.26	.10	.13	-.07	-.26	-.21	-.00		
K	.32	-.20	.16	-.13	-.17	.20	.13	-.43	.24	.29	
Ca/Al	-.20	-.77	-.05	-.79	-.78	.04	.73	-.14	.78	-.16	
Mg/Al	.07	-.64	.27	-.62	-.60	.22	.44	-.44	.66	-.01	
Na	-.45	.23	-.37	.13	.16	-.34	.01	.80	-.26	-.13	
pH	-.15	.23	-.23	.15	.19	-.17	-.22	.52	-.37	.12	
	Zn	Fe	Mn	Al	Ti	Cr	Sr/Al	B	Ba/Al	P	
Ca/Al	.26										
Mg/Al	.41	.77									
Na	.45	-.32	-.53								
pH	-.37	-.33	-.51	.52							
	K	Ca/Al	Mg/Al	Na							

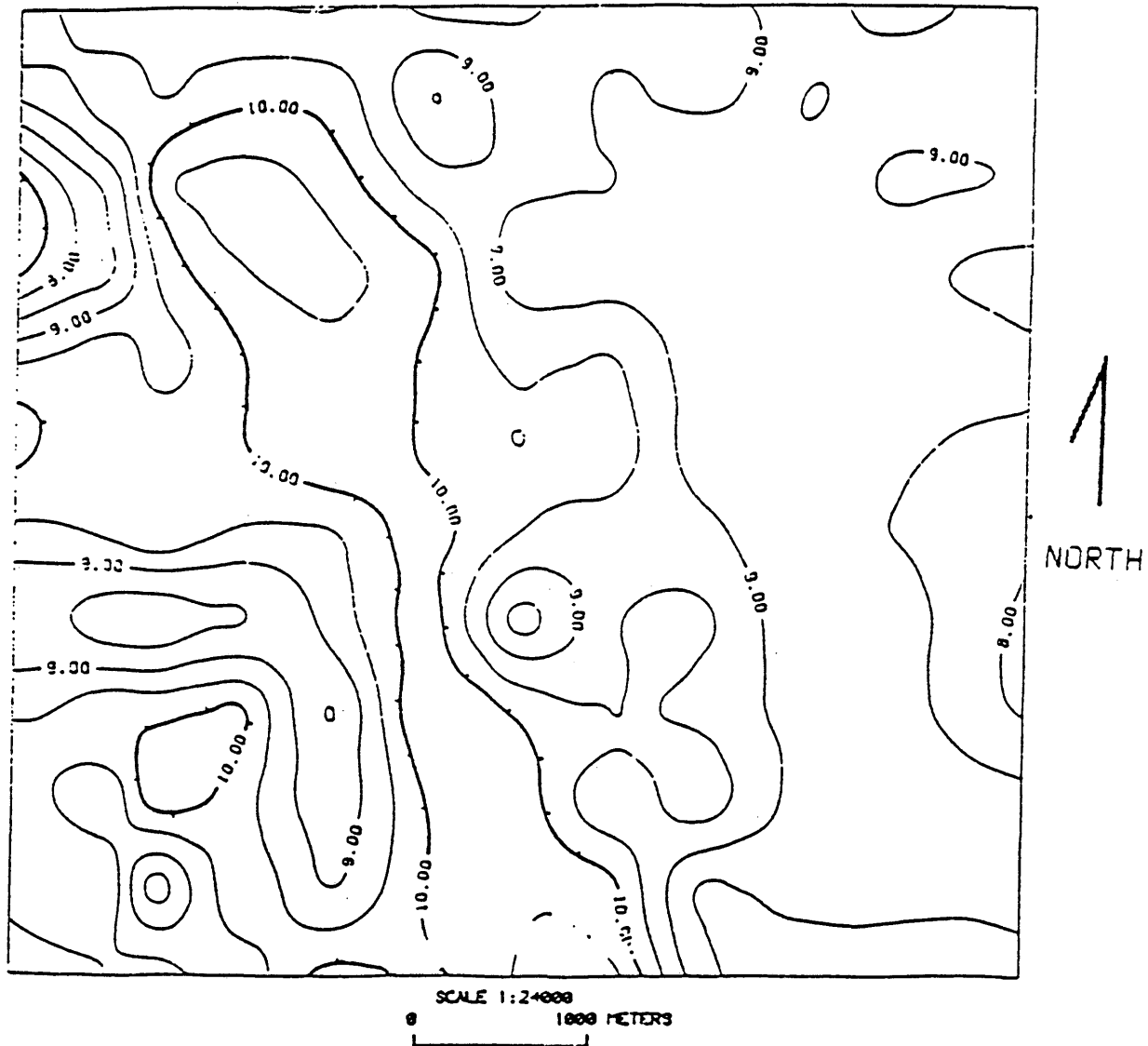


Figure 14. Contour map of the soil pH, Eagle Springs area, Railroad Valley, Nevada.

soil pH shows no relationship to oil production (Figure 14).

A strong positive relationship between Ca/Al, Ba/Al, Sr/Al and to some extent Mg/Al reveals that Ca, Sr, Ba and maybe Mg behave similarly. Also significant, positive relationships are found for Zn, Mn, Cr, Fe and Ti is observed, which suggests that these elements are behaving similarly and from the correlation matrix it can be seen that these elements are negatively correlated with alkaline-earth elements. The negative correlations between redox-sensitive elements and alkaline-earth elements support the principle that oxidation of hydrocarbons creates a reducing environment which resulted in the reduction and mobilization of the redox-sensitive elements, and in turn they become more available for plants. On the other hand, the oxidation of hydrocarbons near the surface has resulted in the precipitation of alkaline-earth carbonates, which make them less available to plants.

Analysis of Variance

The estimates of variance components, as percentages of the total logarithmic variance are given in Table 5. Significant variance components between samples are indicated for Zn, Fe, Mn, Ti, Cr, Sr/Al, Ba/Al, Ca/Al and Mg/Al. There are no significant variance components for phosphorous and potassium. More than 70% of the total variance may be attributed to the regional (between-samples) variance for Zn, Fe, Mn, Ti, Cr, Sr/Al, Ba/Al, Ca/Al and Mg/Al.

Table 5. Total Logarithmic Variance and Variance Components as Percentage of the Total Variance, for Chemical Variables of (Atriplex confertifolia) from Eagle Springs area, Railroad Valley, Nevada

<u>Variable</u>	<u>Total Logarithmic Variance</u>	<u>Variance Components as Percent of Total Variance</u>		
		<u>Regional</u>	<u>Sampling</u>	<u>Analytical</u>
Zn	0.033118	73.88*	1.59	24.53
Fe	0.023447	79.04*	0.00	20.96
Mn	0.018904	79.57*	19.48***	0.95
Al	0.025676	85.57*	11.62**	2.81
Ti	0.026143	80.25*	16.34**	3.41
Cr	0.018012	76.16*	0.00	23.84
Sr/Al	0.16346	80.24*	9.61	10.15
Ca/Al	0.002255	79.29*	8.36	12.35
Ba/Al	0.050017	81.10*	15.90**	3.00
Mg/Al	0.072707	83.08*	15.07***	3.36
P	0.021024	45.24	53.74***	1.01
K	0.011611	64.82	30.46**	4.72
Na	0.041945	87.27**	9.37*	3.36
B	0.075803	89.30*	6.40	4.31

* significant at 95% confidence level
 ** significant at 99% confidence level
 *** significant at 99.9% confidence level

Table 6 lists the variance ratio (V_R) for each of the measured parameters. All variables except P exhibit V_R values greater than 1.0. The variance ratios indicate that with the possible exception of P and K, all the maps constructed constitute a true representation of the geographic variation of that parameter.

Geochemical maps for each of the parameters of primary interest are given in Figures 15 through 21. It is clear that the Sr/Al, Ba/Al, and Ca/Al ratios in plants are lower over the Eagle Springs oil field and extending south-southwest to where a new well has been drilled just out of the survey area. The low ratio extends north-northeast at the edge of the down-dropped block of the basin and range boundary fault. The low ratio is considered to reflect the depletion of alkaline earth elements in the soil solution due to carbonate precipitation as a result of hydrocarbon microseepage and subsequent oxidation over the oil field and along the faults.

Iron, manganese, titanium and chromium in plants show an opposite relationship over the Eagle Springs oil field than alkaline earth elements. These elements show relatively high concentrations over the Eagle Springs oil field. The high values of redox-sensitive elements is considered to reflect the enrichment of redox-sensitive trace elements in

Table 6. Stability estimates for maps

<u>Variable</u>	<u>Variance Ratio (V_R)</u>
Zn	2.473
Fe	3.772
Mn	3.895
Al	5.932
Ti	4.063
Cr	3.194
Sr/Al	4.061
B	8.343
Ba/Al	4.290
P	0.826
K	1.843
Ca/Al	3.827
Mg/Al	4.911
Na	6.855
Mg	7.391
Ca	3.886
Sr	1.521

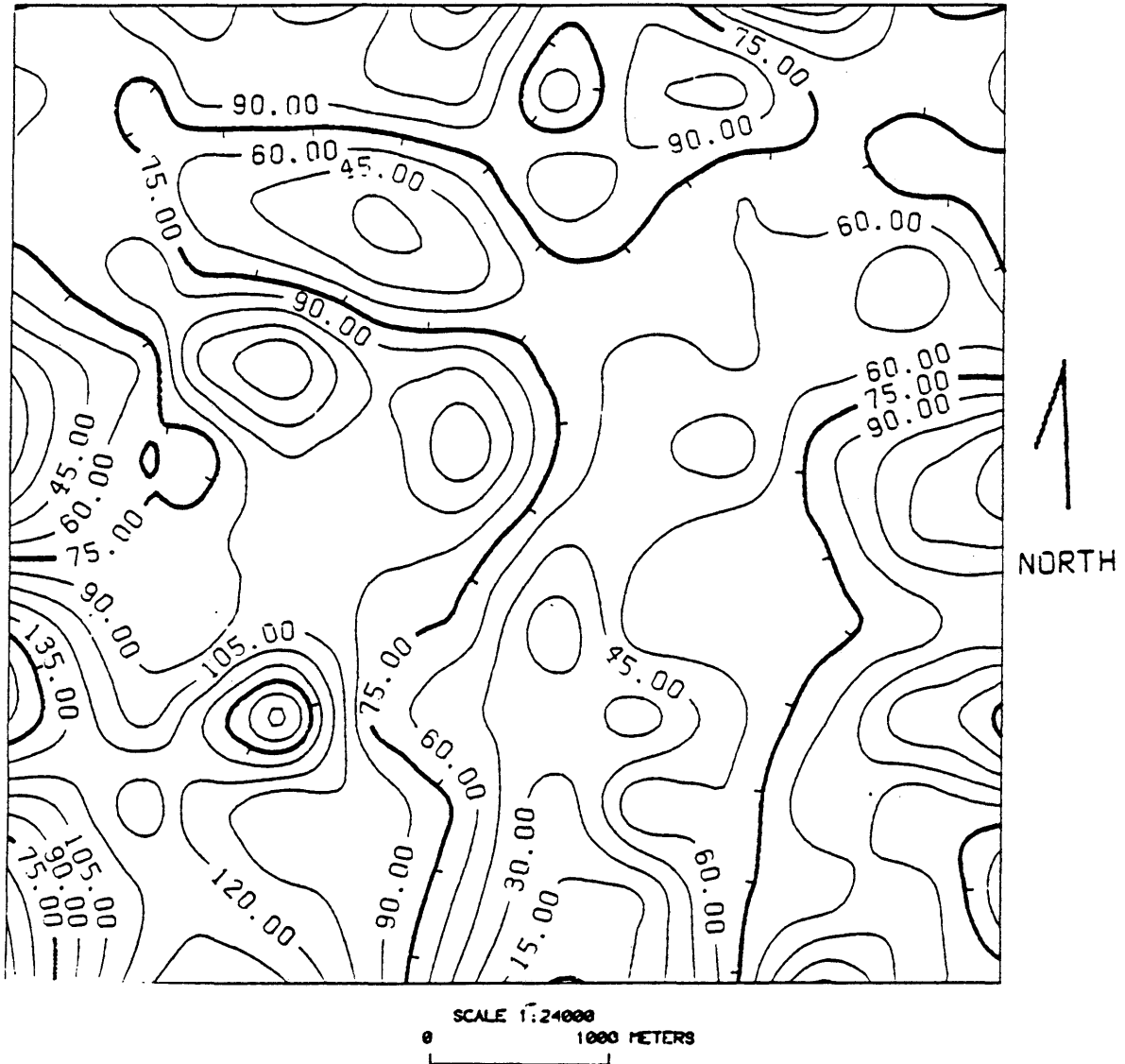


Figure 15. Contour map of Sr/AlX100 in the Atriplex confertifolia Eagle Springs, Railroad Valley, Nevada (CI = 15.0).

