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OFR 75-170

UNITED STATES DEPARTMENT OF THE INTERIOR
GEOLOGICAL SURVEY

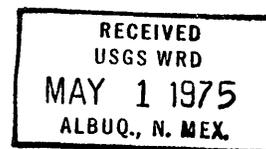
Contributions of Major and Minor Elements to
Soils and Vegetation by the Coal-Fired
Four Corners Power Plant, San Juan County,
New Mexico

By

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Open-File Report No. 75-170
1975

This report is preliminary and has not
been edited or reviewed for conformity
with U.S. Geological Survey standards.



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Contribution of major and minor elements to soils and vegetation
by the coal-fired Four Corners Power Plant,
San Juan Co., New Mexico

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Abstract

The major components in the ash from the Four Corners coal-fired power plant in San Juan County, New Mexico, are K_2O , CaO , MgO , Al_2O_3 , SiO_2 , Na_2O and Fe_2O_3 . Many minor elements, including antimony, arsenic, fluorine, mercury, selenium, tellurium, uranium, and zinc, are enriched in the fly ash relative to bottom ash or coal. The particulate effluvium, however, collected from the crowns of shrubs near the power plant has lower concentrations of the enumerated minor elements, except fluorine and mercury, than the fly ash collected within the generating station. Fluorine and mercury show a relative enrichment in the effluent. In the vicinity of the power plant, the fly ash is currently contributing major and minor elements that are essential to vegetative growth to otherwise deficient soils. The concentrations of potentially harmful minor elements, such as Hg, As, Se, Te, Cd, Be and Pb, that originate from the power plant drop off rapidly with distance from the stacks and are lower than the average contents in U.S. soils at distances greater than 3 kilometres. Lead concentrations from traffic in samples near highways and mercury in samples near gas-well fittings are higher than those near the power plant. Because vegetation tends to exclude noxious

elements, vegetation even within 3 kilometres of the Four Corners Power Plant contains only average concentrations of those elements considered to be hazardous to livestock or to man.

Introduction

By 1971, the people of Farmington and Shiprock, the Navajo tribe, and state officials in New Mexico had become greatly concerned about the large quantities of smoke issuing from the stacks of the new Four Corners Power Plant built near Fruitland, in San Juan County (figs. 1 & 2). Some persons predicted widespread destruction and contamination of large areas of the southwest by the strip mines and power plants slated to be opened up in the near future. To answer these questions and to provide facts on which intelligent decisions could be based, and also because most of the coal to be used as fuel for these plants would be mined on Federal lands, the Department of the Interior initiated a project called the Southwest Energy Study. Three parts of this study were the responsibility of the U.S. Geological Survey--1) to estimate and evaluate the coal resources in southwest United States (Averitt and others, 1972); 2) to determine the composition of the coal to be mined for use in the 10 power plants either already in production or anticipated (Swanson, 1972), and 3) to determine the effects of the effluent from the Four Corners Power Plant on the composition of soil and vegetation in the surrounding area (Cannon and Anderson, 1972).

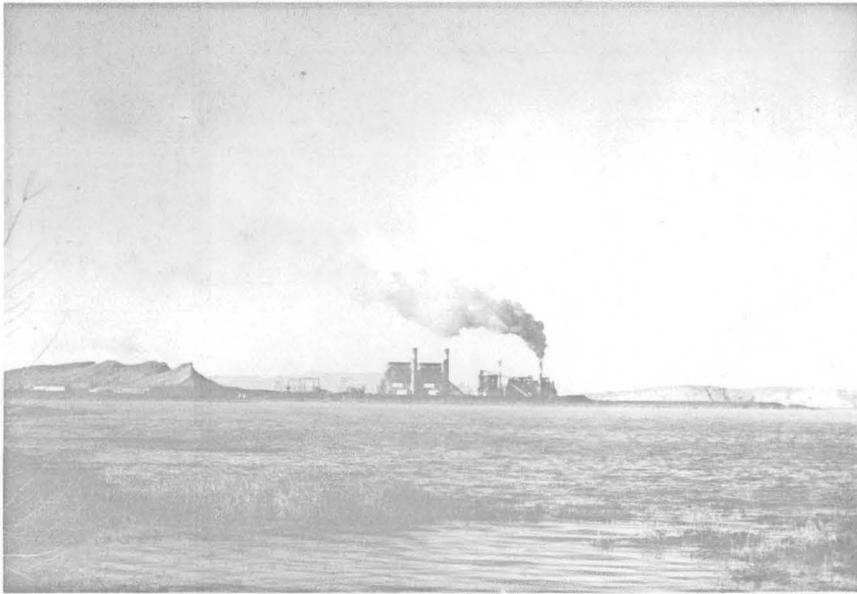


Figure 1. Four Corners Power Plant from east side of Morgan Lake.

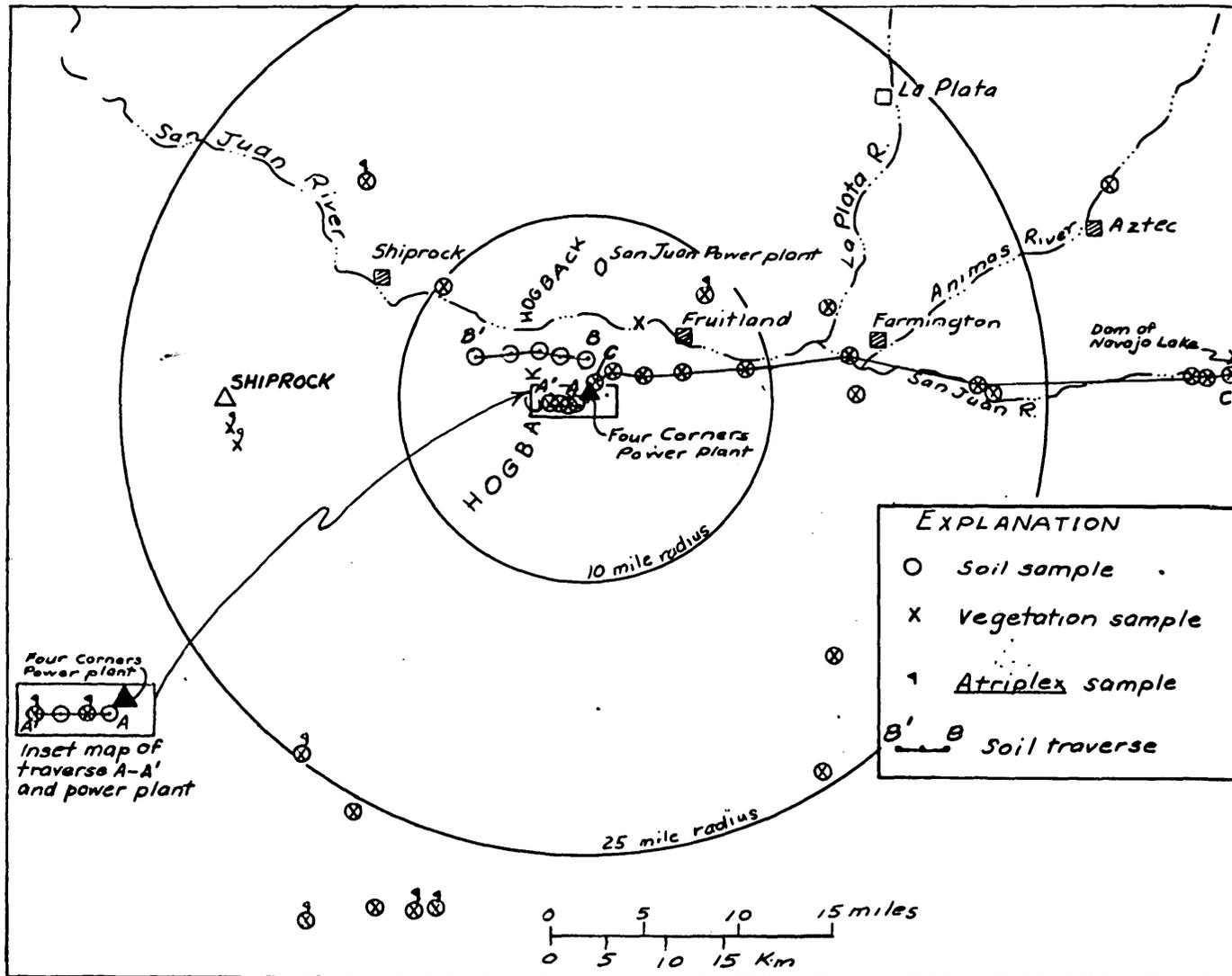


Figure 2 - Map showing sample locations relative to Four Corners power plant San Juan Co., New Mexico

The 2,075 megawatt power plant was built by Arizona Power Company on a semiarid mesa south of the San Juan River on an overgrazed and relatively unpopulated part of the Navajo Reservation. The mesa, which is capped by the Pictured Cliffs Sandstone of Cretaceous age, supports a sparse 10 percent cover of low xerophytic shrubs and grasses growing under considerable moisture stress. The dry unproductive land near the power station has attracted few inhabitants and has been used by the Navajos only for sheep grazing. The artificial Morgan Lake which supplies cooling water for the power station, has improved the appearance of the area and is stocked with fish. Alluvium along the nearby San Juan River, however, is irrigated and cultivated for garden vegetables, fruit, alfalfa, and field corn. The towns of Shiprock, Fruitland, and Farmington are within a radius of 20 miles (32 km) of the plant. At the time of our study the plant was releasing 300 tons of particulate matter a day but corrective measures have now been taken at considerable expense.

The annual precipitation at Fruitland is 6.96 inches (17.8 cm) a year, being greatest in late summer and early fall. The rains are commonly torrential in nature resulting in runoff rather than penetration to the ground water table. Predominant wind directions influenced by the orientation of the valley are from both the east and west, commonly blowing from the east in the morning and reversing in the afternoon.

Sampling and analysis

The objective of the ecologic impact study was to study the coal being used in the power plant and the degradation products and also to recollect soils and vegetation from San Juan County stations that had been studied in 1961-62 before the power plant was constructed, and to reanalyze these samples for comparison with the present collection. Only 11 of the original stations occurred within a 15-mile (24 km) radius of the power plant and therefore samples were collected along several new traverses both east and west from the plant. The species of plants collected were largely xerophyte shrubs. The samples were most contaminated for 2 miles (3.2 km) directly west of the power plant, in a disposal area for ash slurry, which is ditched to ponds at the end of traverse A-A' (fig. 3). The east traverse (C-C') crossed the spoil piles of the Navajo mine (fig. 4) and continued east to Navajo Lake.

The analyses showed that the earlier soil samples contained more metal than later samples because of improved laboratory sample preparation since the earlier samples were analysed. Therefore, the two sets of samples could not be compared for the purposes of this study. Both sets of plant samples, however, were prepared by the same method and were comparable.



