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Element associations in soils of the San Joaquin Valley, California

By

R. R. Tidball, R. C. Severson, C. A. Gent,
and G. O. Riddle

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Abstract

Total chemical analyses of soils on the alluvial fans of Panoche and Cantua Creeks in western Fresno County, California, were studied to identify associations among elements in the soils. Some elements, particularly selenium, have been identified as pollutants in agricultural drainage water from this area. R-mode factor analysis of data for 26 elements suggested five element associations in the soils. Factor 1, predominantly aluminum, titanium, gallium, yttrium, cerium, scandium, iron, and lithium, is interpreted as a felsic-sediment factor. Factor 2, predominantly nickel, magnesium, chromium, cobalt, manganese, and iron, is related to serpentine. Factor 3, selenium and sulfur, reflects the similar chemical behavior of these two elements; sodium is negatively related to this factor. Factor 4, calcium, strontium, carbon, and sulfur is an alkaline-earth factor related to carbonate and sulfate precipitation. Factor 5, carbon and mercury, reflects the common occurrence of these element on the alluvial fan. Evaluation of these element associations and their distributions allows determination of probable sources and sinks for several of the trace elements, including selenium.

Introduction

Subsurface agricultural drainage collected from a part of the San Luis irrigation district (San Luis Drain Service Area, Central Valley Project, San Joaquin Valley) in western Fresno County, California (see Figure 1), contains elevated amounts of several trace elements, of which chromium, mercury, and selenium exceed the specified water-quality criteria for freshwater aquatic life (Deverel, and others, 1984). The drainage is transported through the San Luis Drain to Kesterson National Wildlife Refuge in Merced County (San Joaquin Valley Interagency Drainage Program, 1979) where a high incidence of mortality and birth defects among water fowl has been observed (U.S. Bureau of Reclamation, 1984). This toxicity is believed to result from selenium because high concentrations of this element were found in birds, fish, and plants exposed to the water. The concentrations of selenium found in water in field-drain sumps ranged from 84 to 4200 micrograms per liter; the concentration in San Luis Drain water averaged about 300 micrograms per liter (Presser and Barnes, 1985).

The work of Deverel and others (1984) indicated that field-sump water in the irrigation district near the lower end of the Panoche and Cantua Creek alluvial fans contained higher concentrations of selenium than other localities in the district. Based on this evidence from water, we investigated the distribution of numerous elements in the soils on these same two alluvial fans. The purpose of the present study was to determine the optimum number of element associations which would describe the distribution of elements in the soils and to determine what natural features might control those associations. A second objective was to identify sources and sinks for environmentally important trace elements. R-mode factor analysis was used to classify the elements into associations.

The coalescing alluvial fans head on the west side of the San Joaquin Valley at the base of the Diablo Range and slope to the northeast. Sediments in the valley are derived from both the Diablo Range on the west and the Sierra Nevada range on the east, but the majority probably come from granite and metamorphosed sedimentary and igneous rocks on the east side of the valley (Harradine, 1950). The maximum depth of valley fill under these fans exceeds 1000 feet (Lettis, 1982). The two major fans, from Panoche Creek and Cantua