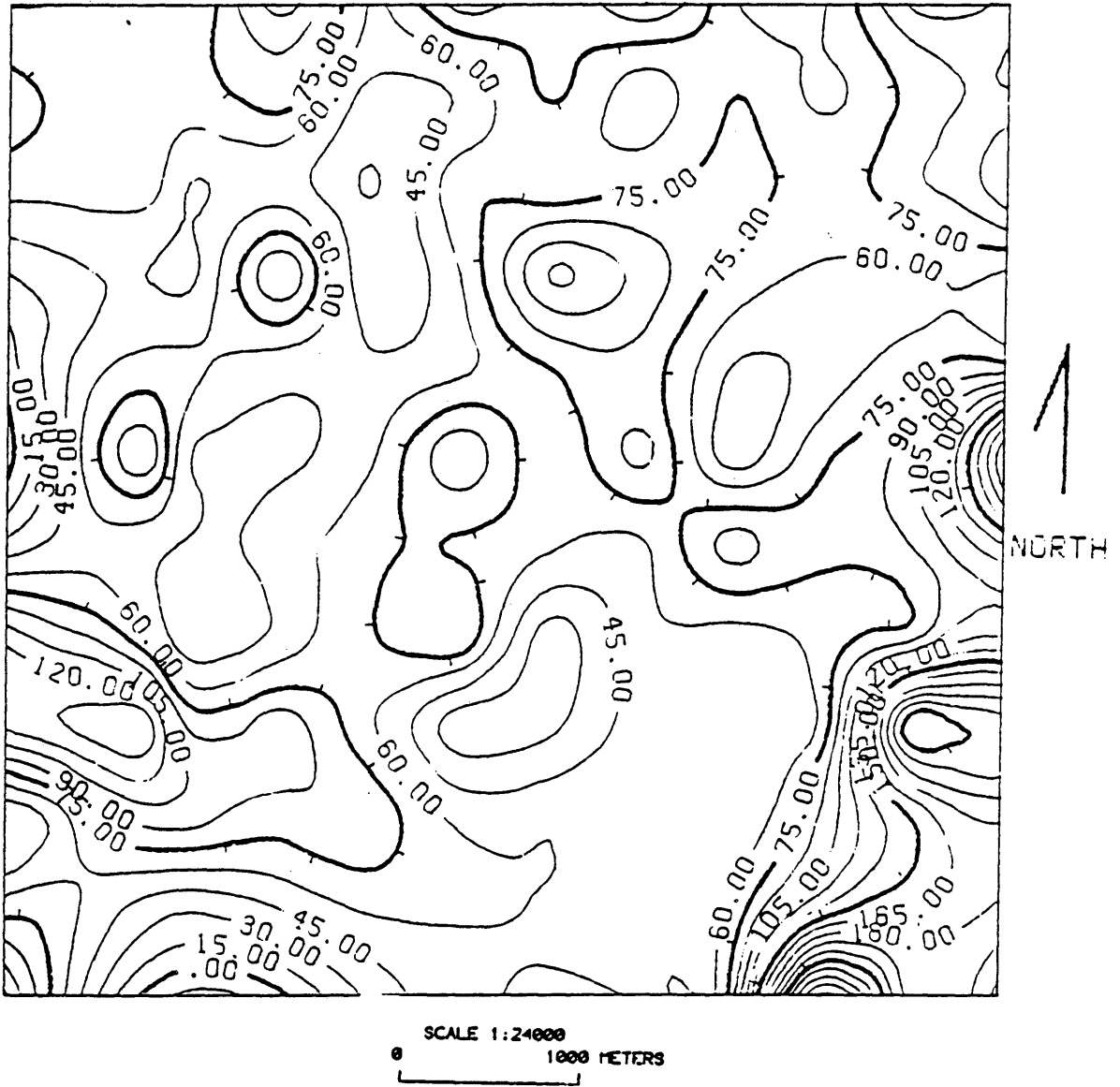


Figure 16. Contour map of Ca/Al in the Atriplex confertifolia, Eagle Springs, Railroad Valley, Nevada (CI = 15.0).

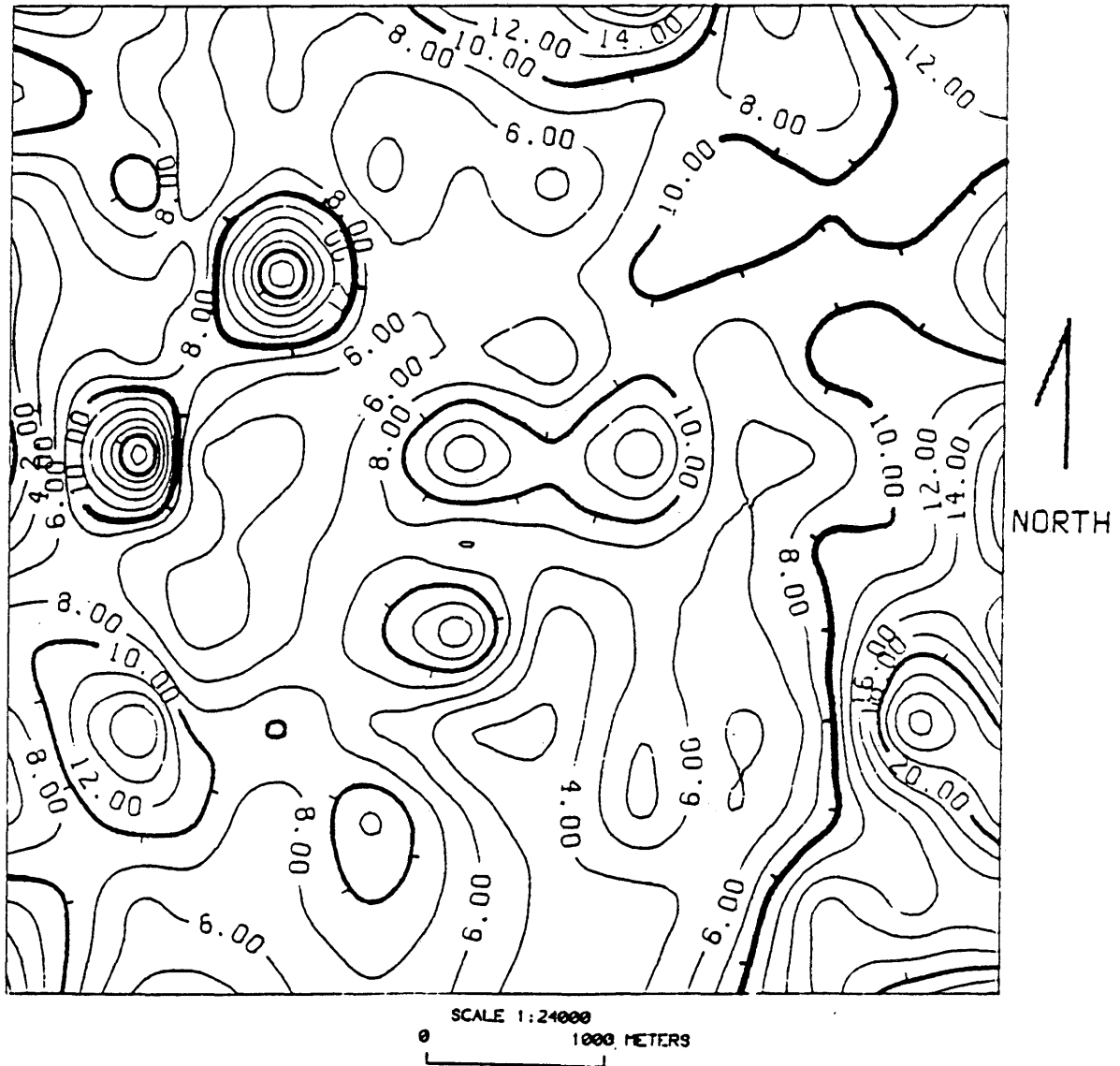


Figure 17. Geochemical map of Ba/Al* 100 in the Atriplex confertifolia, Eagle Springs, Railroad Valley, Nevada (CI = 2.0).

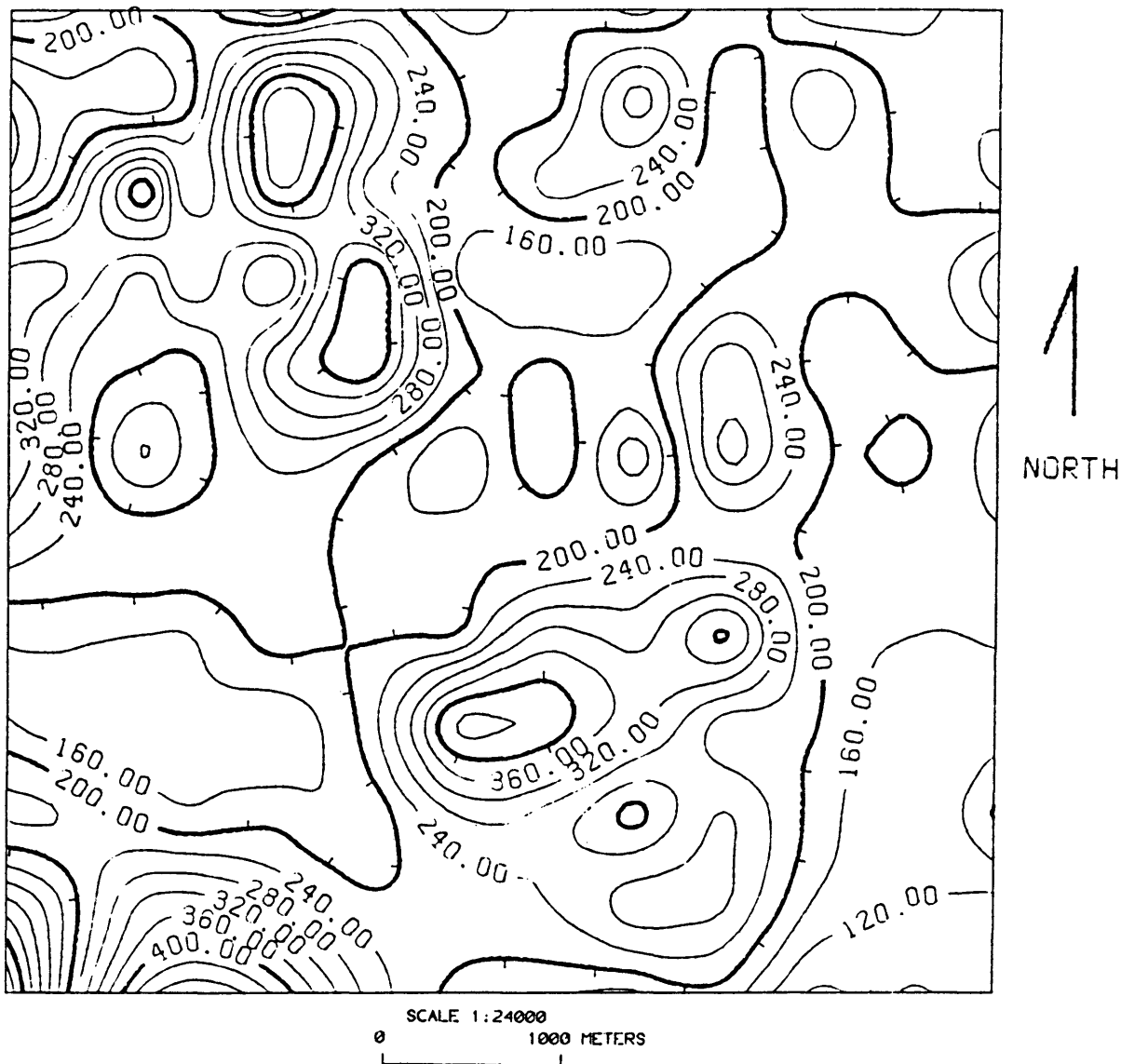


Figure 18. Contour map of iron in the Atriplex confertifolia Eagle Springs, Railroad Valley, Nevada (CI = 40.0).