Figure 3. View looking west from power plant along traverse A-A'
toward ash disposal ponds.



Figure 4. View looking west at Navajo Mine spoil piles from station on traverse C-C'.

Several types of coal samples were collected--channel samples or core splits of the coal beds and plant-feed samples from blend piles or pipeline slurries. The coal and soil samples were dried and ground and the coal samples ashed for spectrographic, X-ray fluorescence and wet chemical analyses. Unwashed vegetation samples were dried and ashed at low temperatures. Ultimate coal analyses were made according to U.S. Bureau of Mines procedures (Staff, U.S. Bureau of Mines, 1967). Lithium, copper, zinc, cadmium, aluminum, calcium, magnesium, mercury, thallium, and total iron (as Fe_2O_3) were determined by atomic absorption spectrometry using acid digestion (Ward and others, 1969). Silicon, aluminum, calcium, potassium, iron, sulfur, phosphorus, and selenium were determined by X-ray fluorescence; arsenic, sodium, silicon, sulfur, nitrogen, iron, antimony, tellurium by specific chemical methods (Ward and others, 1963), and the remainder by the 6-step spectrographic method (Myers, Havens, and Dunton, 1961). By the latter method, the results are reported arbitrarily as the mid-points 1, 1.5, 2, 3, 5, 7, of geometric brackets within each order of magnitude. The precision of a reported value is thus plus or minus one bracket at 68 percent or two brackets at 95 percent confidence. The reported mid-points are used in the tables and graphs. Fewer direct chemical methods were used for soils and plants than for coal and more reliance was placed on the spectrographic method as shown in table 1. The analyses were performed in the Denver laboratories of the U.S. Geological Survey under the direction of Claude Huffman, Jr. and F. N. Ward.

Table 1.--Analytical methods used and limits of detection,
shown in parts per million

Element	Method	Ashed coal	Soil	Plant
Al	emission spectrograph	20	10	20 (ash)
As	spectrophotometry	1.0	10	0.25 (d.w.)
Be	emission spectrograph	2	1	2 (ash)
B	emission spectrograph		20	50 (ash)
Ba	emission spectrograph	3	1.5	3 (ash)
CaO	atomic absorption	100	20	50 (ash)
Cd	atomic absorption	5000	0.2	0.3 (ash)
Co	emission spectrograph	7	3	7 (ash)
Cr	emission spectrograph	2	1	2 (ash)
Cu	atomic absorption	5		
"	emission spectrograph		1	2 (ash)
F	specific ion electrode	50		0.6 (d.w.)
Hg	atomic absorption	0.01	0.001	0.025 (d.w.)
Li	atomic absorption	5		
"	emission spectrograph		50	100 (ash)
Fe	atomic absorption	100		
"	emission spectrograph		10	20 (ash)
Mg	atomic absorption	100	20	50 (ash)
Mo		7	3	7 (ash)
N	elemental analyzer	100		
Na	flame photometer	100		
	emission spectrograph	100	500	

Table 1.--Analytical methods used and limits of detection,
shown in parts per million--Continued

Element	Method	Ashed coal	Soil	Plant	
Ni	emission spectrograph	10	5	10	(ash)
Pb	emission spectrograph	20	10	20	(ash)
S	combustion-iodometric	100			
Sb	spectrophotometer	0.05	1	1	(ash)
Se	X-ray spectrograph	0.1	0.1	0.1	(d.w.)
Sr	emission spectrograph	10	5	10	(ash)
Te	catalysis	0.02			
U	neutron activation	0.06			
V	emission spectrograph	15	7	15	(ash)
Zn	atomic absorption	10	0.5	0.5	

Coal and degradation products

There is an estimated 800 billion tons or more of predominantly high volatile B or C bituminous coal of Late Cretaceous age in the Southwest. The coal is low in sulfur content averaging about 0.6 percent. The Four Corners Power Plant is using coal being strip-mined from 6 to 8 beds in the Fruitland Formation at the nearby Navajo Mine. The major constituents of the ash of southwestern coals, reported in table 2 as oxides, are K, Ca, Mg, Al, Si, N, and Fe. The composition of the various coals is remarkably similar except for the percent of ash. The Four Corners Plant uses coal that is blended to have an average ash content of 21 percent.

The minor element content of air-dried coal compared to that of bottom ash, fly ash and effluent are shown in figures 5a and 5b. Most elements are enriched in the bottom ash, compared to the original coal as might be expected. A considerable amount of the volatile elements, F, As, Se, and Hg has probably been vaporized during the burning of the coal. The trace element content of fly ash collected in the stack by the scrubbers and precipitator is also compared with the effluent being deposited on the soil and vegetation 1 mile (1.6 km) west of the plant. The latter material was more than 1/2 inch (1.3 cm) thick in the crowns of some of the shrubs. Although there has been a certain amount of dilution with windblown silts, the volatile elements mercury and fluorine are considerably higher in the windblow material than in the fly ash taken from the stack. Presumably, the wind-borne material is similarly enriched in arsenic and selenium although no analytical data are available.

