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Effects of processed oil shale on the element content of *Atriplex cancescens*

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ABSTRACT

Samples of four-wing saltbush were collected from the Colorado State University Intensive Oil Shale Revegetation Study Site test plots in the Piceance basin, Colorado. The test plots were constructed to evaluate the effects of processed oil shale geochemistry on plant growth using various thicknesses of soil cover over the processed shale and/or over a gravel barrier between the shale and soil. Generally, the thicker the soil cover, the less the influence of the shale geochemistry on the element concentrations in the plants. Concentrations of 20 elements were larger in the ash of four-wing saltbush growing on the plot with the gravel barrier (between the soil and processed shale) when compared to the sample from the control plot. A greater water content in the soil in this plot has been reported, and the interaction between the increased, percolating water and shale may have increased the availability of these elements for plant uptake. Concentrations of boron, copper, fluorine, lithium, molybdenum, selenium, silicon, and zinc were larger in the samples grown over processed shale, compared to those from the control plot, and concentrations for barium, calcium, lanthanum, niobium, phosphorus, and strontium were smaller.

Concentrations for arsenic, boron, fluorine, molybdenum, and selenium--considered to be potential toxic contaminants--were similar to results reported in the literature for vegetation from the test plots. The copper-to-molybdenum ratios in three of the four samples of four-wing saltbush growing over the processed shale were below the ratio of 2:1, which is judged detrimental to ruminants, particularly cattle. Boron concentrations averaged 140 ppm, well above the phytotoxicity level for most plant species. Arsenic, fluorine, and selenium concentrations were below toxic levels, and thus should not present any problem for revegetation or forage use at this time.

INTRODUCTION

Four-wing saltbush (*Atriplex canescens* [Pursh.] Nutt.), a native browse species for wildlife and livestock, is one of the most widespread and adaptable western shrubs. Because of its preference for saline soils, four-wing saltbush is being used more and more on spoil-pile reclamation sites throughout the arid and semi-arid regions of the Western United States.

Studies of various plant materials from the Colorado State University Intensive Oil Shale Revegetation Study Site by other researchers (Kilkelly and Lindsay, 1979; Lindsay and McFadden, 1978; Schwab and others, 1981) have concentrated on five potentially toxic contaminants (arsenic, boron, fluorine, molybdenum, and selenium) based on their presence in oil shale, their possible mobilization due to processing, and their possible deleterious effects on the biosphere if mobilized.

Four-wing saltbush samples were collected in the fall of 1978 from five test plots at the Study Site. The samples were analyzed for approximately seventy elements with thirty-three elements reporting concentrations above the lower limit of detection (table 1). Twenty-nine elements were determined in the plant ash and four volatile elements (fluorine, mercury, selenium, and sulfur) on dried plant material.

ACKNOWLEDGMENTS

The work was performed in cooperation with Dr. Wayne Cook, Colorado State University, Department of Range Science. Mr. David A. Koehler, Research Associate, Oil Shale Revegetation Research, Colorado State University, assisted in the collecting of the samples. Preparation and analysis of the samples were conducted in the U.S. Geological Survey Laboratories in Denver by T. F. Harms, F. E. Lichte, J. G. McDade, C. Papp, and M. L. Tuttle.

Table 1.--Analyses of four-wing saltbush on dry weight basis grown over Paraho retorted shale, Piceance basin, Colorado

Element	Plot 2 30.5 cm cover-soil	Plot 3 61 cm cover-soil	Plot 4 91.5 cm cover-soil	Plot 5 61 cm cover-soil with 30.5 cm gravel barrier	Plot 6 control (no shale)
Ash pct------	10	9.8	9.7	9.6	11
Al pct-------	.11	.09	.04	.11	.09
As ppm-------	.05	.05	.05	.05	.05
B ppm--------	18	12	13	12	12
Ba ppm-------	17	13	6.9	31	48
Ca pct-------	.74	.84	.83	.94	1.3
Cd ppm-------	.20	.17	.14	.23	.19
Co ppm-------	<.1	.10	.10	<.1	<.11
Cr ppm-------	.90	.80	.53	.92	.70
Cu ppm-------	7.0	7.4	8.7	7.2	6.1
F pct--------	.0009	.0010	.0007	.0007	.0006
Fe pct-------	.04	.03	.02	.02	.03
Hg ppm-------	.06	.03	.03	.02	.06
K pct--------	3.5	3.1	3.3	2.9	3.2
La ppm-------	1.4	1.6	<.97	1.7	2.4
Li ppm-------	18	12	1.5	7.7	.44
Mg pct-------	1.0	.90	.81	.71	.99
Mn ppm-------	110	108	126	125	121
Mo ppm-------	10	7.6	2.4	6.0	1.1
Na pct-------	.06	.05	.03	.03	.04
Nb ppm-------	<.46	<.45	<.45	.53	.94
Ni ppm-------	1.2	1.2	.74	.96	.90
P ppm-------	800	882	1,067	864	1,870
Pb ppm------	.64	.25	<.21	<.21	.28
Tot S pct---	.21	.25	.23	.25	.23
Sc ppm------	<.10	<.10	<.10	.12	<.11
Se ppm------	.15	.10	.10	.10	.08
Si ppm------	2,100	2,156	2,134	1,536	1,760
Sr ppm------	49	38	38	74	68
Ti ppm------	31	28	11	32	25
V ppm-------	.50	.46	.19	.65	.53
Y ppm-------	.47	.37	.25	.56	.58
Zn ppm------	19	19	11	30	10
Zr ppm------	2.1	2.1	1.2	3.7	1.8