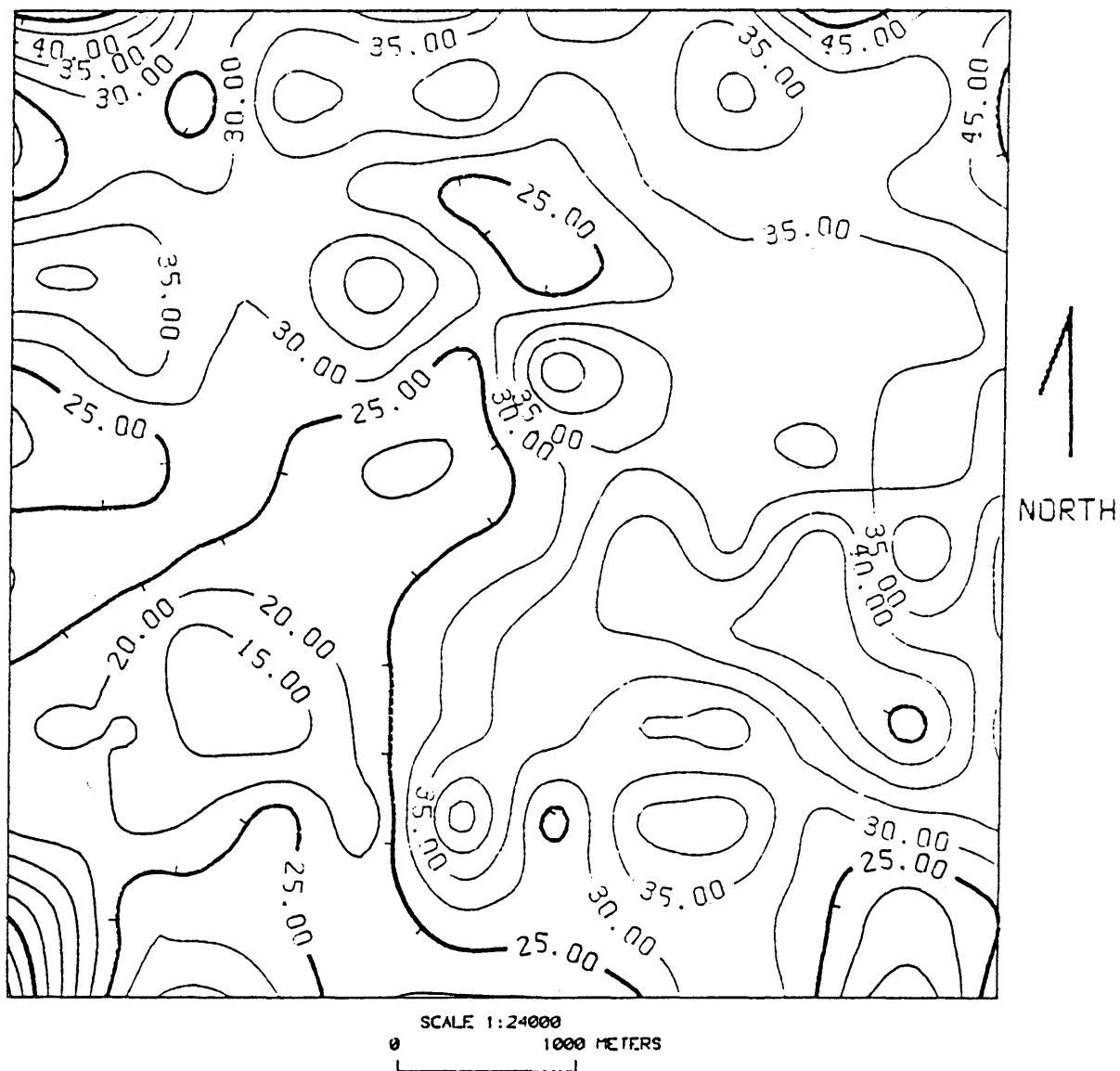


Figure 19. Contour map of Mn in the *Atriplex confertifolia*, Eagle Springs, Railroad Valley, Nevada (CI = 5.0).

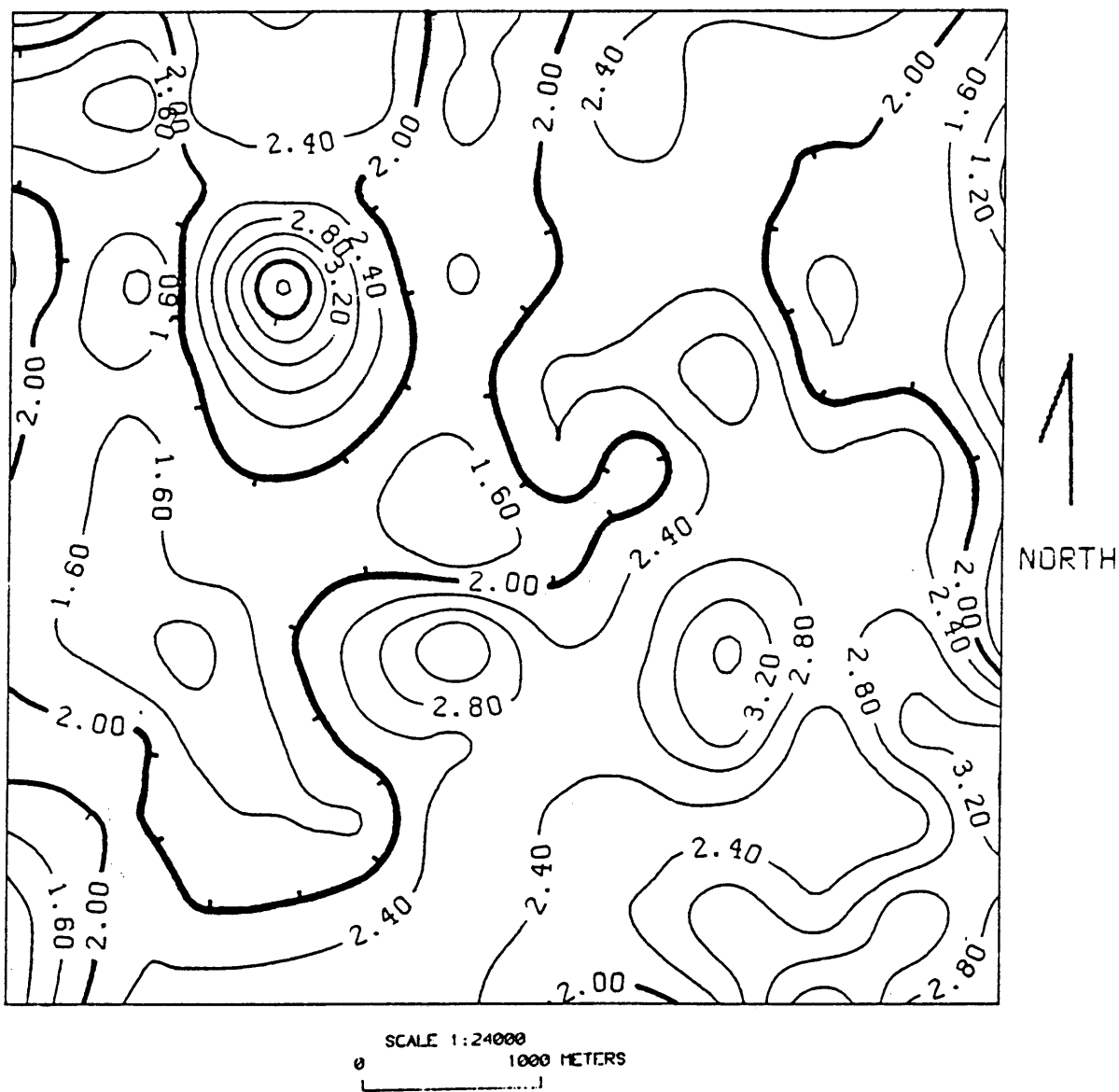


Figure 20. Contour map of Cr in the *Atriplex confertifolia*, Eagle Springs, Railroad Valley, Nevada (CI = 0.40).

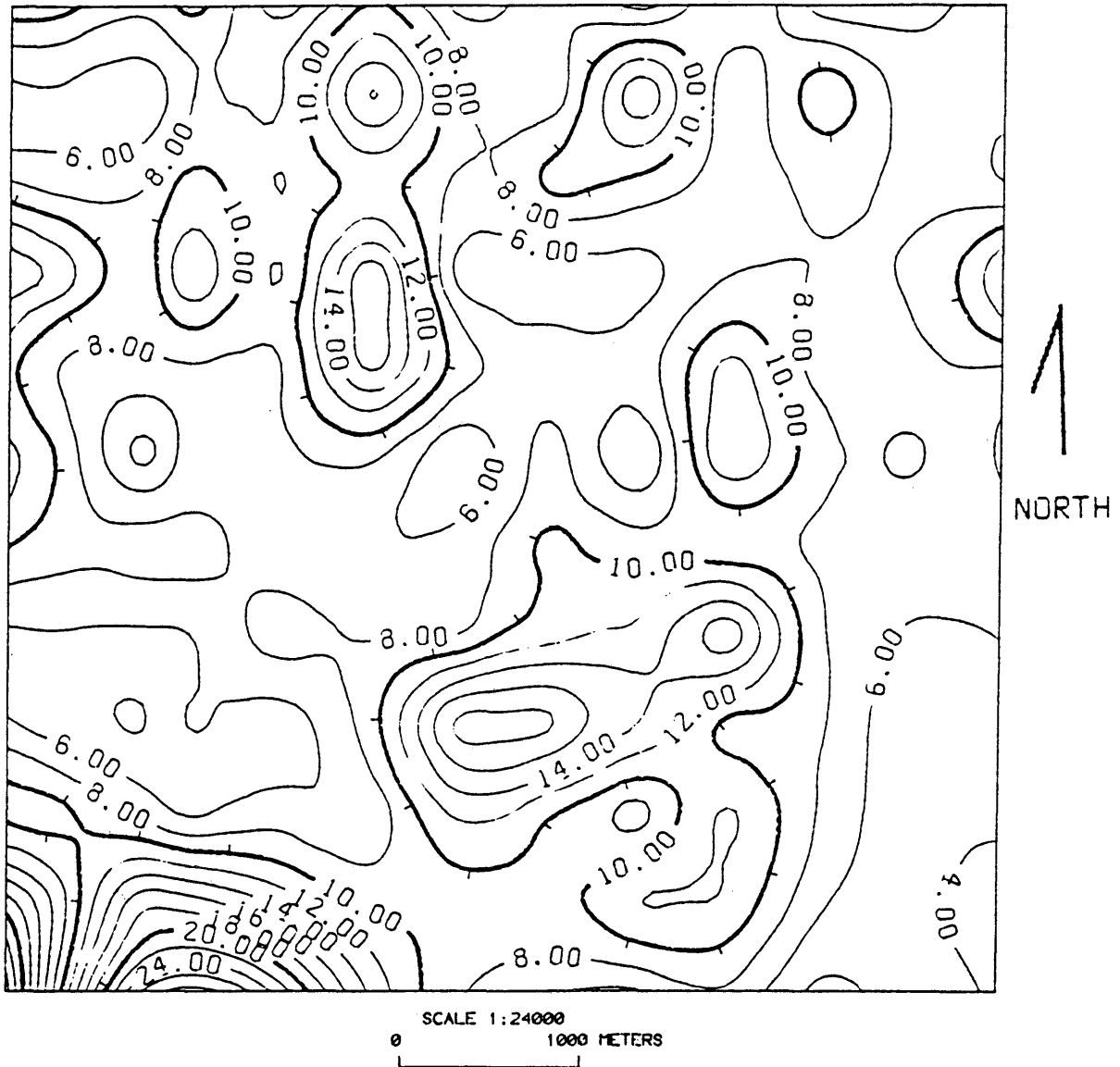


Figure 21. Contour map of Ti in the *Atriplex confertifolia*, Eagle Springs, Railroad Valley, Nevada (CI = 2.0).

the soil solution in the reduced form, which is more available for plants.