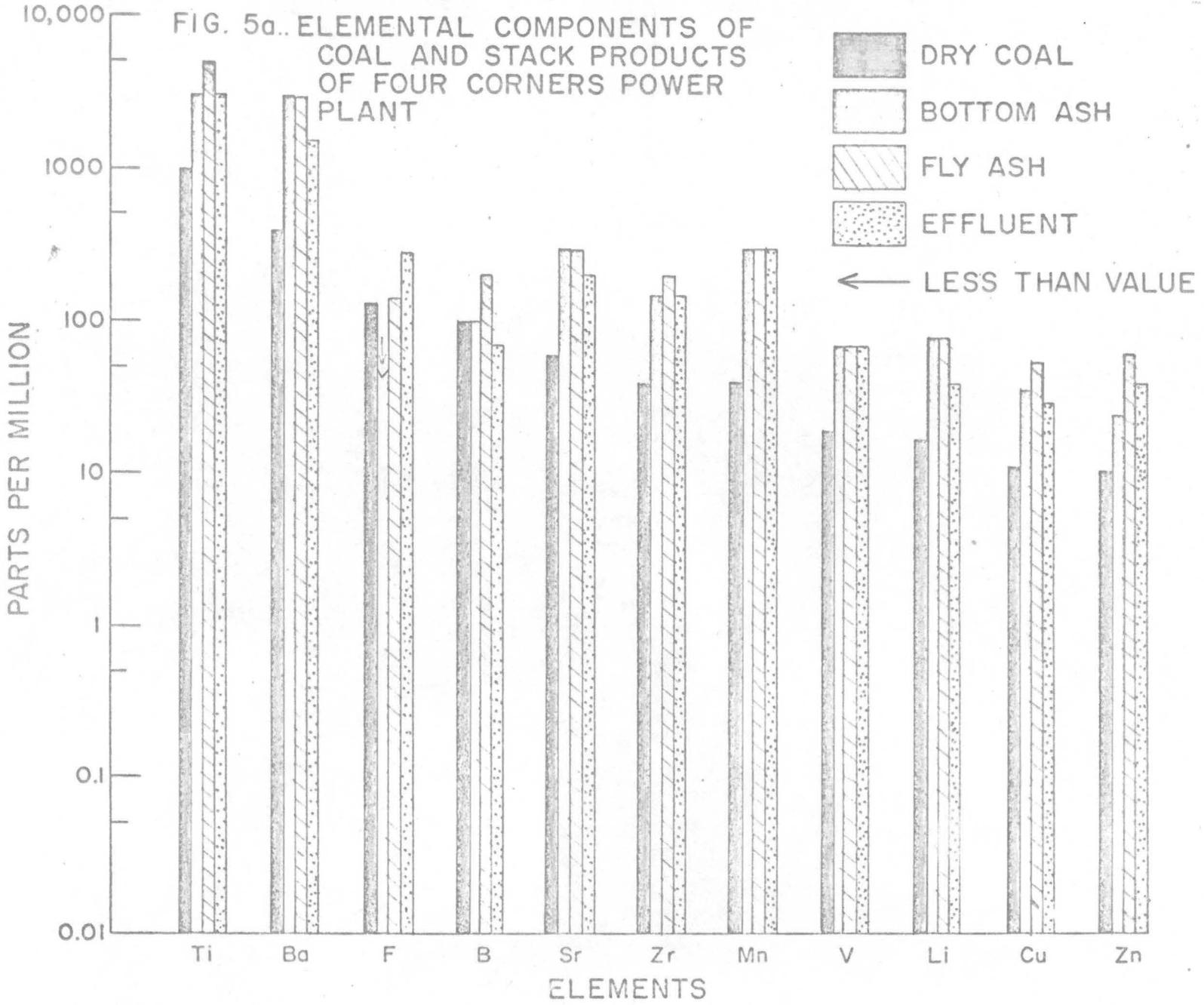


FIG. 5b. ELEMENTAL COMPONENTS
IN COAL AND STACK PRODUCTS
OF FOUR CORNERS POWER
PLANT

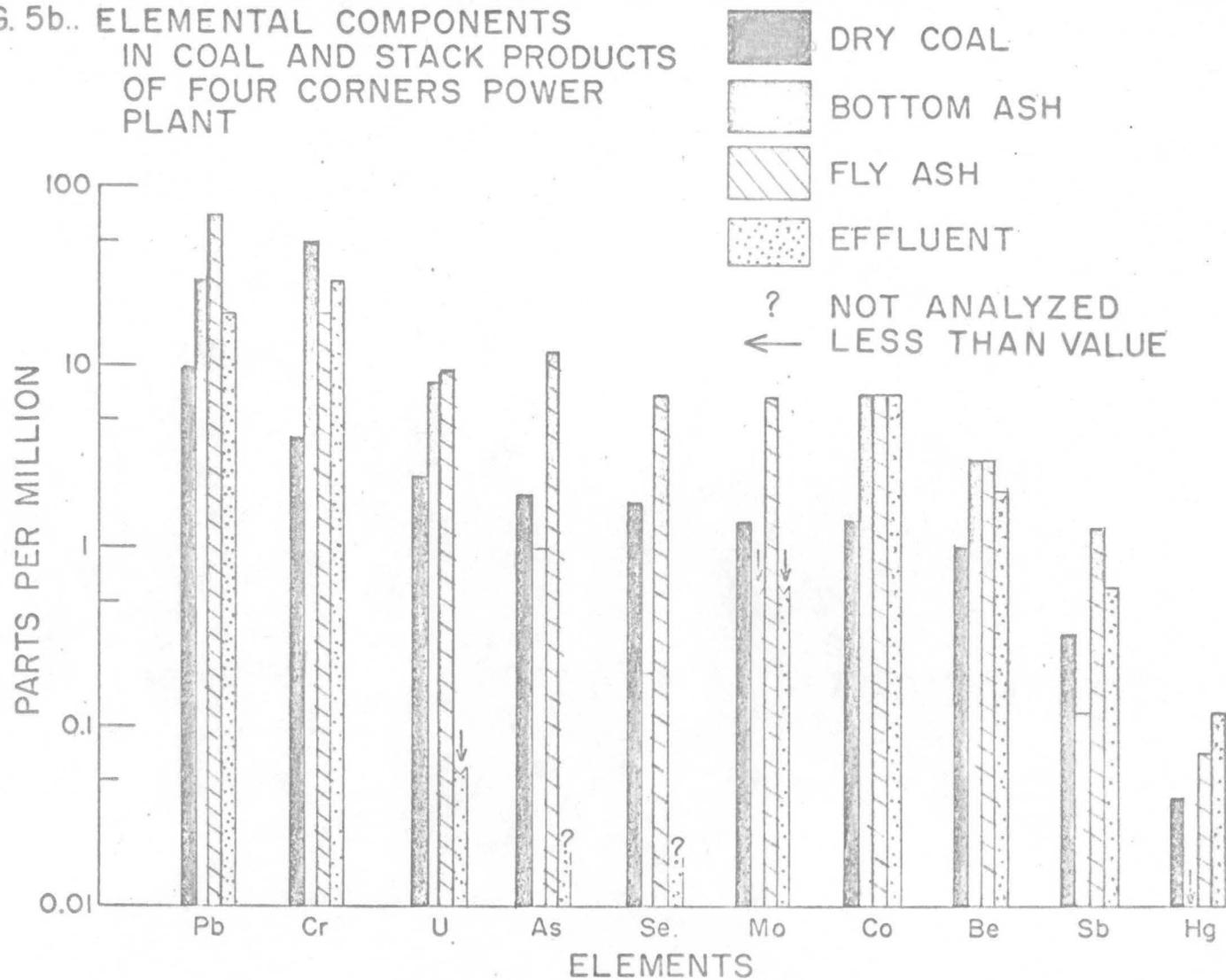


Table 2.--Average major-oxide composition of ash of coal
 (71 samples), southwestern United States
 [from Swanson, 1972]

	<u>Percent</u>
SiO ₂	47.0
Al ₂ O ₃	27.0
Na ₂ O	1.5
K ₂ O	.5
CaO	8.4
MgO	1.7
P ₂ O ₅	.4
Fe ₂ O ₃	4.8
SO ₂	7.7
(Other)	8.0
	<hr/> 100.0

Soils

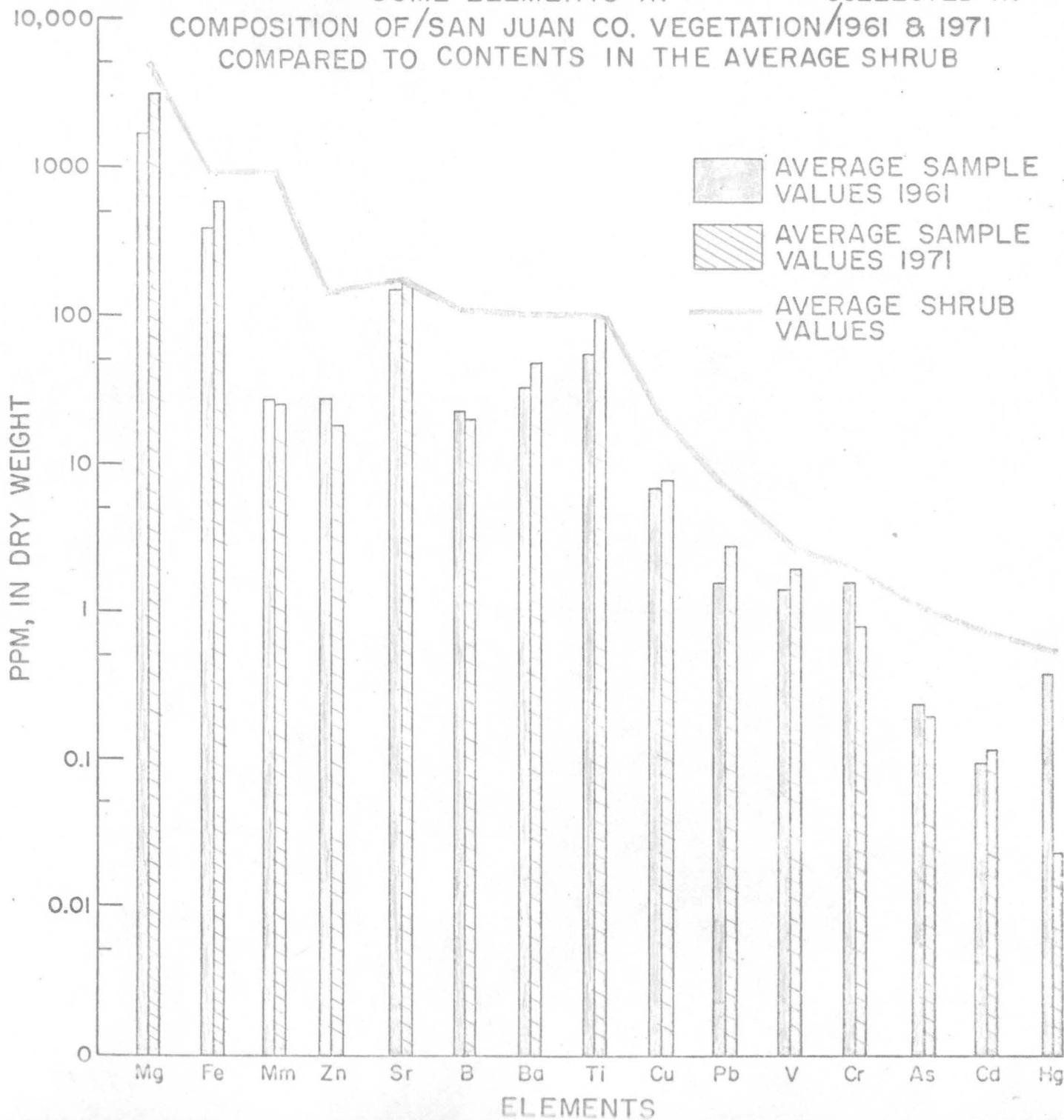
Log-log graphs of the concentration of Zn, Be, Pb, V, Ni, Sr, Ba, Ca, B, Cu, Mn, Hg, Se, and As in the top 1/2 inch of 2 soil samples collected at each station, along 3 traverses west, northwest, and east are shown in figures 6a to 6n. All of these are unusually high on the A-A' traverse in the area of ash disposal except from Pb, Sr, and Hg compared to average soils (Shacklette, Boerngen, and others, 1971). Mercury contamination from a gas well 34 miles east of the power plant was greater than from the power plant itself. V, N, and Mn are below the national average for soils on all traverses (Shacklette, Boerngen, and others, 1971). Zn, Ca, and Cu are above average in soils along traverse A-A' only; Sr, B, and Se for 2-3 miles (3-5 km), on A and B traverses; Be, Ba, Pb, and Hg are elevated on all 3 traverses but other sources of contamination are indicated for Pb and Hg.

Vegetation

Certain elements in the vegetation show a small increase when the 1971 samples are compared with the same species collected at the same stations in 1961 before construction of the power station. There is also a decrease with distance from the stacks. The early samples were mixed randomly with the later collection and reanalyzed as a group. It is apparent in figure 7 that the early samples stored in ice cream cartons were highly contaminated with mercury during the 10 year period of storage in an old munitions bunker at the Federal Center. Although the percentage of mercury is higher in the effluent than in

FIG. 7

SOME ELEMENTS IN COLLECTED IN
COMPOSITION OF/SAN JUAN CO. VEGETATION/1961 & 1971
COMPARED TO CONTENTS IN THE AVERAGE SHRUB



the fly ash collected inside the power station, no mercury values greater than 0.25 ppm in dry weight were reported in the vegetation samples collected in 1971. A later study of mercury in soils, vegetation, and water in the San Juan drainage basin area was made to determine whether the power plant could be the source of mercury that had been detected in fish in Navajo Lake 45 miles (73 km) northeast of the plant (Cannon, J. L. and Swanson, V. E., written commun., 1972). No evidence was found of a definable concentration of mercury in the environment that could be related to the power plant. Uncontaminated soils, in general, contained 0.05 ppm or less mercury, all vegetation contained less than 0.025 ppm, and all water samples contained less than 0.5 ug/l.

The elements that have increased in concentration since the power station was built are Cd, Se, Ba, Cu, Pb, Sr, Fe, Mg, and Ti. Of these, probably only the differences in Cd, Ba, Pb, and Ti may be significant. An important consideration is that vegetation in this general area is actually deficient in trace elements and the additions from the plant are thus largely beneficial. Because the uptake of elements by the various genera varies markedly, the composition of Atriplex samples only have been plotted with distance from the power plant, as shown in figures 8a-8d for Pb, Mo, Se, Zn, V, Cu, Fe, Ba, B, and Cd. The samples do not represent collections along a particular traverse and are thus not direction oriented. Fe, B, and Ba are higher within the first mile (1.6 km) than at any other point on the traverse, but Cu, V, and Zn are high at 9 miles (15 km) and again at 26 miles (42 km). The later station is southwest of the

power plant and on the Mancos shale. The selenium content was also much higher than near the power plant and is presumably geologic in origin. The lead concentrations at 16 and 26 miles (25 and 53 km) are believed to be caused by highway pollution because these stations were both near U.S. Highway 666. Mercury was below detection limits except at a station believed to be contaminated by a gas well.

Tamarix gallica, a phreatophyte, was collected at the edge of Morgan Lake near the power station. The sample contained less of all elements than the Atriplex samples collected from any distance.

Because there is no record in the literature of fluorine concentrations in plants growing near power stations, a few plants and soils were analyzed for fluorine and are shown in table 3. The reason for the concentrations found in alfalfa and grass growing on the alluvial flat of the San Juan River are not know. There appears to be no consistent relationship between fluorine in soils and plants and distance from the power plant. In general, the top one-half inch (1.3 cm) of soil contained less fluorine than the soil at a depth of one-half to 6 inches (15 cm).