DESCRIPTION OF THE INTENSIVE STUDY SITE

Six test plots were constructed by Colorado State University in 1977 at the Intensive Study Site in the Piceance basin, Colorado (fig. 1) to evaluate the effects of processed oil shale geochemistry on plant growth using various thicknesses of soil cover over the processed shale and/or a gravel barrier between the shale and the soil. Natural vegetation was removed from six rectangular plots 23 by 109 m. The soil on the control plot (Plot 6) was disturbed, but left in place. On the other five plots, the soil cover was removed and stockpiled. The five plots were then excavated from 61 to 152 cm depending upon the treatment to be tested (fig. 2). All plots containing shale received 61 cm of Paraho processed shale from the Anvil Points retorting facility near Rifle, Colo. The lower 15 cm of processed shale in each plot was compacted to reduce soil water movement through the material. Plot 5 was constructed with a 30 cm combined fine- and coarse-gravel barrier separating the soil and the processed shale.

All plots were subdivided into smaller units and three fertilizer treatments with varying ratios of nitrogen and phosphorus were applied on each test plot. The test plots were then seeded with three vegetation mixtures using native and introduced species in different combinations (grasses, forbs, and shrubs). Further details on the construction, fertilizing and seeding of the plots are given by Redente and others (1981).

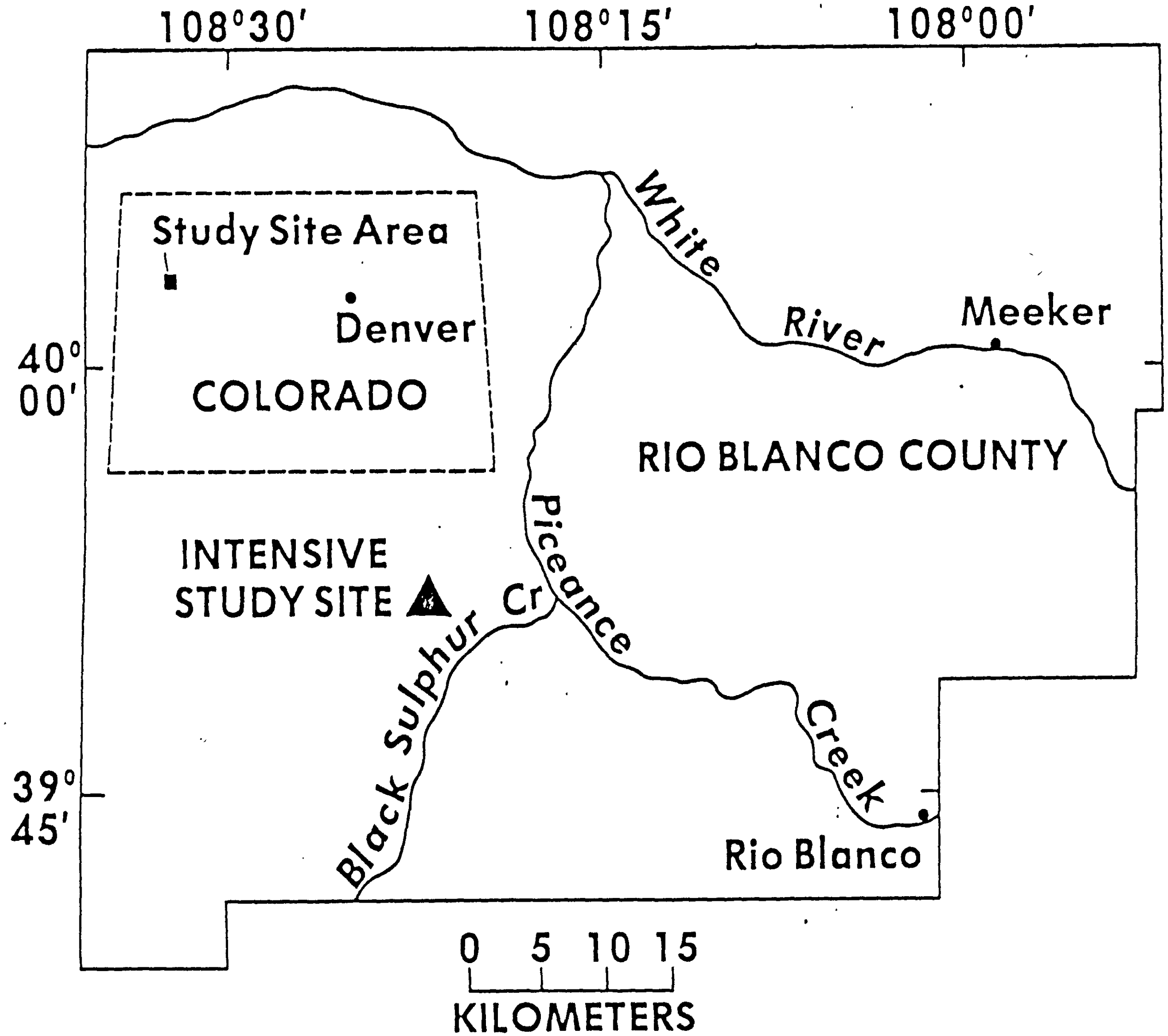

Figure 1.--Location of Colorado State University Intensive Study Site, Piceance Creek basin, Colorado.