R-MODE FACTOR ANALYSIS

The results of the varimax loadings for the two and three factor models as well as the positive eigenvalues are presented in tables 7,8 and 9 respectively. The two-factor model accounts for 72% of the variance and is considered the most appropriate solution because (1) two metal associations can be considered as a measure of geochemical features present in the area, (2) eigenvalues are greater than unity, and (3) a plot of eigenvalues vs. the factor numbers shows a significant break in slope from a linear decrease.

The first factor contains the association of Fe, Ti, Sr/Al, Ba/Al, Ca/Al and Mg/Al. The easy substitution of Ca for Sr and possibly the substitution of Sr for Ba in the alkaline-earth carbonates that may be formed during the hydrocarbons oxidation in the near surface soils is some evidence for the Sr-Ca-Ba and Mg geochemical association. The association of Fe and Ti can be explained by the easy substitution of iron for Ti^{3+} in some accessory minerals like magnetite, which may be found as a result of the hydrocarbon oxidation and subsequent reduction of iron oxides. The negative correlation of Sr/Al, Ba/Al, Ca/Al and Mg/Al to the Fe and Ti can be explained by the strong association of Sr, Ba, Ca and Mg in the alkaline-earth carbonates.

The second factor contains the association of Zn, Mn, Cr and Sr/Al. This can be explained by the coprecipitation of Zn,

Cr and Sr by manganese, and the oxidation of hydrocarbons creating a reducing zone which in turn makes them more available for plants.

Table 7. Communalities and Varimax Loadings for The Two-Factor Model (X100) from the Atriplex confertifolia Samples from Eagle Springs area, Railroad Valley, Nevada

<u>Elements</u>	<u>Communalities</u> <u>(2 Factors)</u>	<u>Factor</u> <u>1</u>	<u>Factor</u> <u>2</u>
Zn	56.9	19.5	72.9*
Fe	84.5	87.0*	29.7
Mn	61.3	7.3	77.9*
Ti	82.3	85.9*	29.3
Cr	40.3	-7.5	63.1*
Sr/Al	75.0	-75.9*	-41.8*
Ba/Al	71.7	-84.4*	-6.8
Ca/Al	91.2	-95.5*	-0.8
Mg/Al	85.6	-87.7*	29.6

Eigenvalues %	72.13		

*Significant varimax loadings

Table 8. Communalities and Varimax Loadings for the Three-Factor Model (X100) From the Atriplex confertifolia Samples from Eagle Springs Oil Field area, Railroad Valley, Nevada

<u>Elements</u>	<u>Communalities</u>	<u>Factor_1</u>	<u>Factor_2</u>	<u>Factor_3</u>
Zn	68.1	14.8	80.7*	-9.1
Fe	87.6	87.7*	21.6	-24.5
Mn	76.6	2.1	87.2*	-7.8
Ti	84.6	86.3*	22.7	-22.1
Cr	96.3	-1.5	13.5	-97.2*
Sr/Al	75.4	-74.2	-43.7*	11.5
Ba/Al	71.7	-84.2*	0.6	-9.0
Ca/Al	91.8	-94.4*	-10.8	-12.4
Mg/Al	85.7	-87.6*	-17.8	24.2

Eigenvalues %	82			

* Significant varimax loadings

Table 9 . Positive EigenValues for Three-Factor Model
Computed from the Atriplex confertifolia Samples from
Eagle Springs area, Railroad Valley, Nevada

<u>Factor Number</u>	<u>Eigen Values</u>	<u>Cumulative % Data Variance</u>
1	4.679	51.99
2	1.813	72.13
3	0.888	82.00

CONCLUSIONS

1. In arid environments, like that found at Eagle Springs oil field, Railroad Valley, Nevada, geochemical exploration for petroleum using shallow soil sampling techniques are unreliable because the depth of carbonate formation and the redox zone is generally too deep to be reached with hand tools.
2. Geochemical exploration for petroleum using biogeochemistry is more reliable in such environment because deep rooted plants reach further below the surface into the microseepage oxidation zone and can be sampled easily.
3. Iron, manganese, chromium and titanium (redox-sensitive elements) show relatively high concentrations over the Eagle Springs oil field in Atriplex confertifolia plants and extend north-northeast at the edge of the down-dropped block of the basin and range boundary fault. The high concentrations also extend south-southwest to where a new well has been drilled just out of the survey area. Relatively high concentrations are shown in the northwestern sections, which may be considered as a possible target for a follow up study. The high concentrations of these transition elements reflect their enrichment in the soil solution as a result of

the reducing conditions which resulted from the hydrocarbon microseepage and subsequent oxidation.

4. The alkaline earth elements to aluminum ratios in Atriplex confertifolia show low concentrations over the oil field . The low ratios are considered to reflect the depletion of alkaline earth elements in the soil solution due to the precipitation of carbonates during the hydrocarbon oxidation over the oil field and along faults. The anomalous areas shown by alkaline earth elements to aluminum ratios generally coincide with areas of high concentration of the redox sensitive elements as theory would predict if microseepage is occurring.

RECOMMENDATIONS FOR FURTHER STUDY

The following recommendations could be considered if a follow up study is to be done:

1. Deep soil samples should be collected in order to get more reliable geochemical results for soils.
2. More soil and plant samples could be collected from around the newly drilled wells in the southwestern portion of the area and the northwestern sections of the study area because of the observed undrilled anomalies in those areas.
3. Sampling density is adequate in the study area.
4. Sampling density should be increased in the subsequent study of the southwestern and northwestern sections to verify and better define the anomalous areas.

REFERENCES CITED

- Bartlett, M. S. (1947). The use of transformations. Biometrics, 3(1), pp. 39-52.
- Bortz, L. C. and Murray, D. K. (1979). Eagle Springs oil field, Nye County, Nevada. In: Newman, G. W. and Goode, H. D., eds., RMAG-1979. Basin and Range Symposium and Great Basin Field Conference, pp. 441-453.
- Chapman, R. P. (1976). Limitations of correlation and regression analysis in geochemical exploration. Inst. Min. Metall. Trans., Sect. B, 85, pp. 279-293.
- Crow, E. L., Davies, F. A., and Maxfield, M. W. (1960). Statistics Manual: New York, Dover Publications, 241 p.
- Dalziel, M. C. and Donovan, T. J. (1984). Correlations of suspected petroleum-generated biogeochemical and aeromagnetic anomalies, Bell Creek Field, Montana. In: Unconventional Methods in Exploration for Petroleum and Natural Gas III. Dallas, Southern Methodist University Press, pp. 59-69.
- Dalziel, M. C. and Donovan, T. J. (1980). Biogeochemical evidence for subsurface hydrocarbon occurrence, Recluse oil field, Wyoming: Preliminary Results. U. S. Geological Survey Open File report 80-837, 10 p.
- Dolly, D. E. (1979). Geological techniques utilized in Trap Spring field discovery, Railroad Valley, Nye County, Nevada. In: Newman, G. W. and Goode, H. D., eds., RMAG-1979 Basin and Range Symposium and Great Basin Field Conference, pp. 455-467.
- Donovan, T. J. (1974). Petroleum microseepage at Cement, Oklahoma - Evidence and Mechanism: AAPG-Bull., 58, pp. 429-446.
- Duchscherer, W., Jr. (1985). Bell Creek Oil Field, Montana: A further geochemical confirmation. Assoc. Petrol. Geochem. Explor., 1, pp. 57-84.

- Duchscherer, W., Jr. (1980). Geochemical methods of prospecting for hydrocarbons. Oil and Gas Journal, Dec. 1, pp. 194-208.
- Duey, H. D. (1979). Trap Springs oil field, Nye County, Nevada. In: Newman, G. W. and Goode, H. D., eds., RMAG-1979 Basin and Range Symposium and Great Basin Field Conference, pp. 469-476.
- Foster, N. M. (1979). Geomorphic exploration utilized in the discovery of Trap Spring oil field, Nye County, Nevada. In: Newman, G. W. and Goode, H. D., eds., RMAG-1979 Basin and Range Symposium and Great Basin Field Conference, pp. 477-486.
- Garrett, R. G. (1969). The determination of sampling and analytical errors in exploration geochemistry. Econ. Geol., 64, pp. 568-569
- Garrett, R. G. (1973). The determination of sampling and analytical errors in exploration geochemistry: A reply. Econ. Geol., 68, pp. 282-283.
- Green, R. O. and Roberts, D. A. (1985). Detection of hydrocarbon microseepage and related geobotanical anomalies using multi-data image subtraction, Railroad Valley, Nevada. 19th International Symposium on Remote Sensing of Environments, October 21-25, Ann Arbor, MI, 9 p.
- Havlin, J. L. and Soltanpour, P. N. (1980). A nitric acid plant tissue digest method for use with inductively coupled plasma spectrometry. Comm. in Soil Sci. and Plant Analysis, 11(10), pp. 969-980.
- Howarth, R. J. (1973a). The pattern recognition problem in applied geochemistry. In: Jones, M. J. (ed.) Geochemical Exploration 1972. Institution of Mining and Metallurgy, London, pp. 259-273.
- Jobson, A. M., Cook, F. D., and Westlake, D. W. S. (1979). Interaction of aerobic and anaerobic bacteria in petroleum biodegradation. Chem. Geol., 24, pp. 355-365.

- Jones, V. T., Burtell, S. G., Modgson, R. A., Whelan, T., Milan, C., Ando, T., Okoda, K., Agatsuma, T. and Takono, O. (1985). Presented at the Fourth Thematic Conference, Remote Sensing and Surface Geochemical Study of Railroad Valley, Nye County, Nevada, presented at the Fourth Thematic Conference: Remote Sensing for Exploration Geology, San Francisco, California, April 1-4.
- Klusman, R. W. (1986). CUMFREQ for a computer program written for the VAX 8600 computer to compute the chi-square statistics and cumfrequency plots. Unpublished research, Colorado School of Mines, Golden, CO.
- Krauskopf, K. B. (1979). Introduction to Geochemistry: McGraw-Hill, Inc., New York, 719 p.
- LePeltier, C. (1969). A simplified statistical treatment of geochemical data by graphical representation. Economic Geology, 64, pp. 538-550.
- Levinson, A. A. (1980). Introduction to Exploration Geochemistry. 2nd ed., Wilamette, IL, Applied Publishing Ltd., 924 p.
- Lindsay, W. L. and Norvell, W. A. (1978). Development of a DTPA soil test for zinc, iron, manganese, and copper. J. Soil Sci. Am., 42, pp. 421-428.
- Lindsay, W. L. (1979). Chemical Equilibrium in Soils. John Wiley and Sons, New York, 449 p.
- Miesch, A. T. (1976). Geochemical Survey of Missouri - Methods of Sampling, Laboratory Analysis and Statistical Reduction of Data. U. S. Geological Survey, PP954-A, 39 p.
- Mitchell, R. L. (1972). Trace elements in soils and factors that affect their availability. Geological Society of American Bulletin, 83, pp. 1069-1076.
- Oehler, D. Z. and Sternberg, B. K. (1984). Seepage-induced anomalies, "false" anomalies and implications for electrical prospecting. AAPG 68(9), pp. 1121-1145.
- Peech, M. (1965). H⁺ activity. In: Soil Analysis, Part 2: Chemical and Microbiological Properties. Am. Soc. Agron. (Agron. #9), Madison, WI, pp. 922-923.