Table 3.--Fluorine analyses in soils and vegetation in relationship to the Four Corners Power Plant,
shown in parts per million

[Analysts: T. F. Harms, F. N. Ward]

Distance and direction from plant	Genus and species	Plant		Soil		Depth
		Lab. no.	F in dry weight	Lab no.	F in dry weight	
0.5 mile (1 km) west	----			153500	390	1/2 in.
1 mile (1.7 km) west	<u>Atriplex corrugata</u> (saltbush)	415658	3.0	153493	300	1/2 in.
2 miles (3.3 km) northwest	<u>Atriplex nuttali</u> (saltbush)	415653	7.0	153496	340	1/2 in.
4 miles (6.7 km) northwest				154644	90	1/2 in.
5.5 miles (9 km) east (San Juan alluvium)	<u>Sporobolus airoides</u> (alkali sacaton)	414912	25.0	415966	280	1/2 in.
				415969	270	1-6 in.
				415972	290	1/2 in.
				415967	340	1-6 in.
9 miles (15 km) east (San Juan alluvium)	<u>Calamagrostis inexpansa</u> (reedgrass)	415916	7.0	415971	300	1/2 in.
				415974	330	1-6 in.
				415977	290	1/2 in.
				415981	340	1-6 in.

Table 3.--Fluorine analyses in soils and vegetation in relationship to the Four Corners Power Plant,
shown in parts per million--Cont.

Distance and direction from plant	Genus and species	Plant		Soil		Depth
		Lab. no.	F in dry weight	Lab. no.	F in dry weight	
10 miles (17 km) northwest (San Juan alluvium)	<u>Medicago sativa</u> (alfalfa)	415741	20.0	153479	510	0-6 in.

Note: Fluorine in plants may be compared with other anomalous areas: Gila River reservation, Arizona (high F in water) plants contained 0.6-3.0 ppm.
Basin and Range closed basins, Nevada-California plants contained 6-20 ppm.
Tailings of Augusta gold mine, Colorado containing 5.7 percent fluorine, plants contained 220-1500 ppm.
F accumulators such as camellia may contain as much as 3060 ppm.

Summary

In conclusion, three lessons have been learned from this study. The first is the importance of storing unground splits of the original samples as carefully as possible in low level areas in containers that cannot absorb volatile elements because the need for studies of the changes with time in our environment will most certainly increase.

Second, the present treatment of fly ash in the Four Corners plant reduces the contents of harmful metal in the effluent except for fluorine and mercury, which are increased. The levels of elements present in the effluent drop off rapidly with distance; barium, strontium, beryllium, and lead are the most widespread of the contaminants. Both soils and vegetation in San Juan County, however, are very deficient in most essential elements. In such an area of deficiency, the addition of nutrient elements may actually be beneficial, and the tendency of vegetation to exclude unnecessary or harmful elements prevents toxic quantities from getting into the food chain. Levels of harmful metals in vegetation are very low or even below the limits of detection in vegetation except for lead which appears to have increased throughout the area since 1961 and is highest near highways as might be expected. Third, mercury, which has been detected in Navajo Lake, is not coming from the power plant.

With the installation of equipment for further treatment of the fly ash, much of which has already been installed, the Four Corners power plant effluent cannot be considered detrimental, except for visibility and possibly effects of SO_2 which were not investigated in this study. However, in areas where there are already high levels of metals in the geologic substrate and related biosphere, increments from industrial plants should be carefully monitored.

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Figure 6a and 6b.--Ba and B values and mean values of soil sample pairs collected at stations along three traverses from power plant. Mean value is lighter weight line. V, signifies values less than limit of detection.

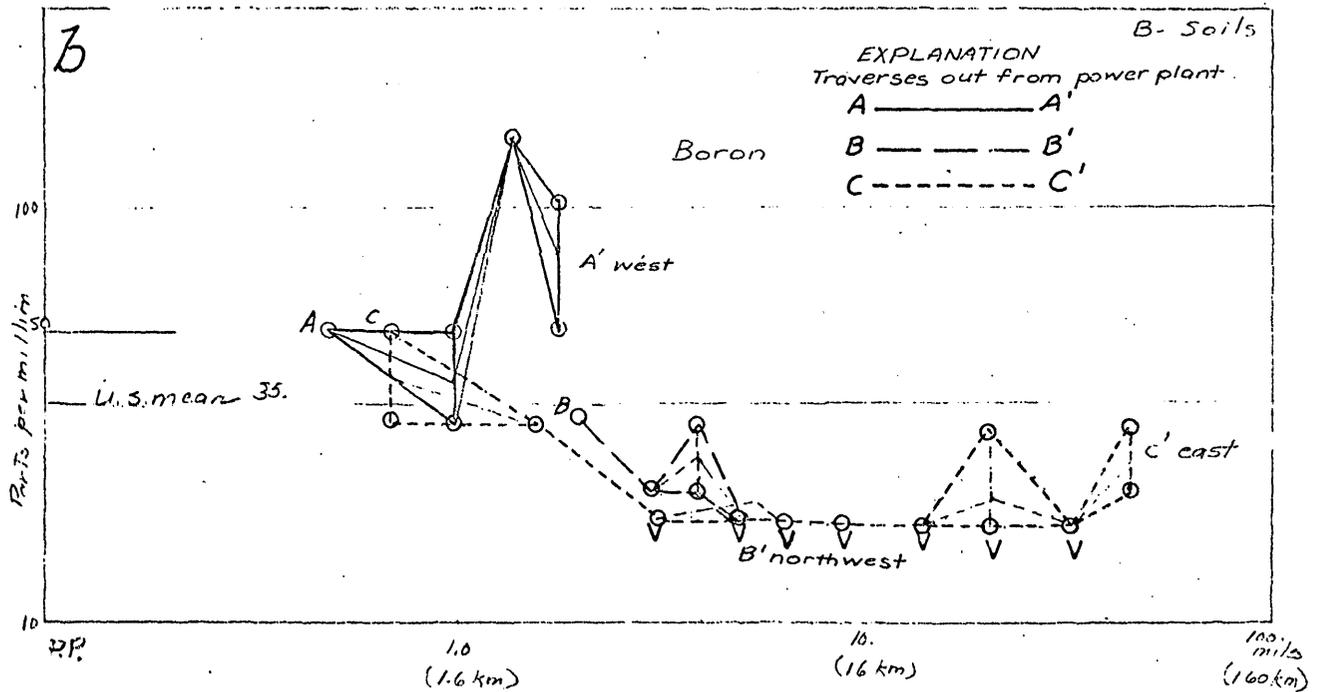
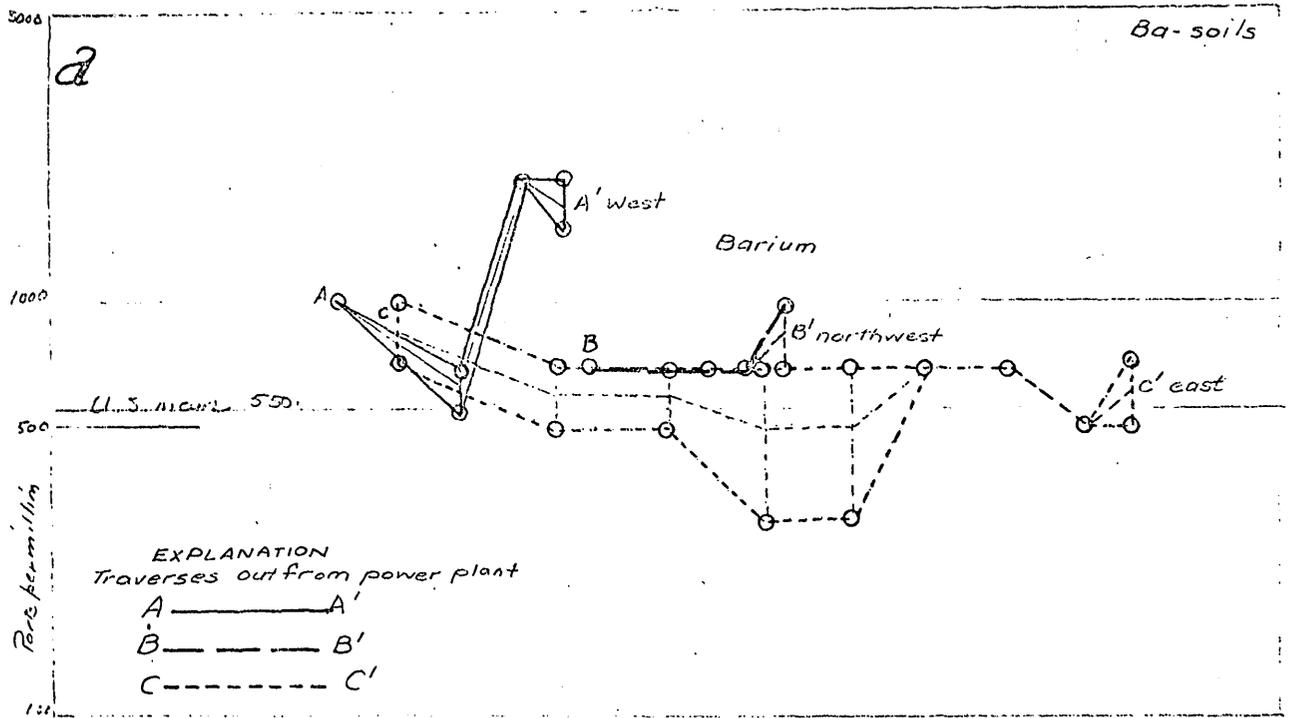


Figure 6c.--Be values and mean values of soil sample pairs collected at stations along three traverses from power plant. Mean value is lighter weight line. V, signifies values less than limit of detection.