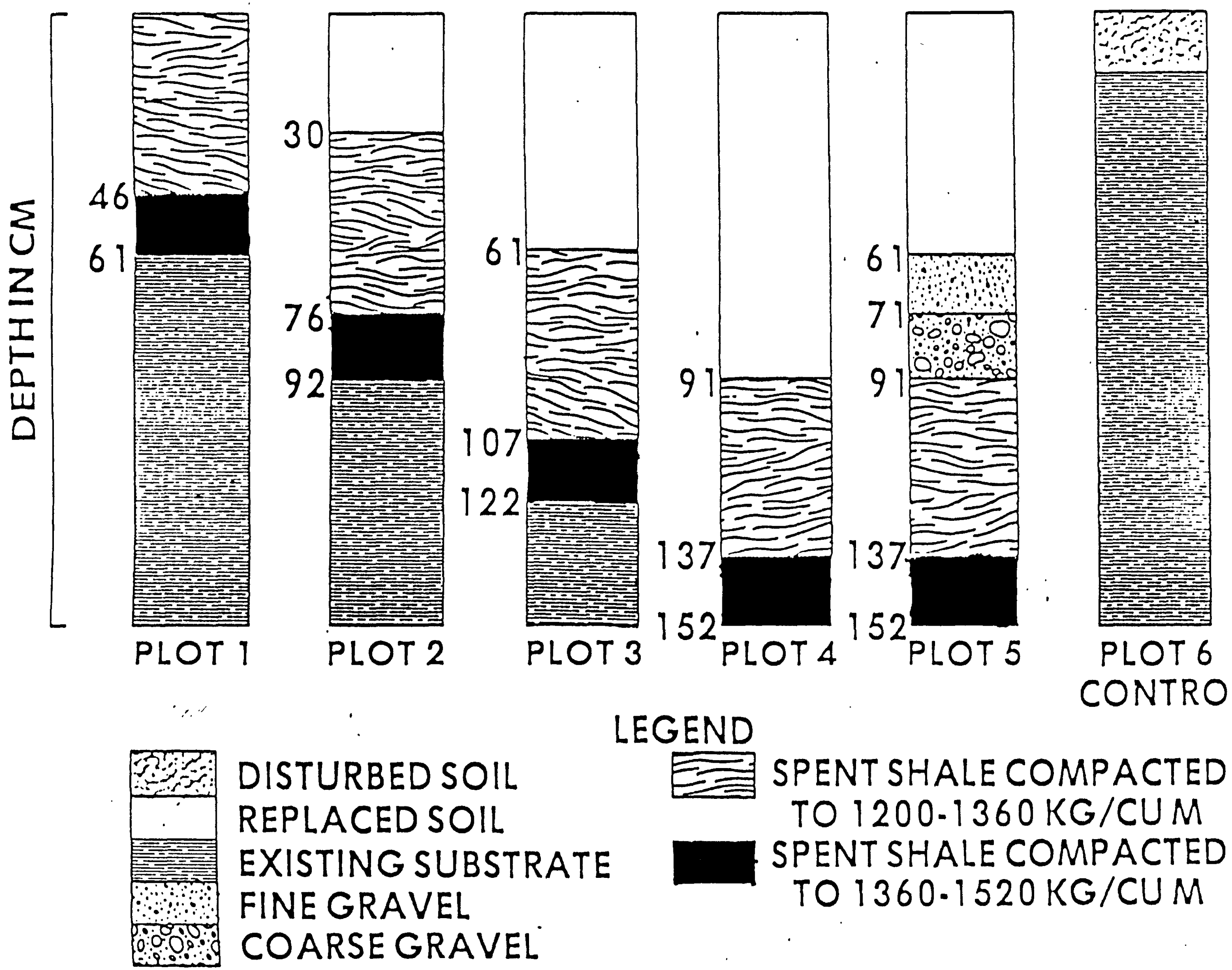

Figure 2.--Profile configurations for Colorado State University Intensive Study Site test plots, Piceance Creek basin, Colorado (modified from Schwab and others, 1981).

FIELD AND LABORATORY METHODS

No sample of four-wing saltbush could be collected on the first plot (no soil cover over the processed shale) because it was barren of vegetation except for a few grass seedlings no more than 3 cm in height. Composite samples of four-wing saltbush were collected on each of the other five test plots in the fall of 1978, approximately 1 year after seeding. The composite samples were collected by clipping the top 18 to 25 cm of randomly located plants with stainless steel clippers. By selecting the plants randomly, the effects of the different fertilizing treatments on each plot were averaged. The number of plants clipped to fill a cloth sampling bag 25 by 40 cm from each plot varied, as the amount of growth available for clipping varied.