- Roeming, S. S. and Donovan, T. J. (1985). Correlations among hydrocarbon microseepage, soil chemistry and uptake of micronutrients by plants, Bell Creek oil field, Montana. Jour. Geochem. Explor., 23, pp. 139-162.
- Satterthwaite, F. E. (1946). An approximate distribution of estimates. Biometrics, 2(2), pp. 110-114.
- Stumm, W. and Morgan, J. J. (1981). Aquatic Chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters. 2nd Ed., John Wiley and Sons, 780 p.
- Tietjen, G. L. and Moore, R. H. (1968). On testing significance components of variance in the unbalanced nested analysis of variances. Biometrics, 24(2), pp. 423-429.

APPENDIX 1

ANALYTICAL METHODS
MEASUREMENT OF SOIL pH

Add water in small increments to a sufficient quantity of soil to allow immersion of an electrode until a "saturation paste" is formed. A saturation paste is obtained when the surface just begins to glisten or when a groove created by dragging a stirring rod through the paste just closes behind it. The pH is measured after immersion with a Sargent-Welch Electrode (S-30072-15) and meter (Model IP). The method is that of Peech (1965).

Notes

1. Check meter with buffers every 10th sample.
2. If paste is not wet enough, errors may result from poor soil-electrode contact and the high electrical resistance of the soil.
3. Excess water will normally give high readings.
4. Soils should be equilibrated with atmospheric CO₂
5. If soils are calcareous, a thin calcium carbonate film may form on the electrode. It can be removed with dilute HCl.
6. Electrodes which are easily cleaned are desirable.
7. Varying amounts of water may be needed due to clay content and grain size, resulting in pH fluctuations.

DTPA Extraction of Surface Soils

Preparation of the extracts was carried out at Colorado State University Soil Testing Lab, Fort Collins, and analyzed by ICP-AES (Jarrell-Ashatom Comp 750). The method used was described by Lindsay and Norvell (1978).

Ten grams of air dried soil were weighted into a 125 ml conical flask. Twenty ml of DTPA extracting solution were added to each soil sample. The soil mixture was then shaken on a mechanical shaker for 2 hours. The extracts were then filtered with Whatman No. 42 filter paper. The filtered solution was then analyzed for the elements.

Reagents

DTPA extraction solution was obtained by dissolving 149.2 g of reagent-grade triethanolamine (TEA), 19.67 g of DTPA, and 14.7 g of calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$) in deionized water. Since DTPA is not very soluble in water, DTPA was placed in a small amount of water and then dissolved in the TEA solution. When DTPA was dissolved, it was diluted to approximately 9 liters. The pH was adjusted to 7.3 with 1:1 HCl and the solution was diluted to 10 liters. The DTPA extractable solution is unstable with regard to pH; however, pH should be checked periodically, because pH of 7.3 is critical for the extraction.

Standard Solutions

A series of standards in DTPA solution for the different elements were prepared and calibrated.

Nitric Acid Digestion of Plant Samples

The dried plant materials were ground to -20 mesh. One gram was weighed into a 50 ml Taylor digest tube (graduated 25 mm x 200 mm, Corning No. 7952). Ten ml of concentrated nitric acid were added to each tube and allowed to digest overnight. The tubes were placed in aluminum heating blocks, which were capable of holding 45 tubes per block. The nitric acid digests were heated in the same aluminum block at 125°C for 4 hours. When the volume was reduced to 2-3 ml, the solution was clear but not colorless due to the presence of nitrogen oxides. The digests were then brought to 12.5 ml with concentrated nitric acid and then diluted to 50 ml with distilled water. The standards were prepared with the same acid to water ratio as the samples.

Analysis was then done by aspiration directly into the plasma for ICP-AES analysis. The detection limits for the ICP-AES are shown in Table 10.

Table 10. Detection Limits for ICP-AES

<u>Element</u>	<u>Detection Limit</u>
Zn	1
Fe	1
Mn	1
Cu	1
Al	5
Ni	1
Mo	1
Cd	0.5
Ti	1
Cr	1
Sr	0.5
B	1
Ba	1
P	0.0005
K	0.01
Ca	0.01
Mg	0.005
Na	0.01

All values in ppm except P, K, Ca, Mg and Na
which are in percent

APPENDIX 2
ANALYTICAL RESULTS

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

.....

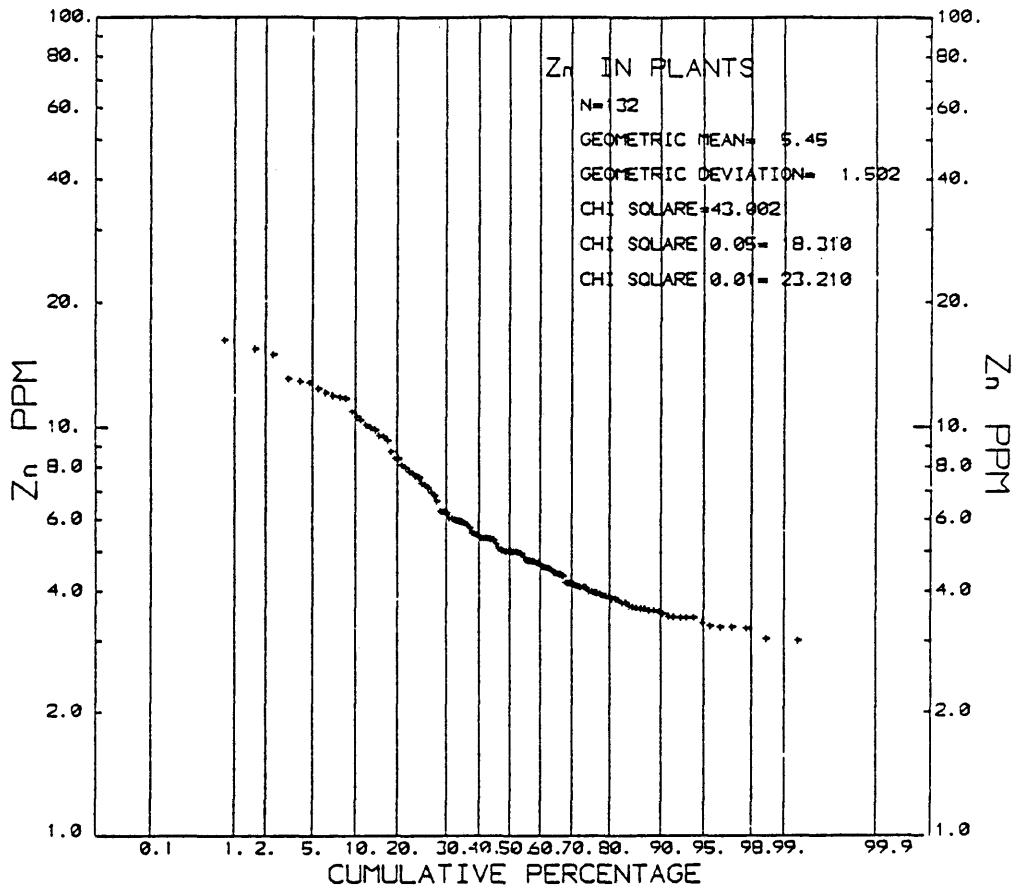
.....

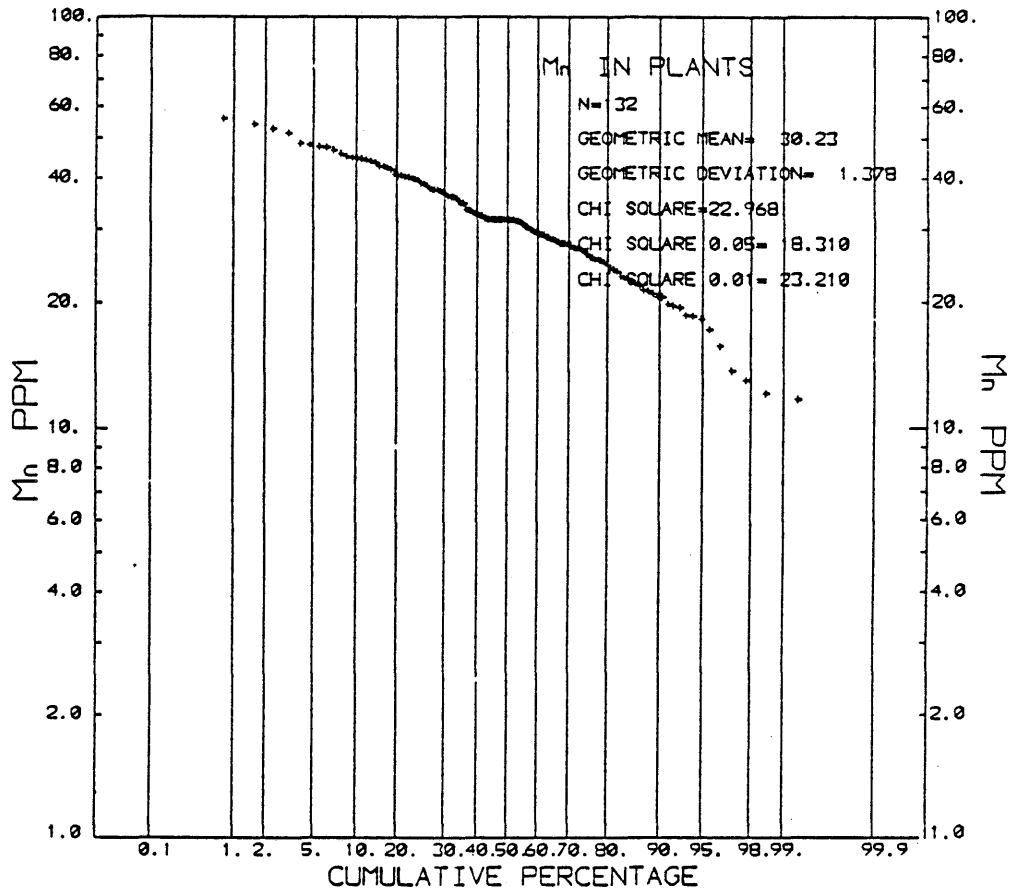
.....

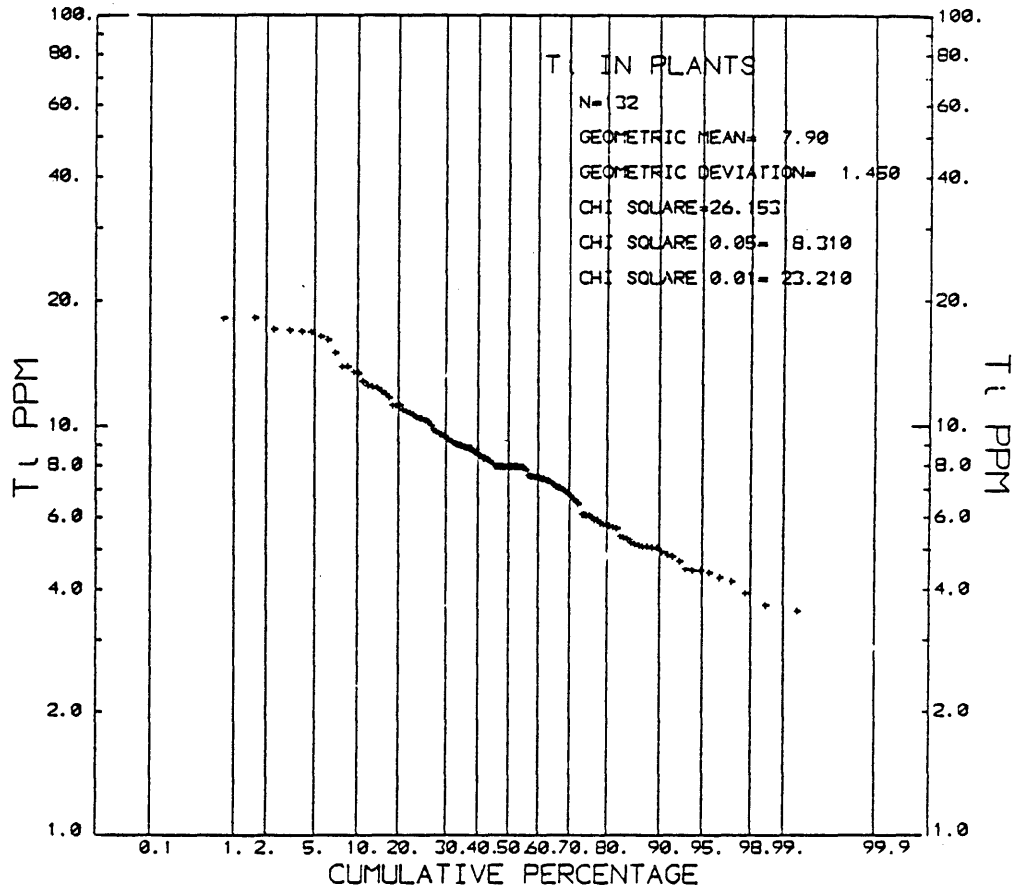
.....