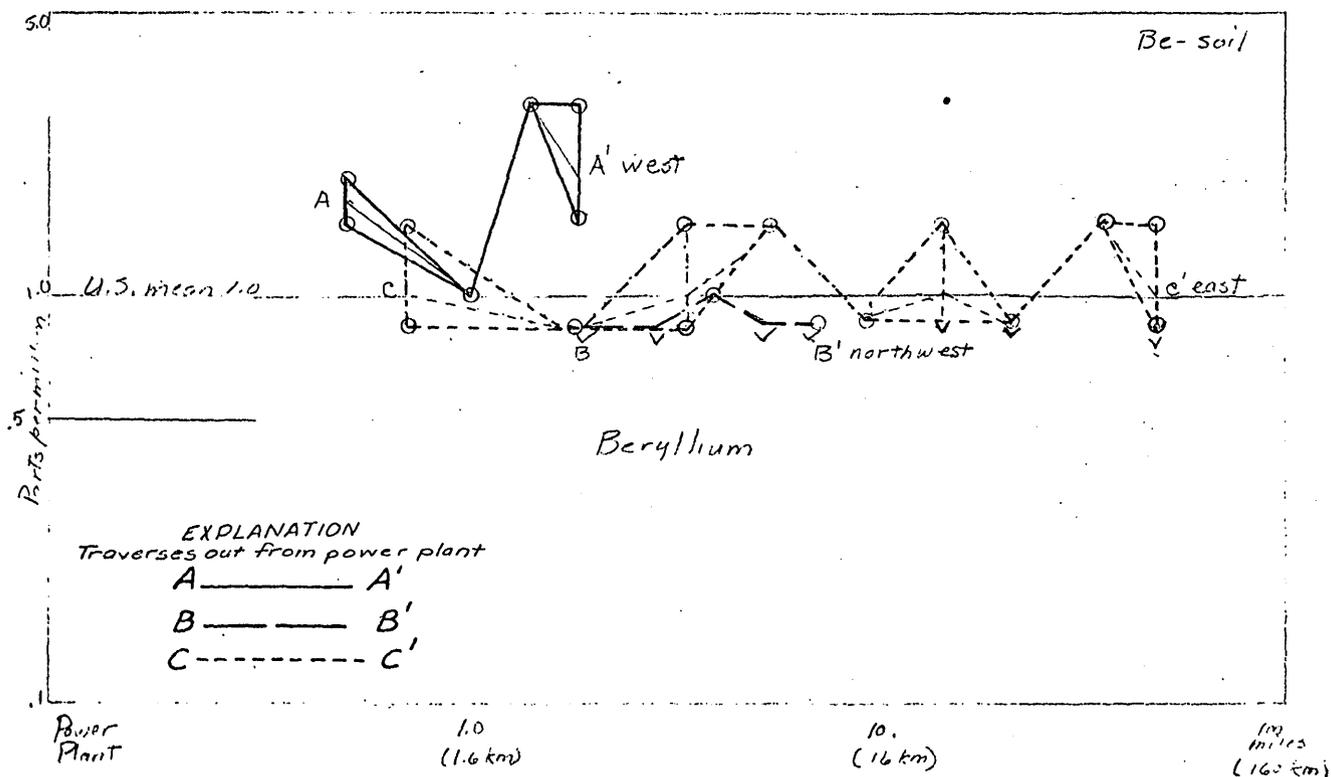


Figure 6d.--Ca values and mean values of soil sample pairs collected at stations along three traverses from power plant. Mean value is lighter weight line.

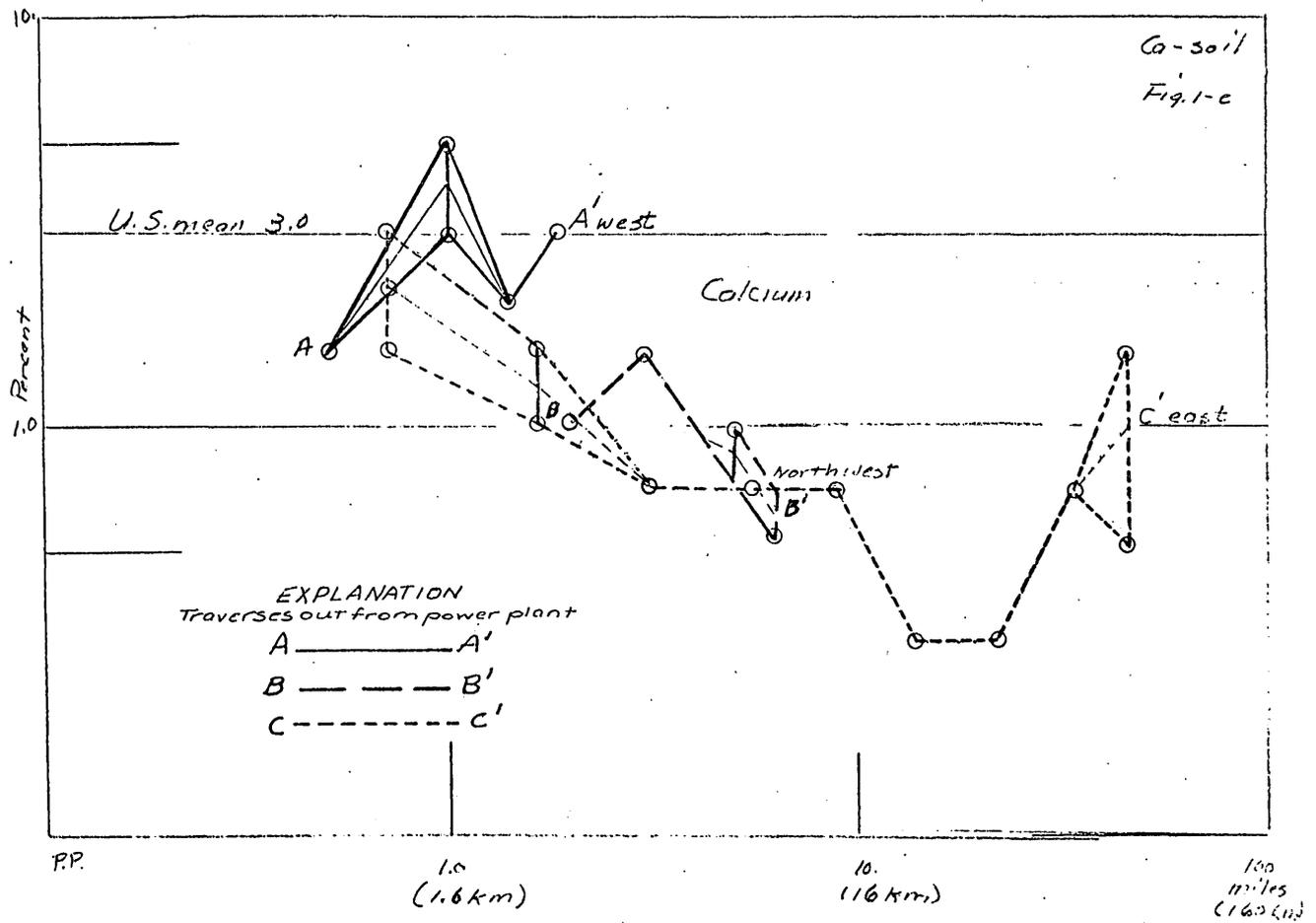


Figure 6e and 6f.--Pb and Ni values and mean values of soil sample pairs collected at stations along three traverses from power plant. Mean value is light weight line. V, signifies values less than limit of detection.

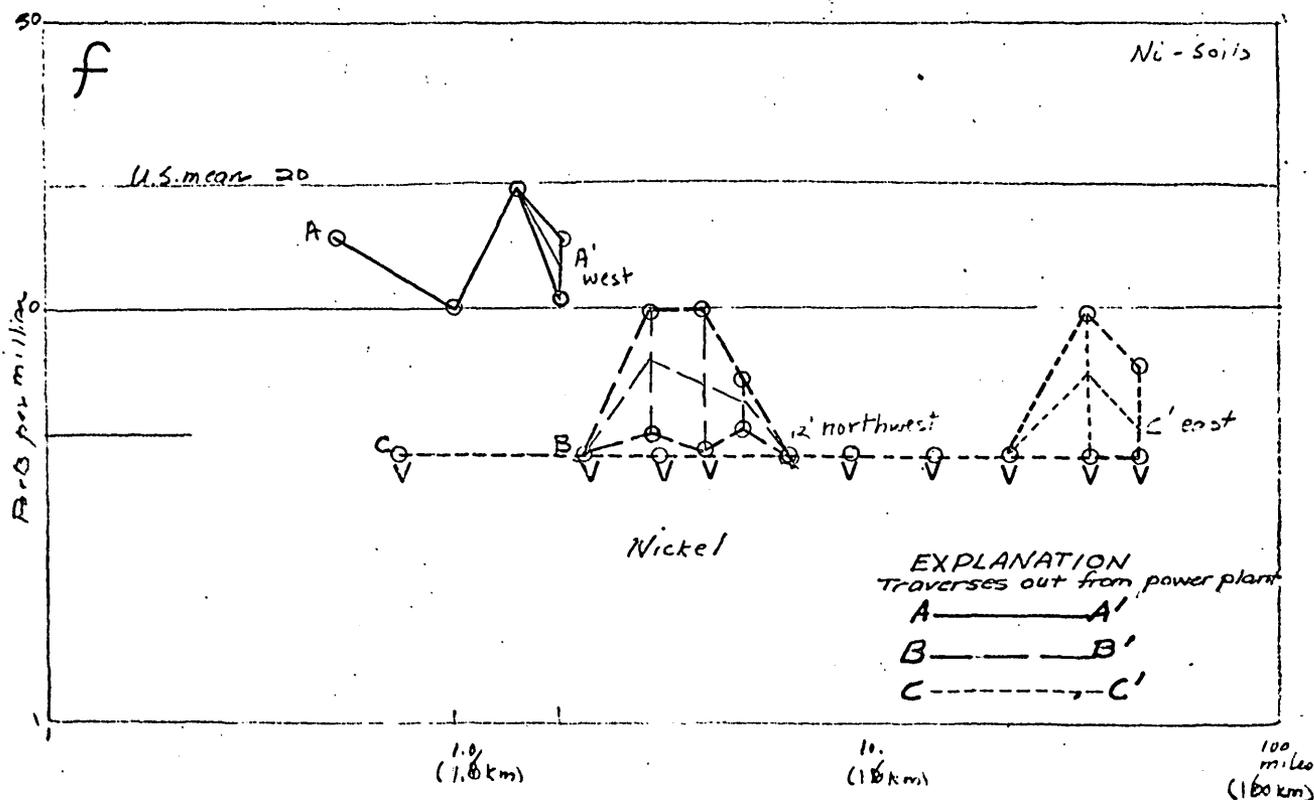
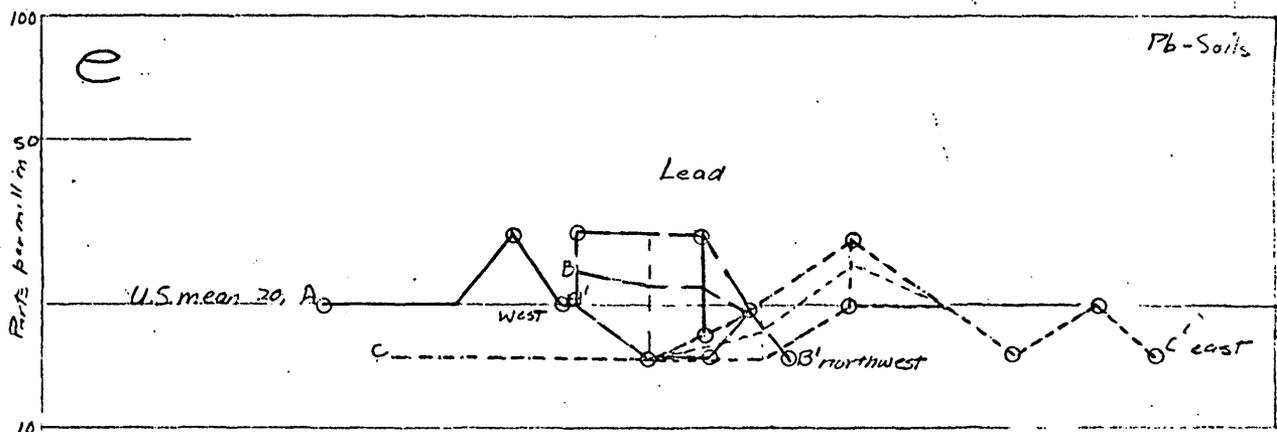


Figure 6g and 6h.--Mn and Cu values and mean values of soil sample pairs collected along three traverses from power plant. Mean value is light weight line.