In the laboratory, the samples were dried at 45°C for one week, pulverized in a Wiley mill,[1] ashed by dry ignition at 500°C for 24 hours, or wet digestion, and analyzed by methods described by Miesch (1976). The analytical methods used for each element and approximate lower limits of detection are listed on table 2.

[1]Use of trade names in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

Table 2.--Analytical methods and approximate lower limits of determination for thirty-three elements reported in the ash of four-wing saltbush

[All values reported on an ash-weight basis, except where noted]

Element	Analytical method[1]	Approximate LLD[2] (ppm)	Element	Analytical method[1]	Approximate LLD[2] (ppm)
Aluminum---	ES	200	Nickel---------	ES	2
Arsenic[3]---	AA	0.05	Niobium--------	ES	9.2
Barium-----	ES	4.4	Phosphorus-----	COL	100
Boron------	ES	10	Potassium------	AA	100
Cadmium----	AA	0.4	Selenium[3]------	Fluor.	0.01
Calcium----	AA	100	Sodium---------	AA	25
Chromium---	ES	1	Scandium-------	ES	2
Cobalt-----	AA	1	Silicon--------	AA	100
Copper-----	AA	1	Strontium------	ES	1
Fluorine[3]--	IE	1	Sulfur (total)[3]	Turb.	100
Iron-------	ES	200	Titanium-------	ES	90
Lanthanum--	ES	9.2	Vandium--------	ES	2
Lead-------	ES	4.4	Yttrium--------	ES	2
Lithium----	AA	4	Zinc-----------	AA	1
Magnesium--	AA	20	Zirconium------	ES	4.4
Manganese--	ES	2			
Mercury[3]--	AA	0.01			
Molybdenum	ES	2			

[1]ES, plate-reader emission spectrography; AA, flame atomic-absorption spectrography; IE, ion electrode; COL, colorimetric; Turb., turbidimetric; and Fluor., fluorometric.
[2]LLD, lower limit of determination.
[3]Analyses determined on dry material not ash.

RESULTS AND DISCUSSION

Figure 3 illustrates the concentrations for eight elements (boron, copper, fluorine, lithium, molybdenum, selenium, silicon, and zinc) which are generally larger in the samples of four-wing saltbush grown over the processed shale then in the control plot sample. In contrast, the barium, calcium, lanthanum, niobium, phosphorus, and strontium concentrations are smaller in the samples grown over the processed shale (fig. 4). Concentrations for the remaining seventeen elements and the percent of ash (aluminum, arsenic, cadmium, cobalt, chromium, lead, mercury, magnesium, manganese, potassium, scandium, sodium, total sulphur, titanium, vanadium, ytterbium, and zirconium) do not seem to be significantly affected by the presence of the processed shale or the response is variable (fig. 5).

On plot 5 (gravel barrier betwwen the soil and shale), twelve element concentrations (aluminum, boron, cadmium, chromium, fluorine, lithium, molybdenum, scandium, strontium, vanadium, zinc, and zirconium) in the four-wing saltbush sample were larger and another eight elements (copper, iron, potassium, manganese, nickel, selenium, Tot. sulfur, and yttrium) slightly enriched compared to the control sample concentrations (fig. 3, 4, and 5). A much higher soil water content was reported for this plot by Klein and others (1981), and the larger element concentrations, therefore, maybe due to an increase in availability for plant uptake caused by the interaction between the percolating water and the processed shale.

Sixteen element concentrations in the four-wing saltbush sample from Plot 4 (thickest soil cover above shale) were smaller than the sample concentrations from the plots with less soil covering. Concentrations for another five elements (lead, magnesium, mercury, niobium, and phosphorus) and the percent of ash were even smaller than the control sample.

Figure Number	Plot 4 element concentrations lowered closest to or below the control sample
3	Li, Mo, Zn
4	Ba, La, Nb, P, Sr
5	Ash, Al, Cd, Cr, Hg, Mg, Na, Pb, Ti, V, Y, Zr

Thus it appears that the thicker the soil cover over the processed shale, the less the influence of the processed oil shale geochemistry on the element concentrations in four-wing saltbush. However, the small number of samples in this study and the unknown effect of time on the element concentrations must be considered.