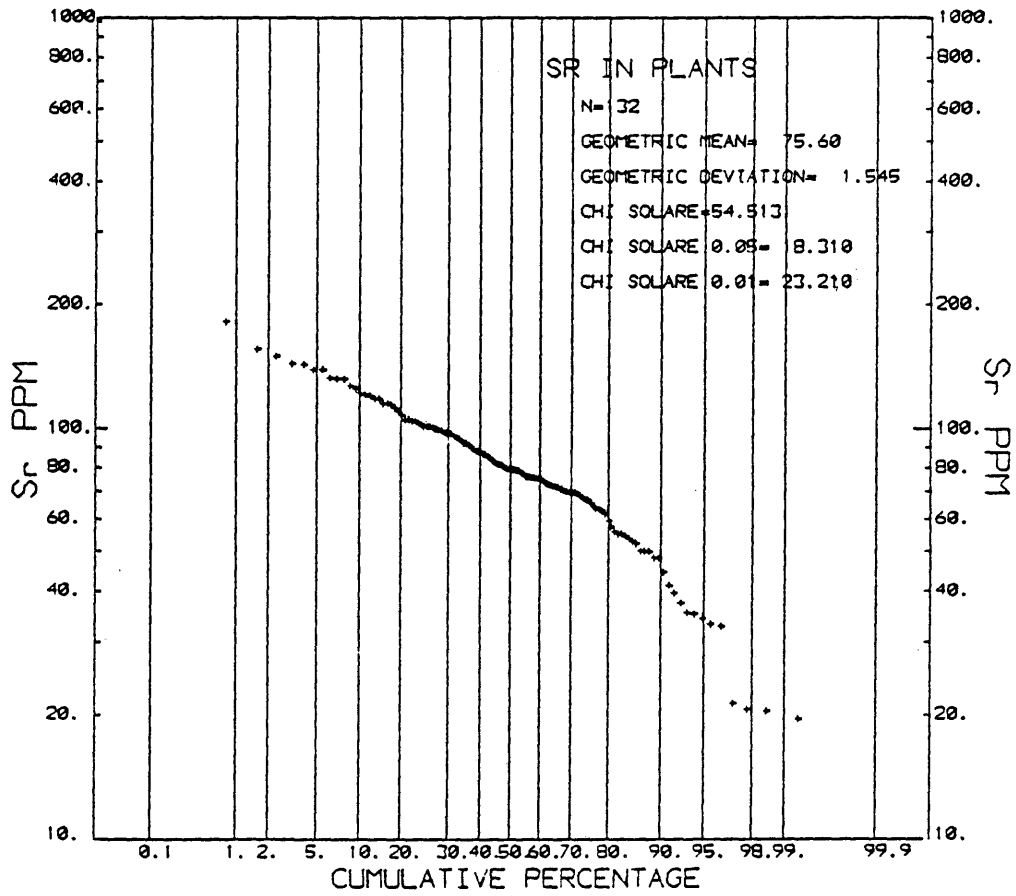
.....

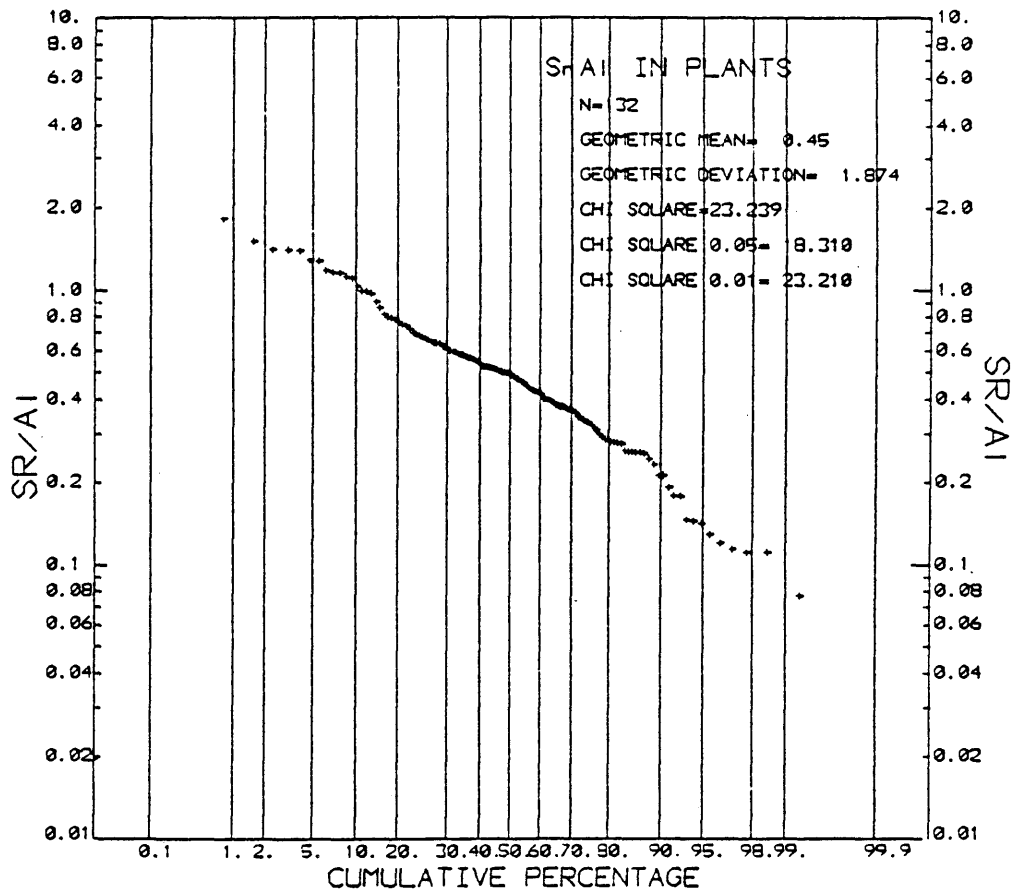
APPENDIX 3
Geochemical Maps and
Cumulative Frequency