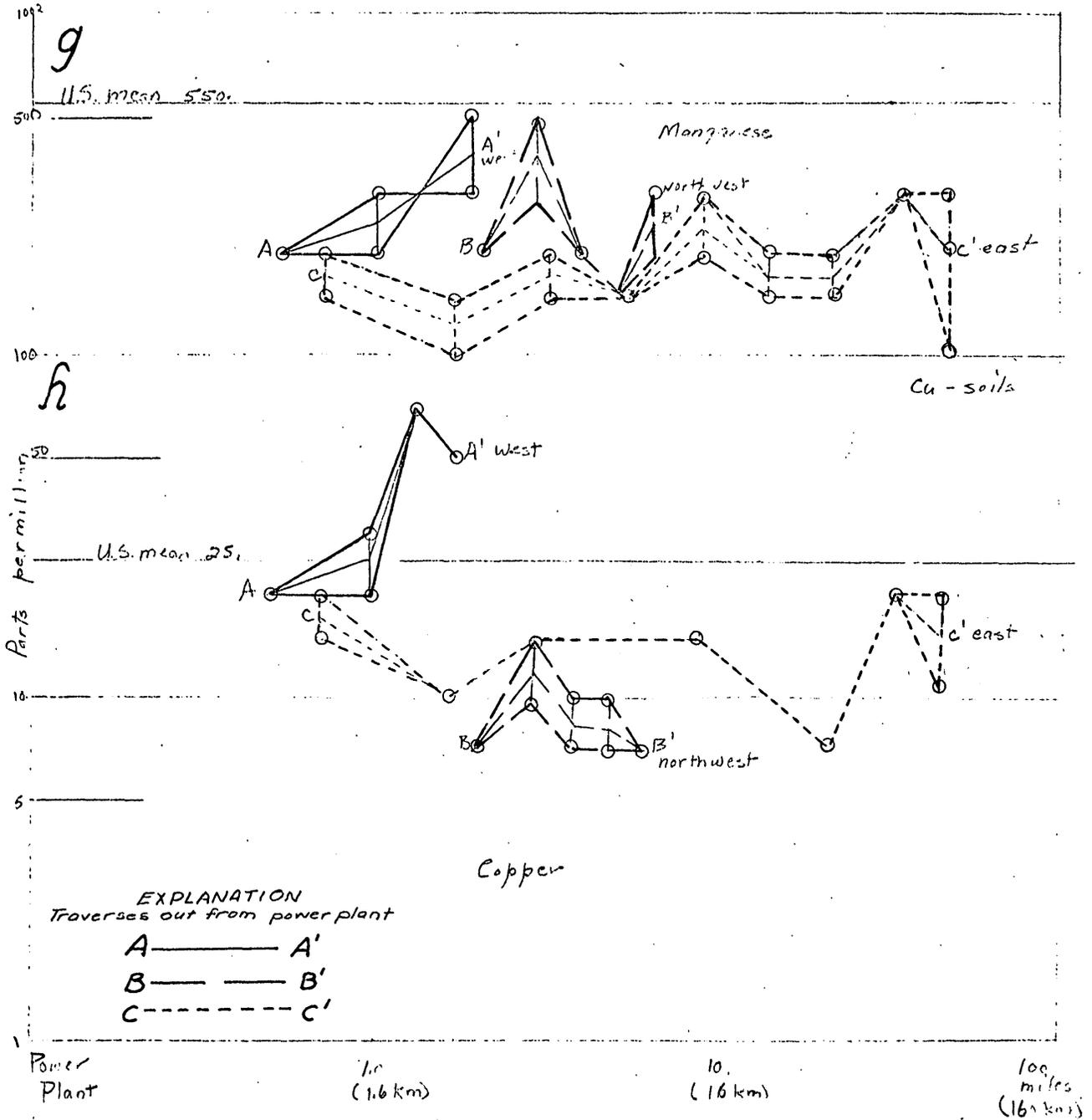


Figure 6i.--Hg values and mean values of soil sample pairs collected at stations along three traverses from power plant. Mean value is light weight line. V, signifies values less than limit of detection.

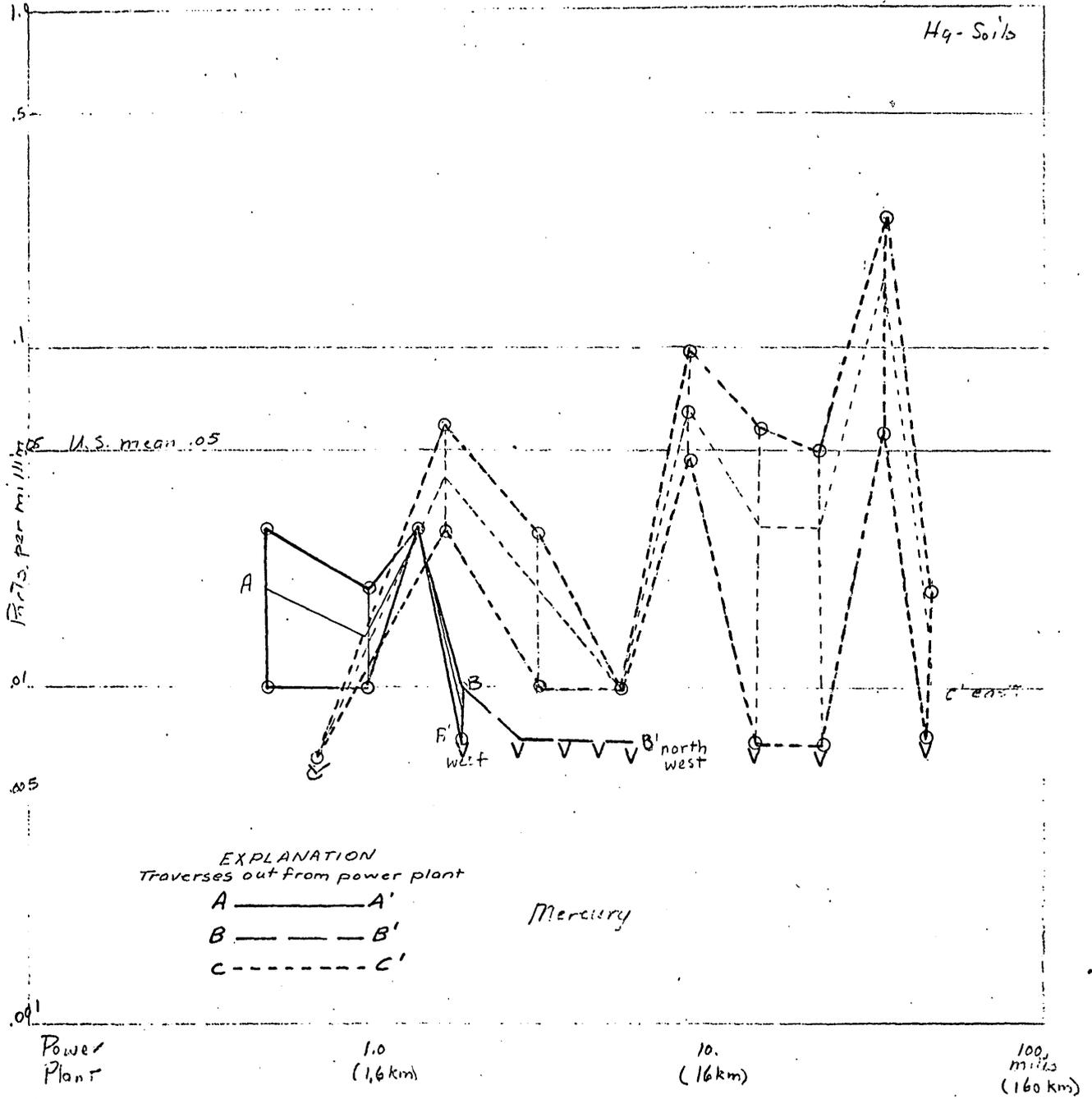


Figure 6j.--Se values and mean values of soil sample pairs collected at stations along three traverses from power plant. Mean value is lighter weight line. .V, signifies values less than limit of detection.

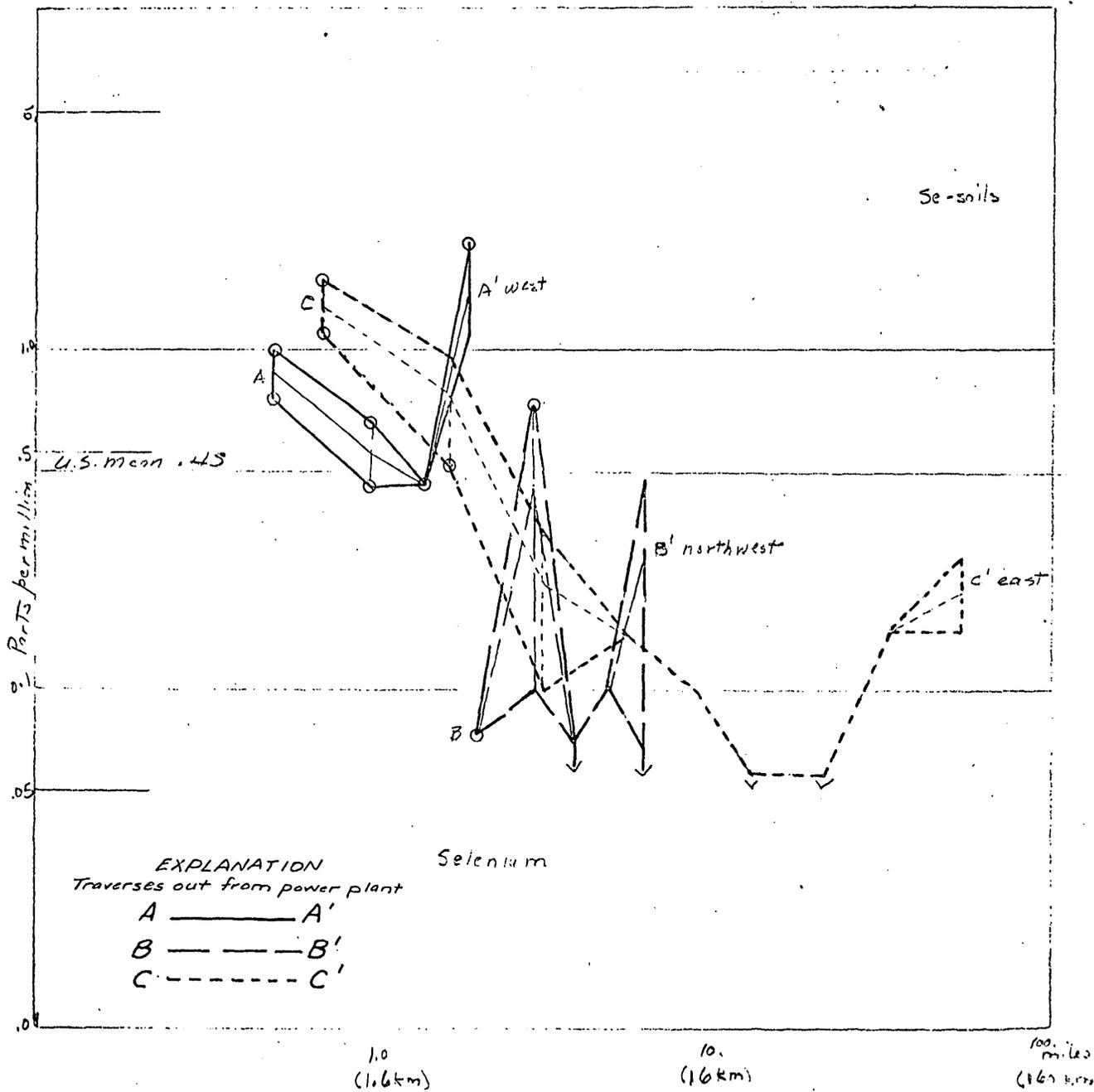


Figure 6k and 6l.--Sr and V values and mean values of soil sample pairs collected at stations along three traverses from power plant. Mean value is lighter weight line.