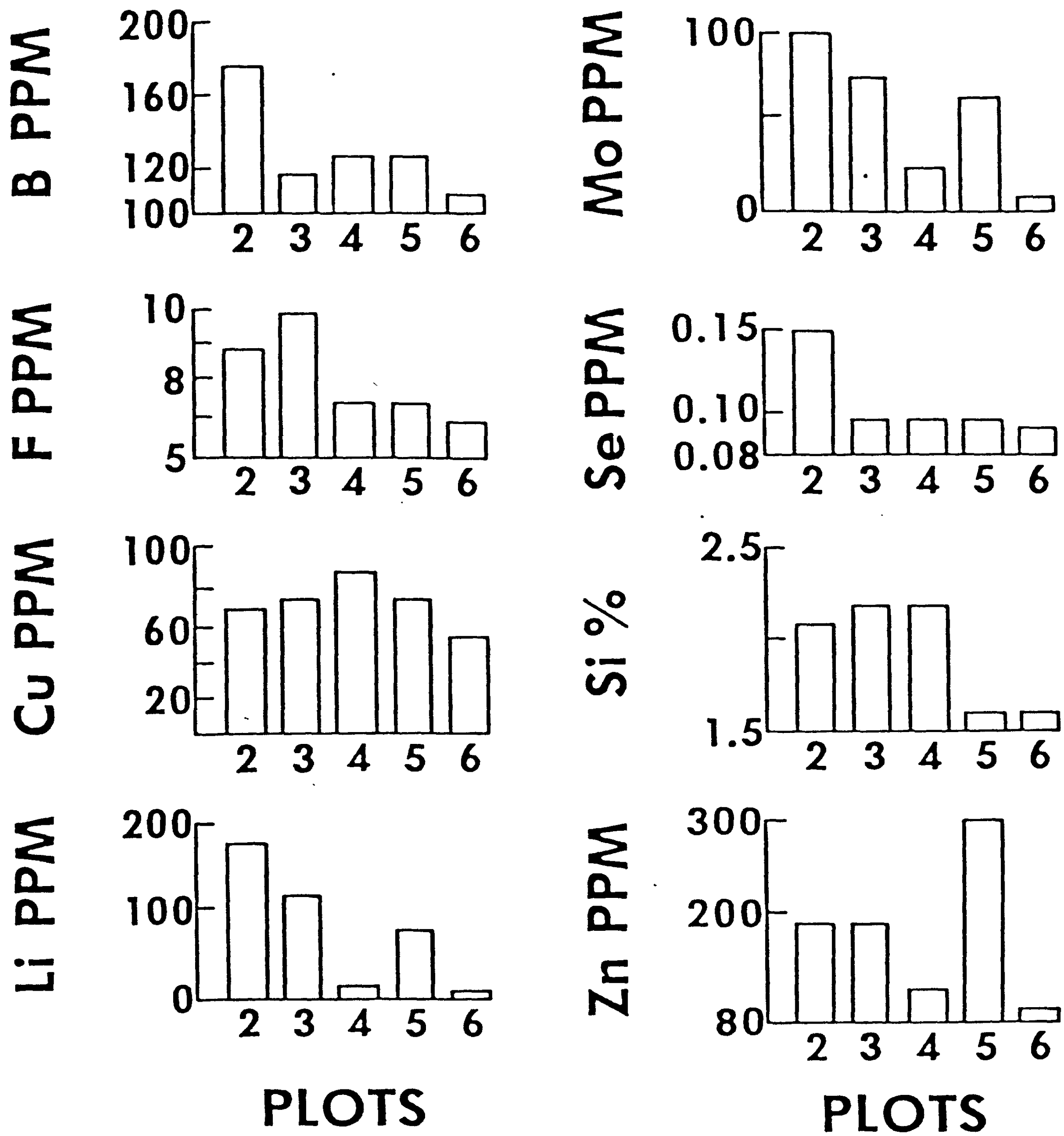

Figure 3.--Eight elements with larger concentrations in the ash of four-wing saltbush samples grown over processed oil shale compared to the control plot samples. Plot 2 (30 cm cover soil), Plot 3 (61 cm cover soil), Plot 4 (91 cm cover soil), Plot 5 (61 cm cover soil over 30 cm gravel barrier), and Plot 6 (disturbed soil, no processed shale). Analyses of F and Se determined on dry material not ash.