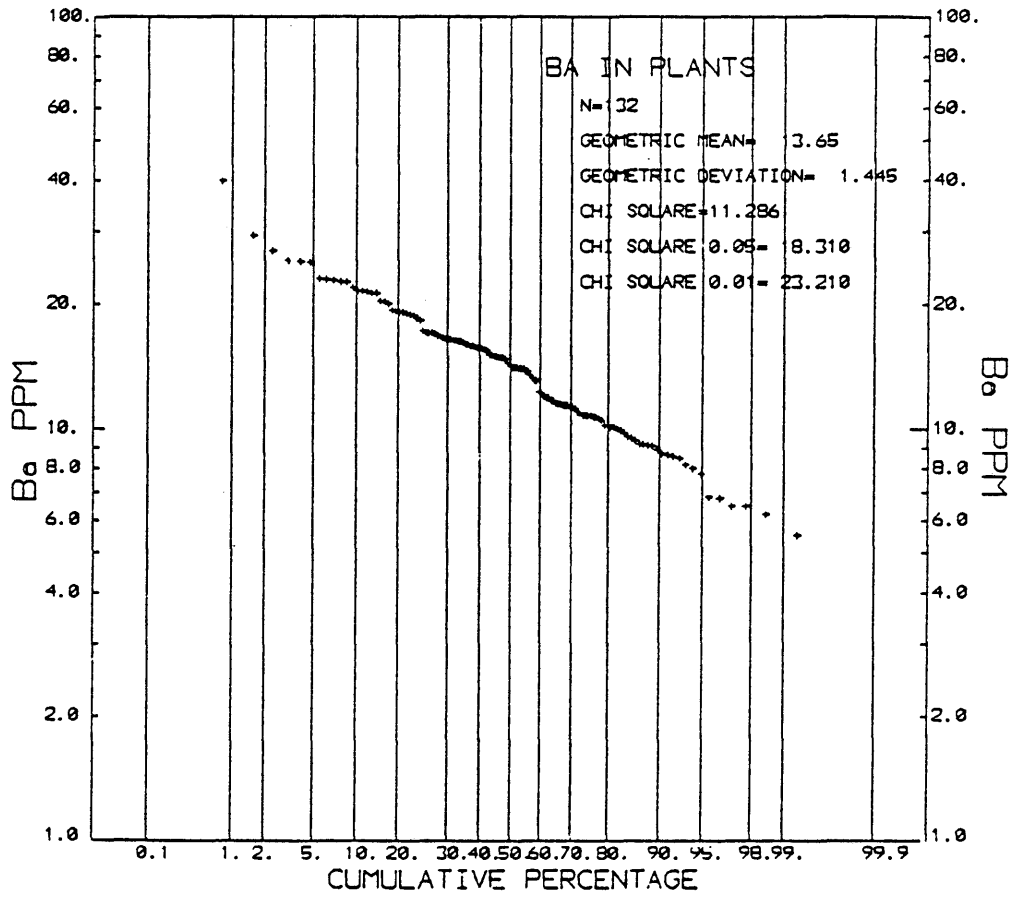


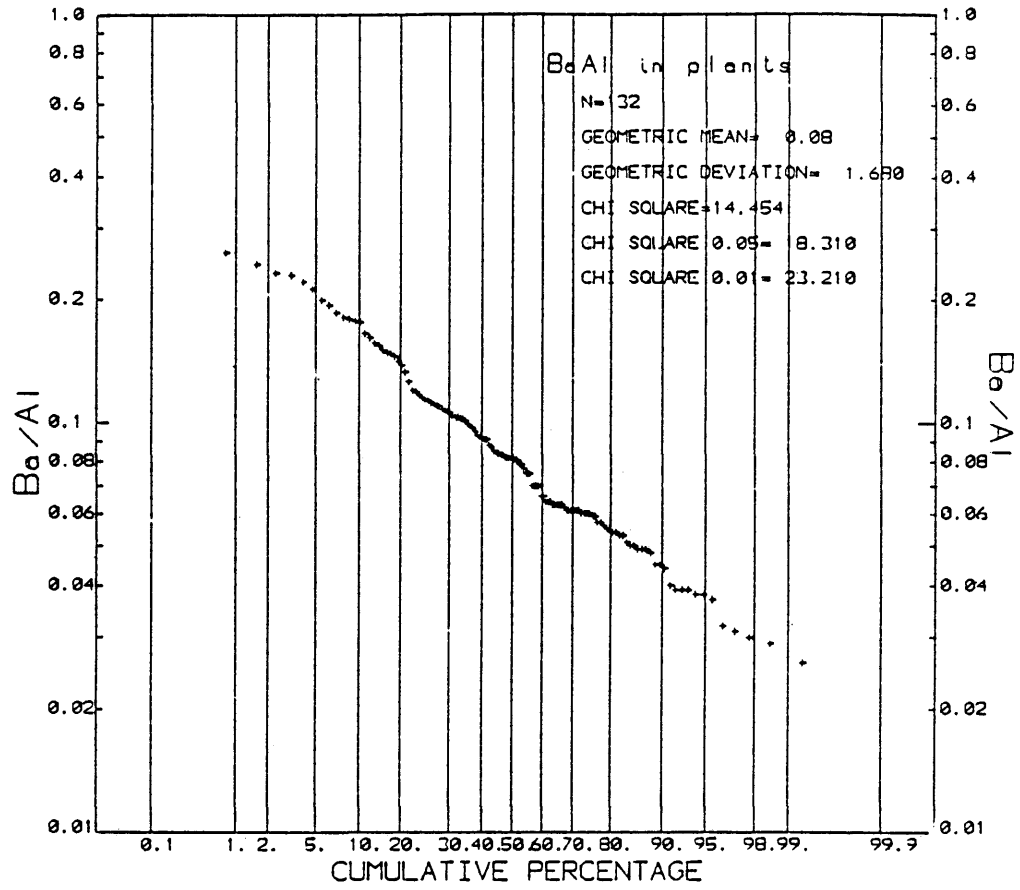


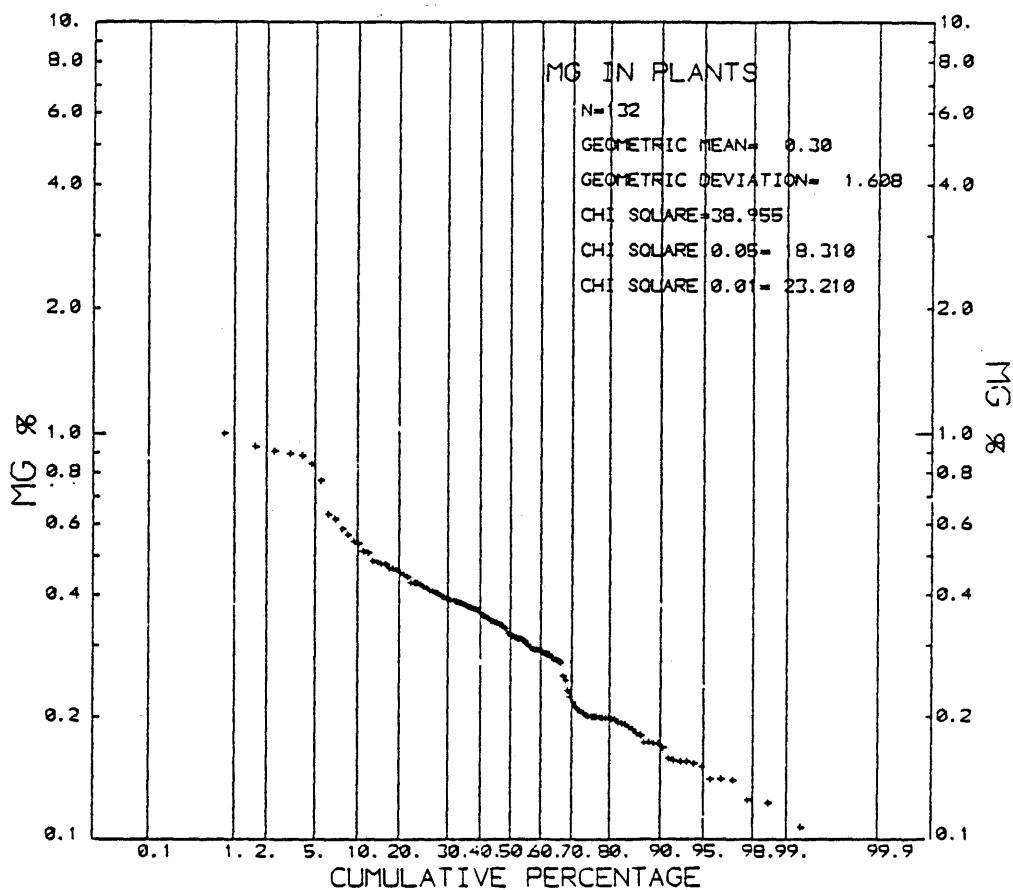


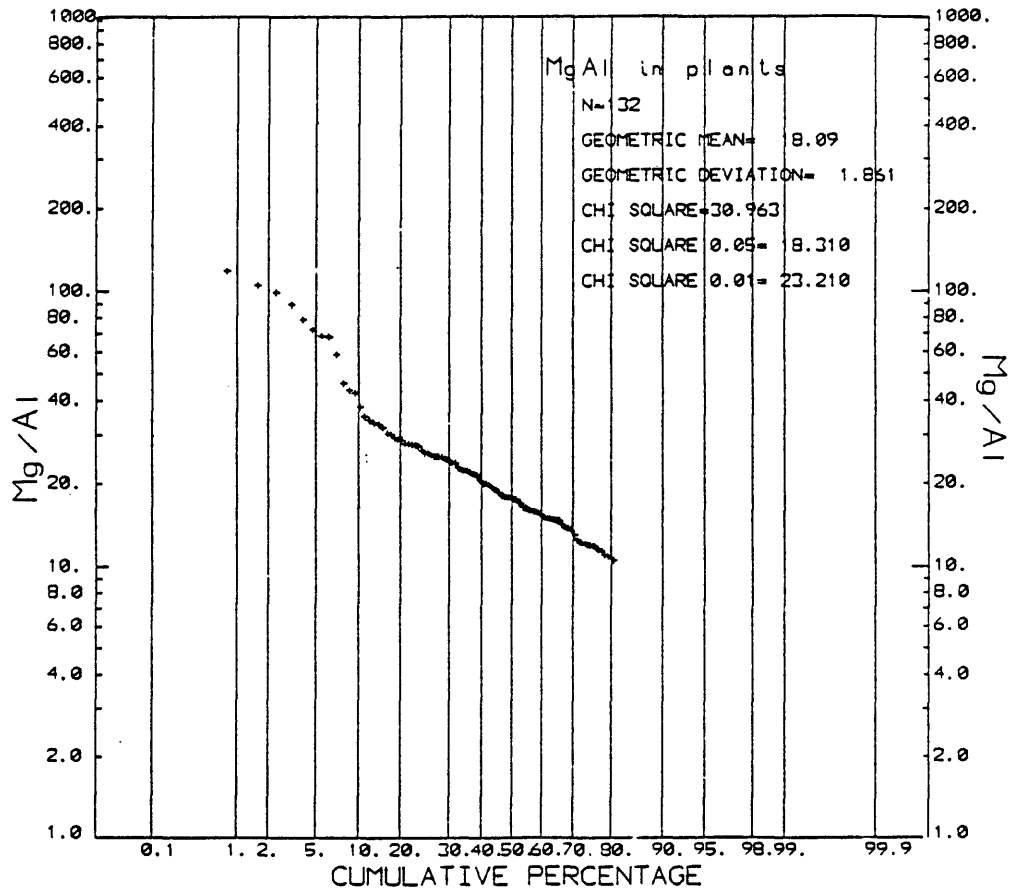


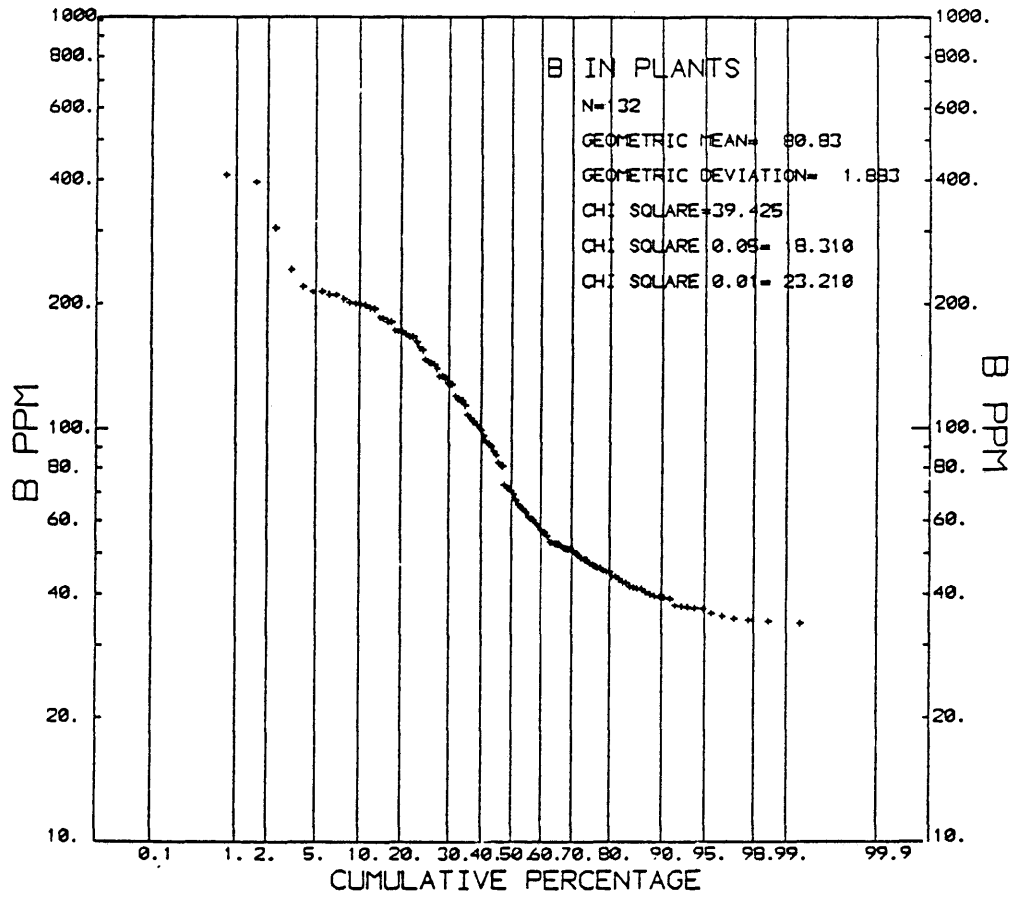


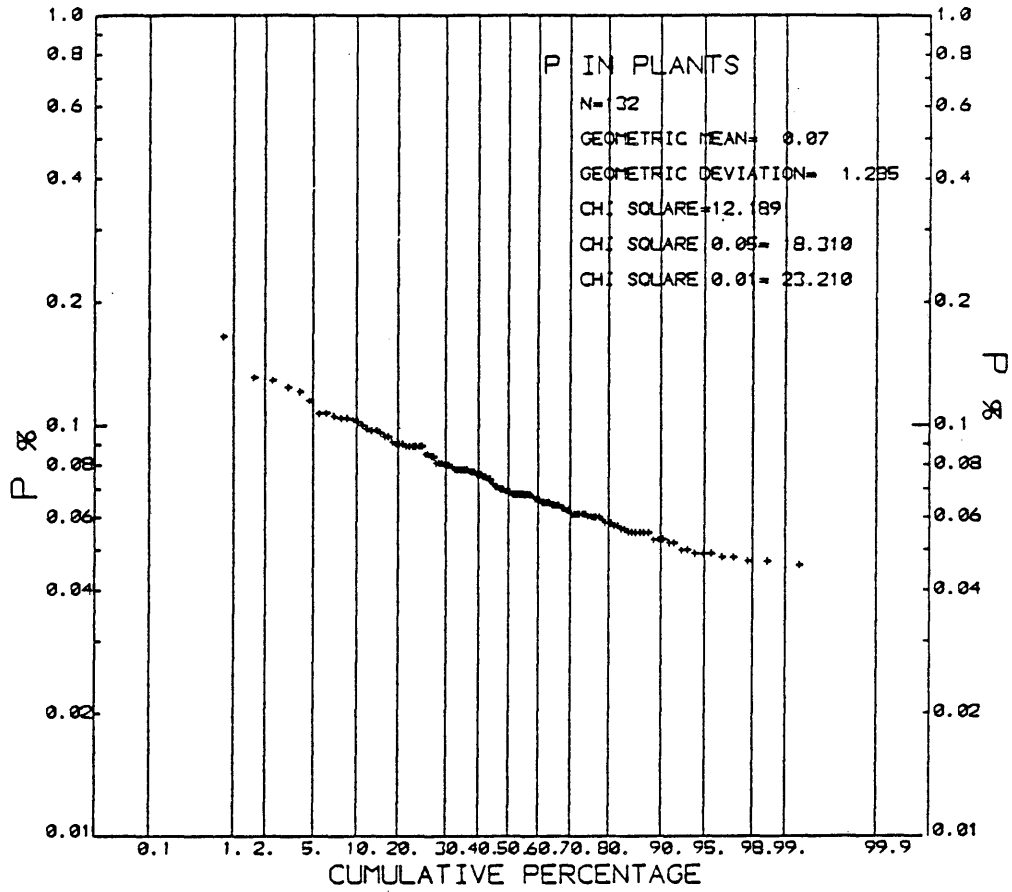


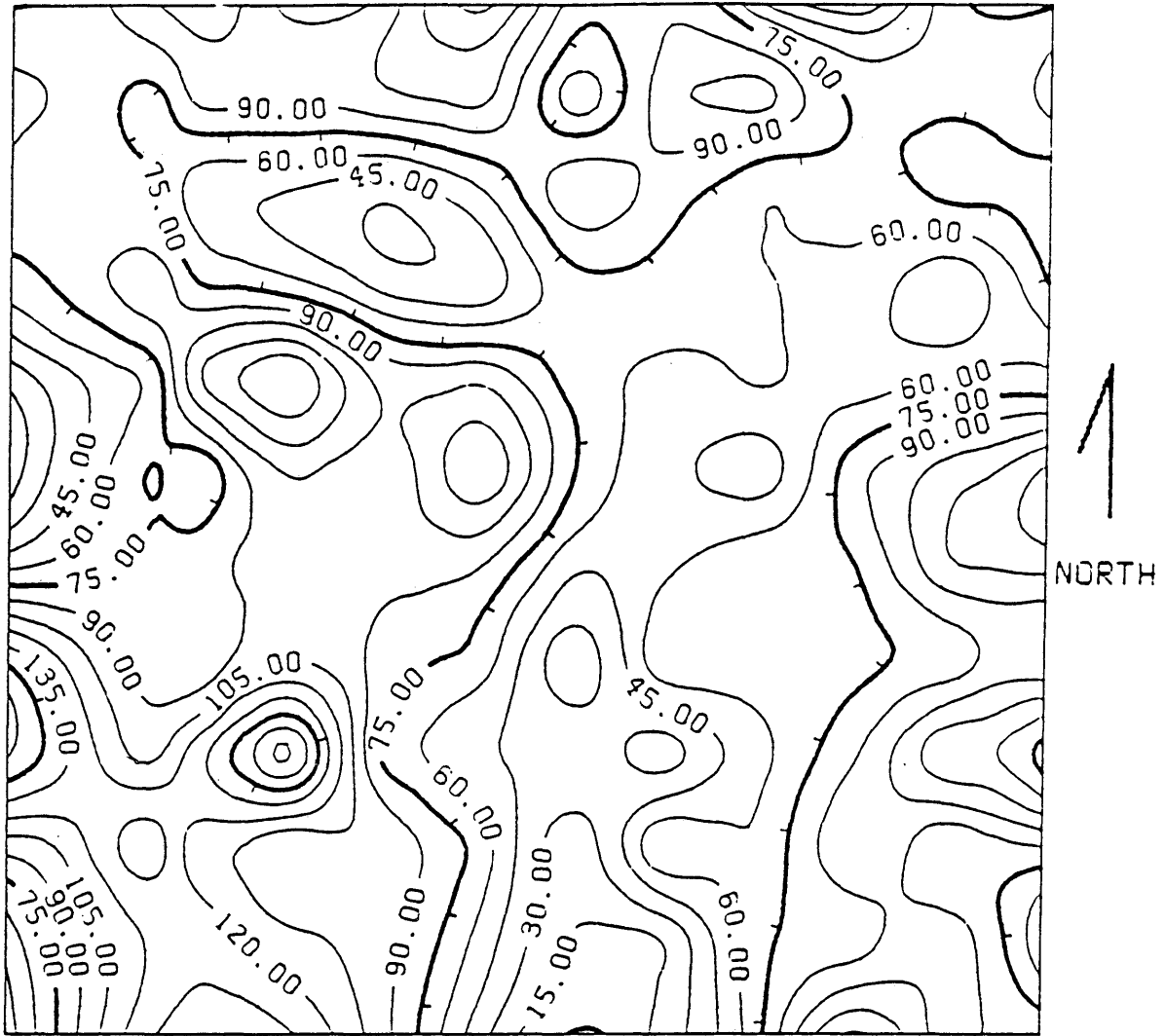






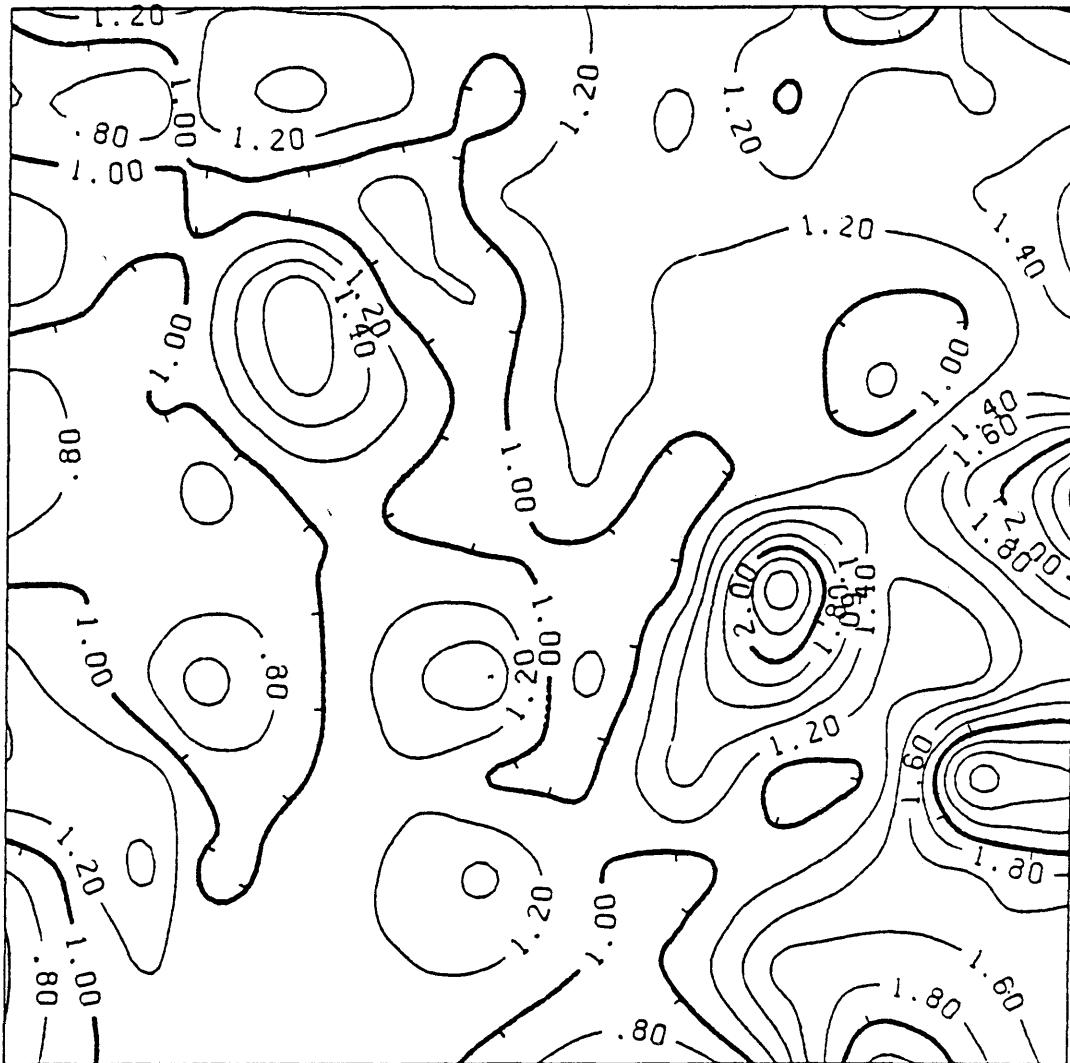