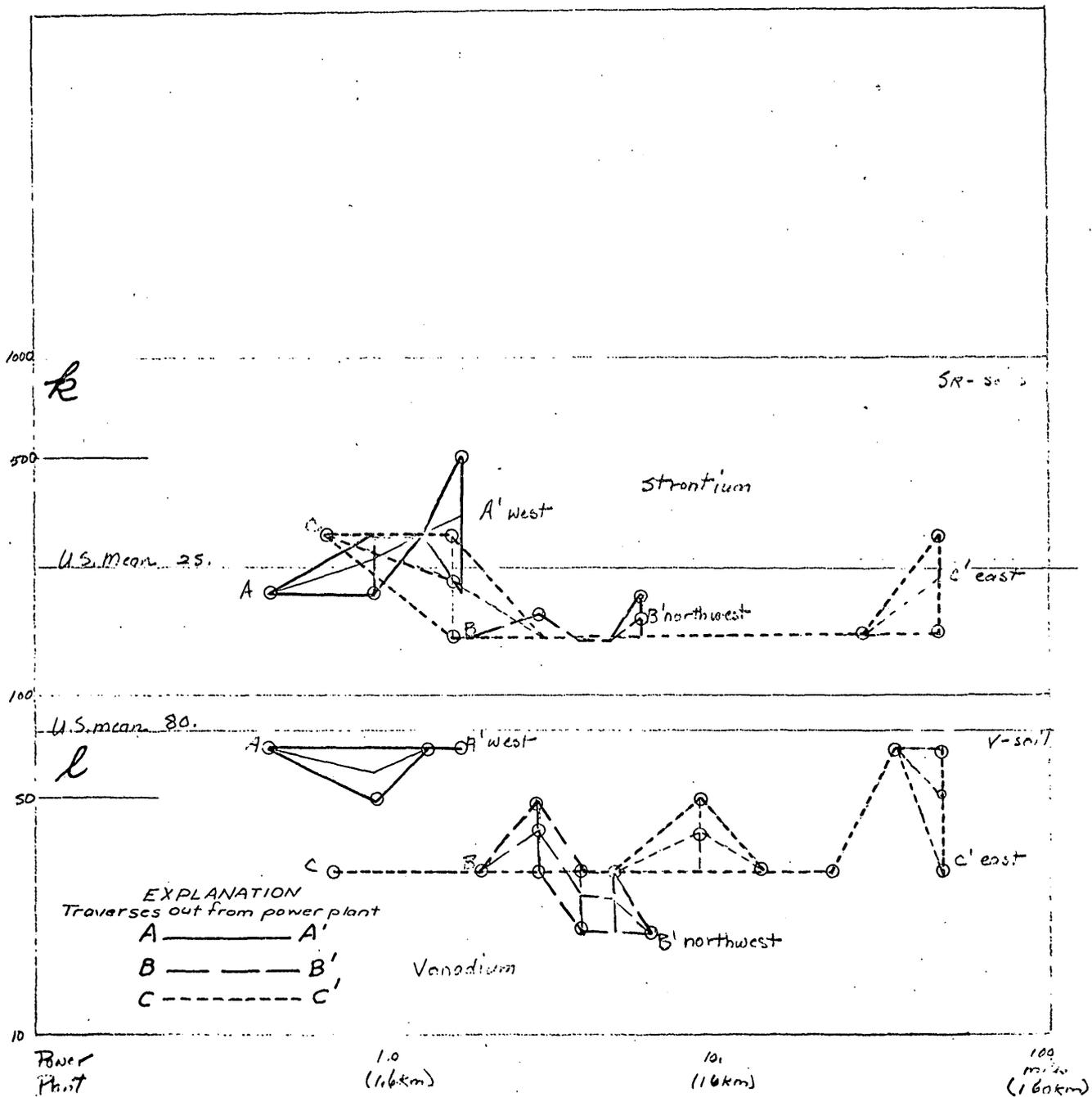


Figure 6m and 6n.--Zn and As values and mean values of soil sample pairs collected at stations along traverses A-A' and B-B' from power plant. Mean value is lighter weight line.

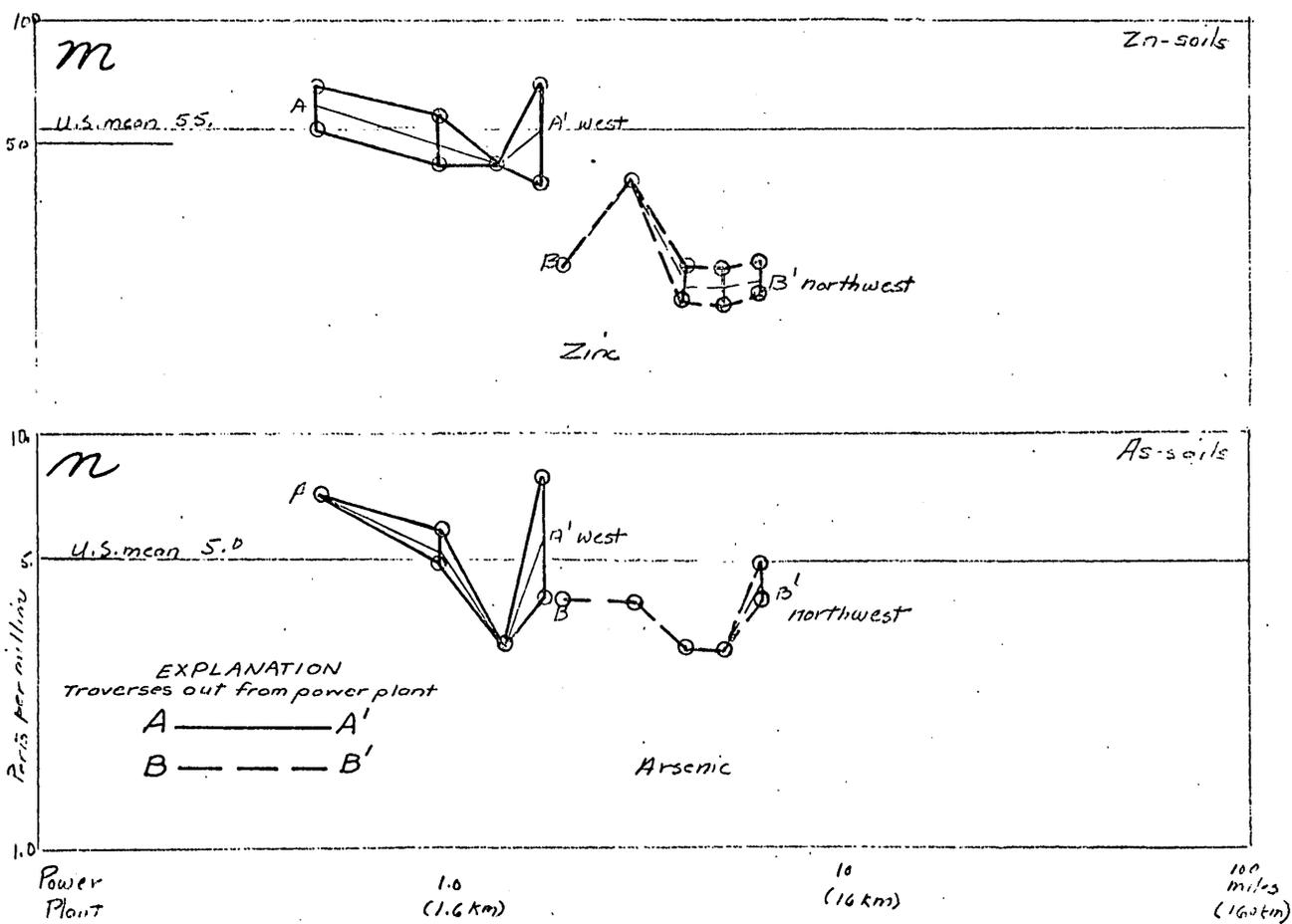


Figure 8a.--Cd values and mean values (where 2 samples) in Atriplex collected at various distances from the power plant (direction not shown). Mean value is lighter weight line.