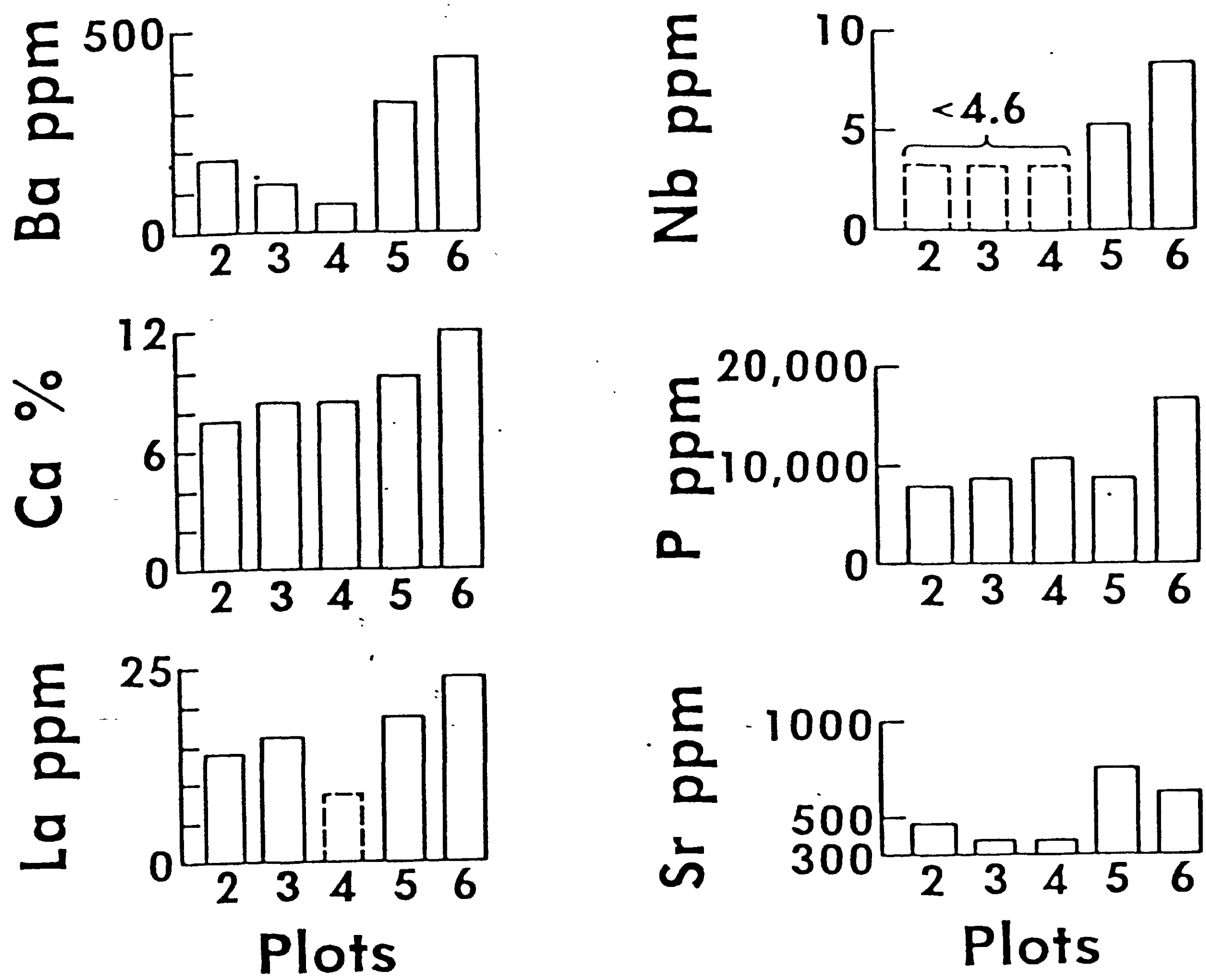

Figure 4.--Six elements with smaller concentrations in the ash of four-wing saltbush samples grown over processed oil shale compared to the control plot sample. Plot 2 (30 cm cover soil), Plot 3 (61 cm cover soil over 30 cm gravel barrier), and Plot 6 (disturbed soil, no processed shale). Dashed bars indicate the sample values were less than the lower limit of detection.