CONTOUR MAP OF SR IN PLANTS (CI=15.0)

SCALE 1:24000
1000 METERS



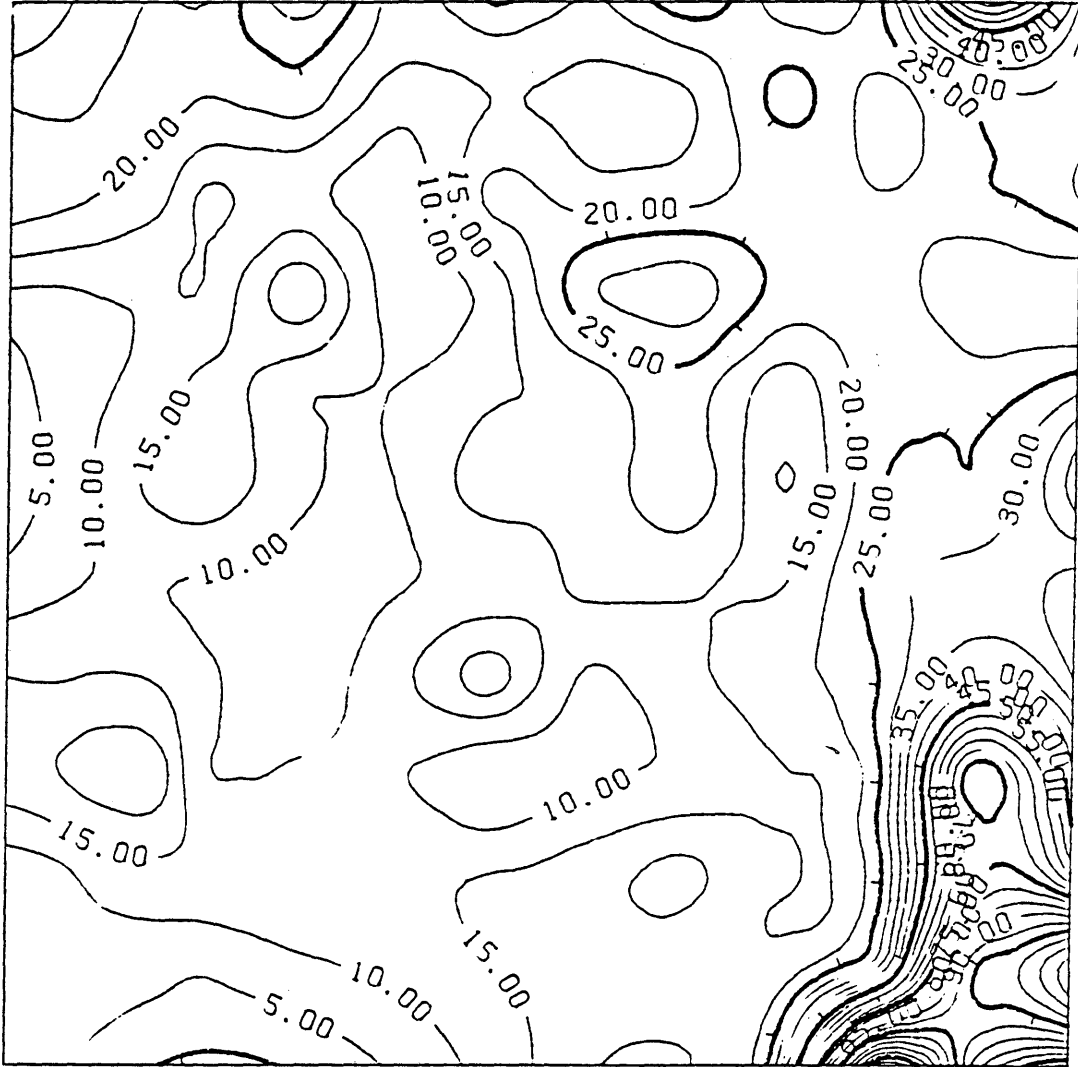
CONTOUR MAP OF CA IN PLANTS (CI=.20)

SCALE 1:24000
0 1000 METERS



CONTOUR MAP OF BA IN PLANTS (CI=5.0)

SCALE 1:24000
0 1000 METERS



CONTOUR MAP OF MGAL IN PLANTS (CI=5.0)

SCALE 1:24000
0 1000 METERS