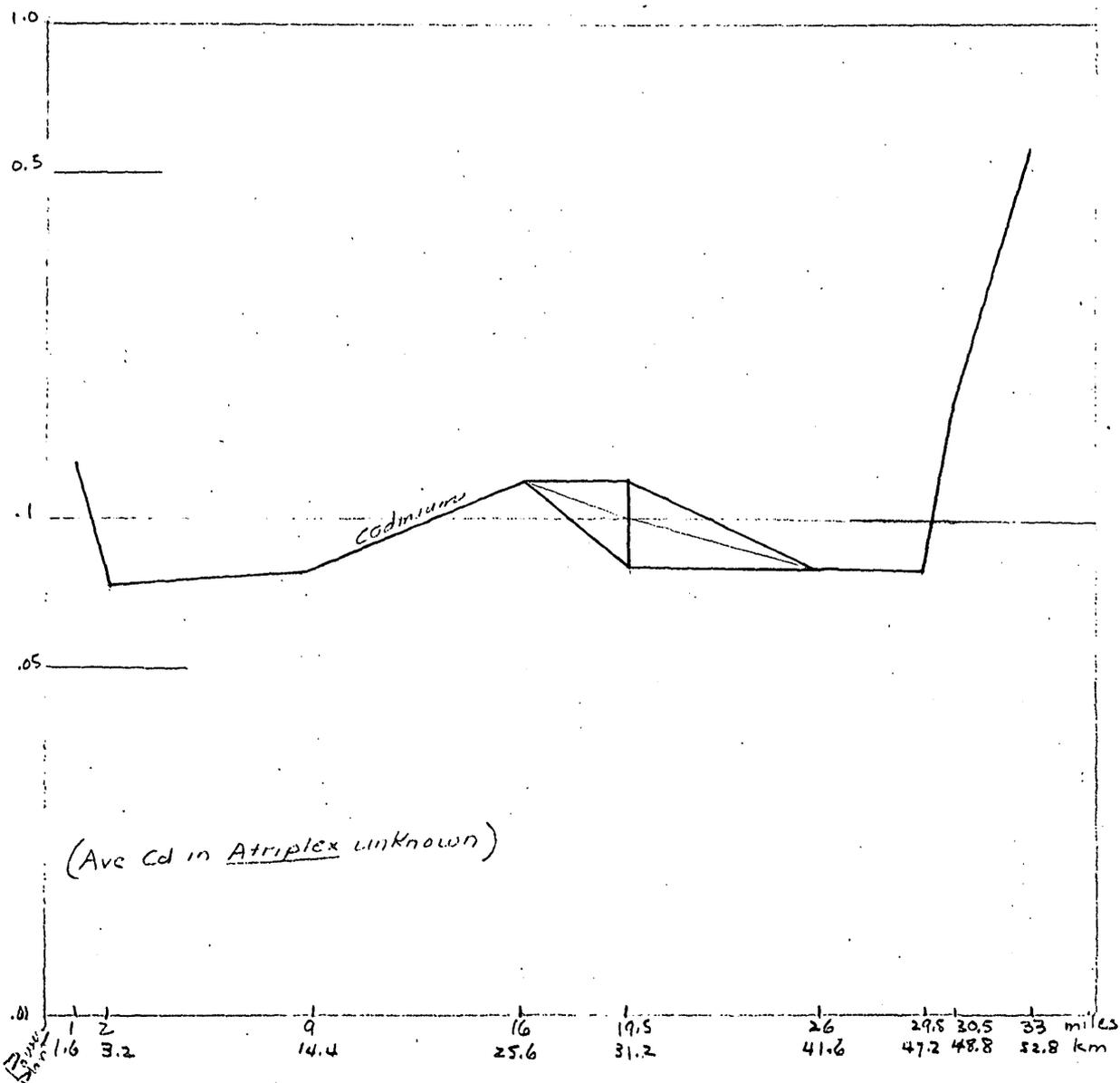


Figure 8b.--Pb, Mo, and Se values and mean values (where 2 samples) in Atriplex collected at various distances from the power plant (direction not shown). V signifies values less than limit of detection.

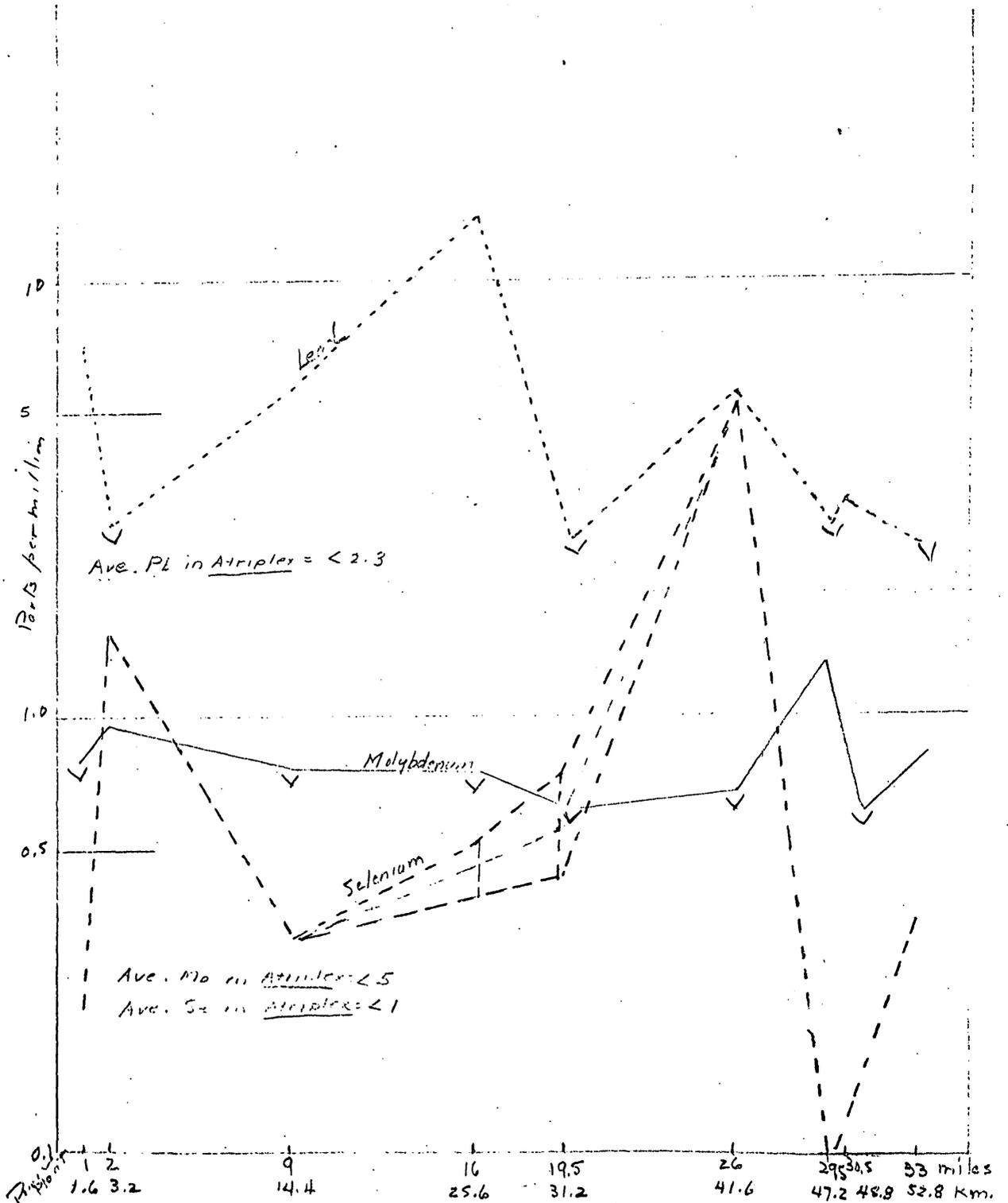


Figure 8c.--Fe, Ba, and B values and mean values (where 2 samples) in Atriplex collected at various distances from the power plant (direction not shown). Mean value is lighter weight and line.

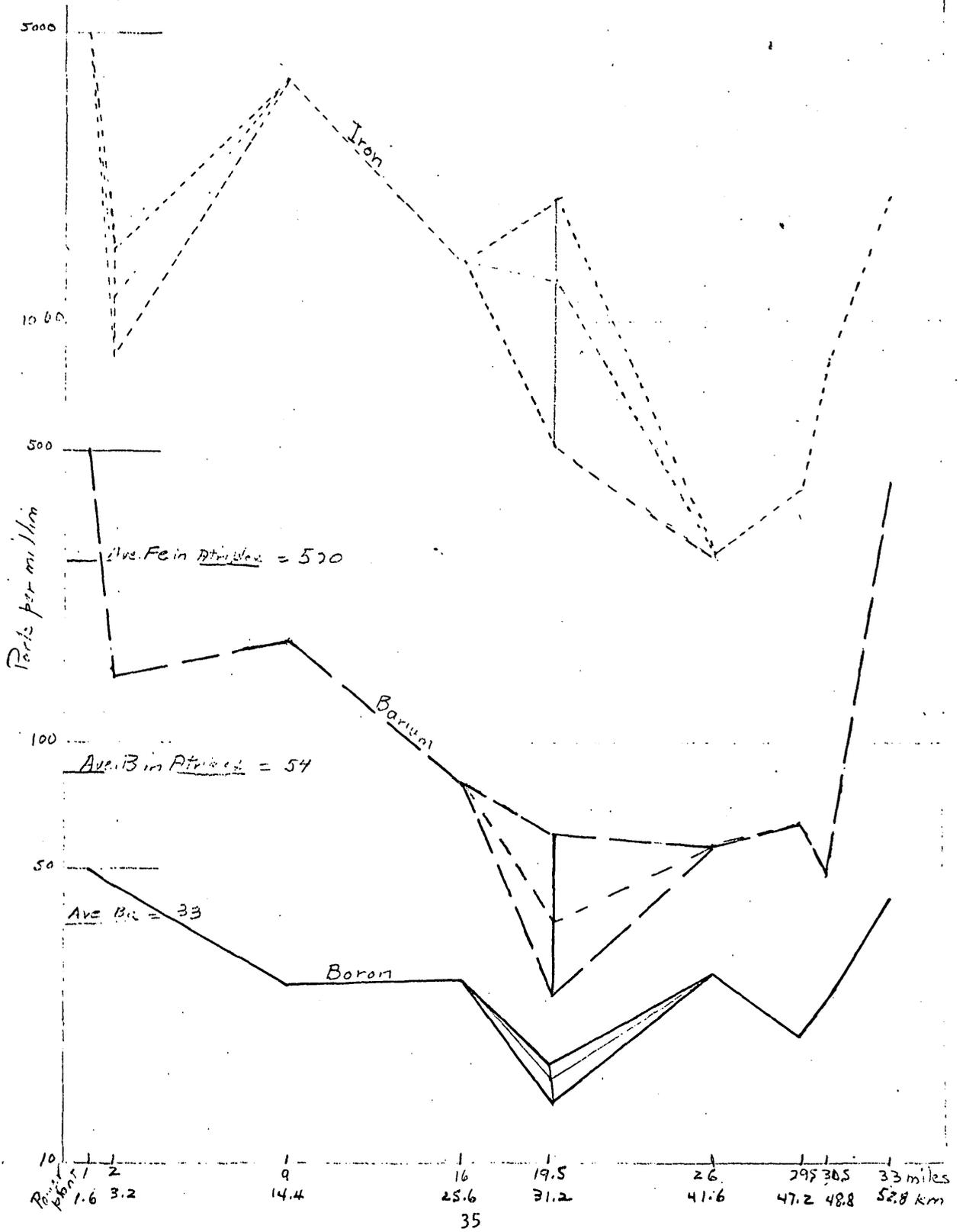


Figure 8d.--Zn, V, and Cu values and mean values in Atriplex collected at various distances from the power plant (direction not shown). Mean value is lighter weight line. V signifies values less than limit of detection.