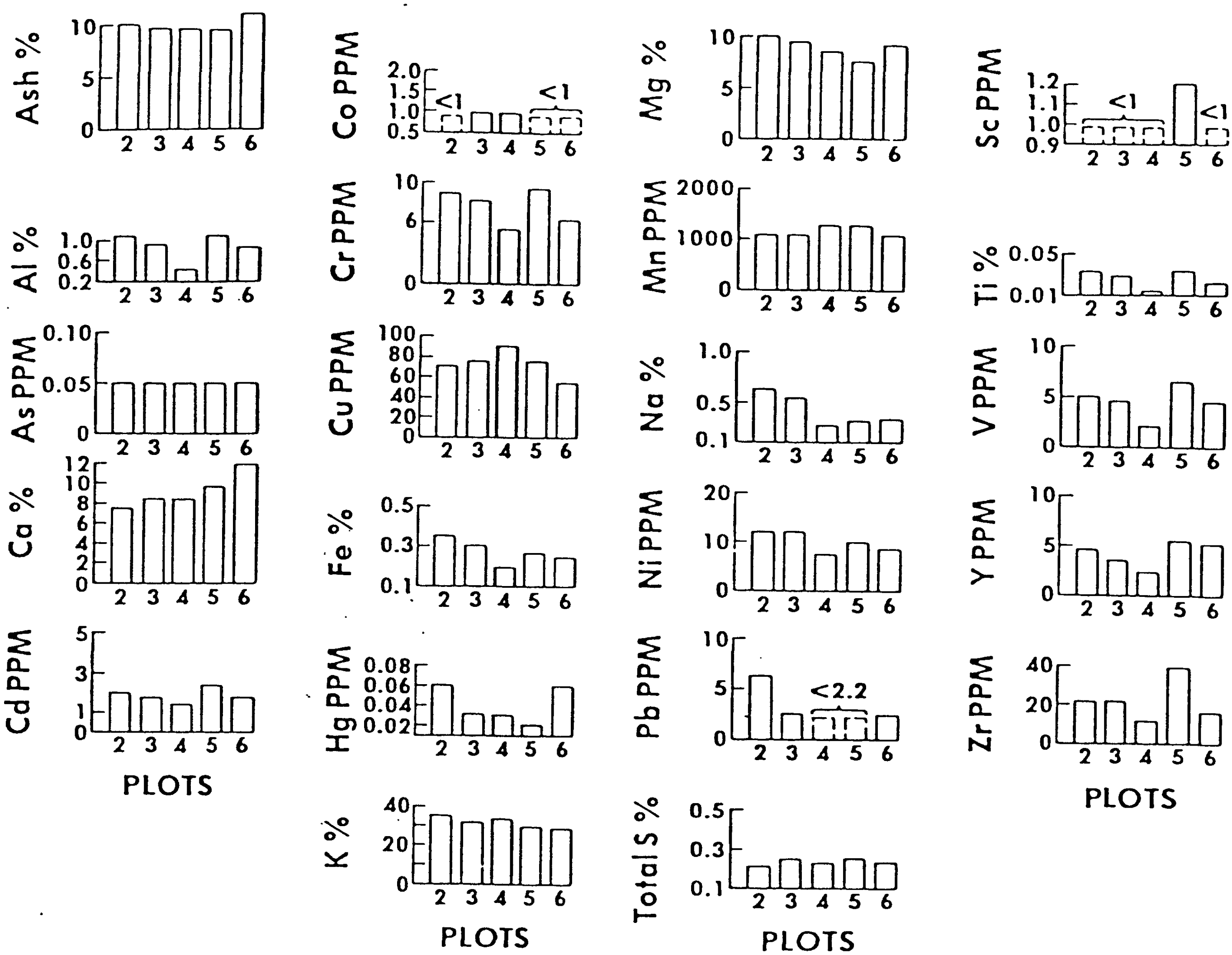

Figure 5.--Percent of ash and concentrations of seventeen elements in the ash of four-wing saltbush which do not appear to be significantly affected by the presence of the processed oil shale or respond variably to it. Plot 2 (30 cm cover soil), Plot 3 (61 cm cover soil), Plot 4 (91 cm cover soil), Plot 5 (61 cm cover soil over 30 cm gravel barrier), and Plot 6 (distrubed soil, no processed shale). Analyses of Hg, total S, and As determined on dry material not ash. Dashed bars indicate the sample values were less than the lower limit of detection.

Potentially Toxic Contaminants

Molybdenum

Molybdenum concentrations (dry weight basis) in the four-wing saltbush samples grown over processed shale decreased with increasing soil thickness from 10 ppm in Plot 2 (thinest soil) to 2.4 ppm in Plot 4 (thickest soil). The molybdenum concentration from Plot 5 (gravel barrier between soil and shale) increased to 6.0 ppm (see table 3, fig. 3). The copper concentrations in the four-wing saltbush samples grown over processed shale were larger than the control sample, but remained about the same regardless of thickness of soil above the shale. Gough and Severson (1981) reported observed background ranges for copper and molybdenum of 3.3 to 7.0 ppm and .24 to 1.5 ppm (dry weight basis) respectively for four-wing saltbush in the San Juan basin, New Mexico. The control sample copper and molybdenum concentrations were both within the reported ranges; however, the concentrations in the samples grown over the processed shale were all larger except for copper on plot 2 (table 1).

Copper to molybdenum ratios less than two can cause sway-back in sheep and/or hypocuprosis in cattle (Miltimore and Mason, 1971). Due to the rather high molybdenum concentrations, the copper to molybdenum ratios for three of the four samples of four-wing saltbush growing over the processed shale were less than two. Only on plot 4 (greatest soil thickness) was the ratio above two. All vegetation species collected at the Intensive Study Site by Schwab, and others (1980) had copper to molybdenum ratios less than two. They also observed a decrease in concentration for most elements from 1979 to 1980, but not for copper and molybdenum. In fact, they found that the copper to molybdenum ratio decreased significantly with time, indicating the possibility of an even more severe copper to molybdenum imbalance in the future.

Boron

Tolerance levels for boron vary greatly with vegetation species. A small 5-15 ppm boron concentration range for grasses and monocots and an intermediate range of 15-50 ppm for oats has been reported by Richards (1954). Toxicity symptoms in oats have been observed when boron concentrations exceeded 54 ppm (Bradford, 1973).

Boron concentrations averaged 50 ppm for four-wing saltbush samples collected at the Intensive Study Site in 1976 by Schwab, and others (1980). The samples collected in 1978 from plots 2, 3, 4, and 5 (processed shale present) averaged 140 ppm in ash (13.8 ppm dry weight basis). The San Juan basin, New Mexico, observed background range of 17 to 770 ppm (dry weight basis) is larger than the average 13.8 from the Study Site. However, Prather (1977) predicted a gradual decrease in shale pH with weathering, which would increase the solubility of boron, making it more readily available for plant uptake. Thus, the increase in boron concentrations in the four-wing saltbush samples from 1976 and 1978 indicate that maintaining vegetation on oil shale reclamation areas might be more difficult in the future because of boron.

Table 3.--Copper and molybdenum concentrations (dry weight basis) and ratios for the four-wing saltbush samples from the Study Site test plots

Plot	Soil thickness (cm)	Copper ppm	Molybdenum ppm	Ratio
2-----	30	7.0	10	0.70
3-----	61	7.4	7.6	0.97
4-----	91	8.7	2.4	3.63
5-----	61 and 30.5 gravel barrier	7.2	6.0	1.20
6-----	Control, no shale	6.1	1.1	5.55

Arsenic

Arsenic concentrations were 0.05 ppm for all of the four-wing saltbush samples, even the control plot (table 3). Similar concentrations have been found in vegetation grown on processed shale (Kilkelly and Lindsay, 1979; Schwab, and others, 1980). Gough and Shacklette (1976) reported the normal concentration in vegetation to be less than 10 ppm. Arsenic appears not to present any environmental problems at this time. However, monitoring should continue as weathering, microbial mobilization, or both may alter the situation.

Fluorine

Fluorine concentrations for the four-wing saltbush samples on Plots 2 thru 6 (table 1) were similar to the concentrations reported for all vegetative species grown over several types of processed shale by Kilkelly and Lindsay (1979).

Concentrations of 30 ppm fluorine and higher, generally reduce growth in vegetation (Gough and Shacklette, 1976). Since all of the four-wing saltbush samples were well below this level, fluorine does not appear to present any problems for revegetating processed oil shale.

Selenium

Selenium also does not appear to present any problems at this time. The four-wing saltbush concentrations ranged between 0.08 and 0.15 ppm (table 1), well below the hazard levels for forages of 4 to 5 ppm (Kubota and Allaway, 1972).

CONCLUSIONS

Two major conclusions may be drawn from this study; (1) the thicker the soil cover over the processed shale, the less the influence of the shale geochemistry on the element concentrations in four-wing saltbush, and (2) the use of a gravel barrier between the soil and the processed shale on one plot increased the amount of water in the soil which seems to have enhanced the interaction with the processed shale increasing the availability for uptake by four-wing saltbush of twenty-one elements.

Arsenic, fluorine and selenium do not seem to present any problems for revegetation or forage use at this time. Boron concentrations in the ash of the four-wing saltbush samples were above the reported toxic levels for most plants. Copper-to-molybdenum ratios in the samples grown over the processed shale were all below two, which could lead to nutritional problems for sheep and cattle.

REFERENCES CITED

Bradford, G. R., 1973, Chapter 4, Boron, in H. D. Chapman, ed., Diagnostic criteria for plants and soils: Abilene, Texas, Quality Printing Co., Inc., p. 33-62.

Gough, L. P., and Severson, R. C., 1981, Biogeochemical variability of plants at native and altered sites, San Juan basin, New Mexico: U.S. Geological Survey Professional Paper 1134-D, 26 p.

Gough, L. P. and Shacklette, H. T., 1976, Toxicity of selected elements to plants, animals, and man--an outline: U.S. Geological Survey, Open-File Report No. 76-746, 46 p.

Kilkelley, M. K., and Lindsay, W. L., 1979, Trace elements in plants on processed oil shale, in Trace Elements in Oil Shale Progress Report, Contract No. EY-76-S-02-4017, Department of Energy, submitted by Center for Environmental Sciences, Environmental Trace Substances Research Program, University of Colorado, Denver, Colo., p. 191-253.

Klein, D. A., Sorensen, D. L., and Brokish, M. 1981, Soil microorganisms and methods of retorted shale reclamation, in Redente, E. F. and Cook, C. W., eds., Revegetation Research on oil shale lands in the Piceance basin: Colorado State University, Research Report #COO-4018-5, p. 33-45.

Kubota, J., and Allaway, M. H., 1972, Geographic distribution of trace element problems, in Mortvedit, J. J., Giordano, P. M., and Lindsay, W. L., eds., Micronutrients in Agriculture: Madison, Wisc., Soil Science Society of America, p. 525-551.

Lindsay, W. L. and McFadden, R. E., 1978, Plant uptake of selected trace elements from processed oil shale, in Third Annual Oil Shale Seminar, December 1, 1978, Denver Botanical Gardens, Denver, Colorado: Colorado State University, University of Colorado, and Colorado School of Mines, 2 p.

Miesch, A. T., 1976, Methods of sampling, laboratory analysis, and statistical reduction of data in a geochemical survey of Missouri, with sections on Laboratory methods by P. R. Barnett, A. J. Bartel, J. I. Dinnin, G. L. Feder, T. F. Harms, Claude Huffman, Jr., V. J. Janzer, H. T. Millard, Jr., H. G. Neiman, M. W. Skougstad, and J. S. Wahlberg: U.S. Geological Survey Professional Paper 954-A, 39 p.

Miltimore, J. E. and Mason, J. L., 1971, Copper to molybdenum ratio and molybdenum and copper concentrations in ruminant feeds: Canadian Journal of Animal Science, 51:193-200.

Prather, R. J., 1977, Sulfuric acid as an amendment for reclaiming soils high in boron: Soil Science Society of America Proceedings 41:1098-1101.

Redente, E. F., Doerr, T. B., Mount, C. B., Grygiel, C. E., Sievers, T. E. and Biondin, M., 1981, Effects of plant species, soil material, and cultural practices upon plant establishment and sucession in Redente, E. F. and Cook, C. W. Eds., Revegetation Research on oil shale lands in the Piceance basin: Colorado State University, Research Report #COO-4018-5, 89 p.

Richards, L. A., 1954, Diagnosis and improvement of saline and alkali soils: U.S. Department of Agriculture Handbook #60, 160 p.

Schwab, A. P., Smith, P. J. and Lindsay, W. L., 1981, Concentration of chemical elements in plants growing on retorted oil shales, in Chappell, W. R., Principal Investigator, Trace Elements in Oil Shale, Progress Report, Contract No. EV-10298, Department of Energy 10298-2, Center for Environmental Sciences, University of Colorado, 324 p.

Schwab, A. P., Lindsay, W. L., and Marx, G. P., 1980, Uptake of Chemical elements by plants growing on spent shale, in Fourth Annual Oil Shale Symposium, March 15, 1980, University of Colorado, Boulder: Center for Environmental Sciences, U.S. Department of Energy, Contract #EV-10298, 16 p.