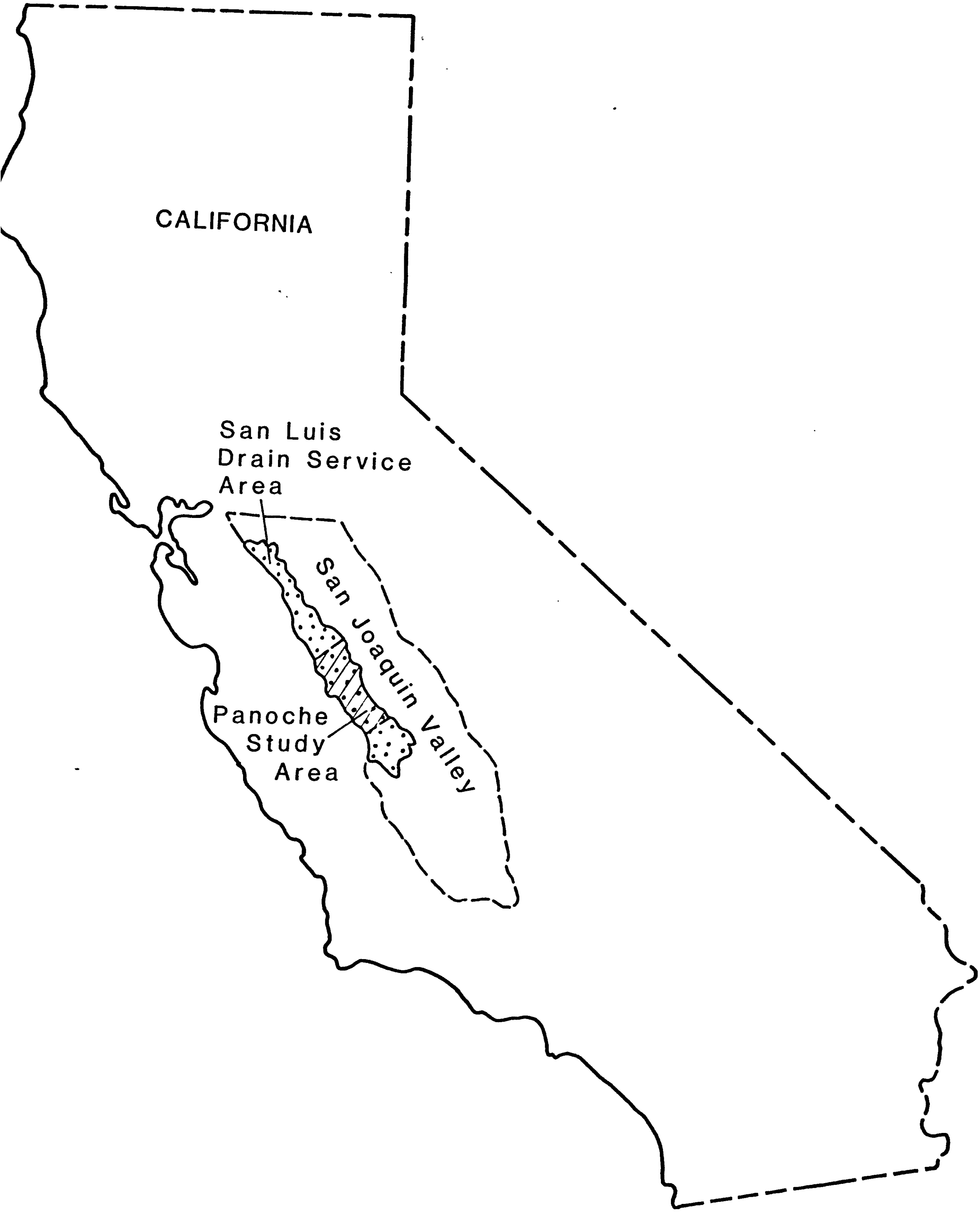

Figure 1. Index map showing the location of the San Luis Drain Service Area and the Panoche Study Area in the San Joaquin Valley, California.

Creek, were fed from extensive drainage basins in the Diablo Range. Several smaller fans were fed by local, intermittent streams in the foothills near Monocline Ridge and Panoche Hills, to the north of Panoche Creek. Monocline Ridge is underlain in part by marine shales that are prone to slumping and sliding. These products of mass wasting are transported onto the alluvial fans during floods as clay-rich mud flows. The resulting fan deposits are subject to subsidence (Bull, 1964).

Acknowledgements

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Methods

Samples of soil were collected from 721 sites located on a one-mile square grid (see Figure 2). Samples were composited from the 168-183 cm (66-72 inch) depth of alluvial soil profiles. This depth was selected because selenium was expected to be water soluble and therefore more concentrated at depth. Severson and others (in press) showed later, however, that the concentration does not vary with depth. Some samples near the lower extremities of the alluvial fans were collected within the saturated zone.

Samples were air dried, disaggregated, and sieved through a 2-mm stainless steel screen. A subsample was ground in a ceramic mill to pass a 100-mesh screen and analyzed for total concentrations of 43 elements. The elements looked for, the analytical methods, the lower limits of detection, and the detection ratios (number of measured values/number of samples analyzed) are shown in Table 1. The following elements were looked for but never detected at the limit shown as mg/kg (ppm) in parentheses: bismuth (10), europium (2), gold (8), holmium (4), silver (2), tantalum (40), tin (20), and uranium (100).

Most elements were determined by inductively coupled argon plasma-atomic emission spectrometry (ICP) after digestion in acids (HF, HCl, HNO_3, $HClO_4$) and bringing to a constant volume in .2M HNO_3 (Crock, Lichte, and Briggs, 1983). Analyses for arsenic, antimony, and selenium were by hydride generation-atomic absorption spectrometry after digestion in acids (HF, HCl, HNO_3, H_2SO_4), and volume adjustment in 2M HCl (Briggs and Crock, 1986; Crock and Lichte, 1982). Mercury was determined by cold vapor atomic absorption after digestion in a Na_2CrO_4/HNO_3 solution (Koirtyohann and Khalli, 1976; Crock and Kennedy, 1986). Analyses for total carbon were done in a Leco automated carbon analyzer and for total sulfur in a Leco automated sulfur analyzer.

The normal range of concentrations for most elements is within the range of detection by the analytical methods, but for some elements numerous samples were reported as below the limit of detection (censored). Censored data were arbitrarily replaced by a value 0.7 times the lower limit of detection for elements where censored data did not exceed 20 percent of the samples so that

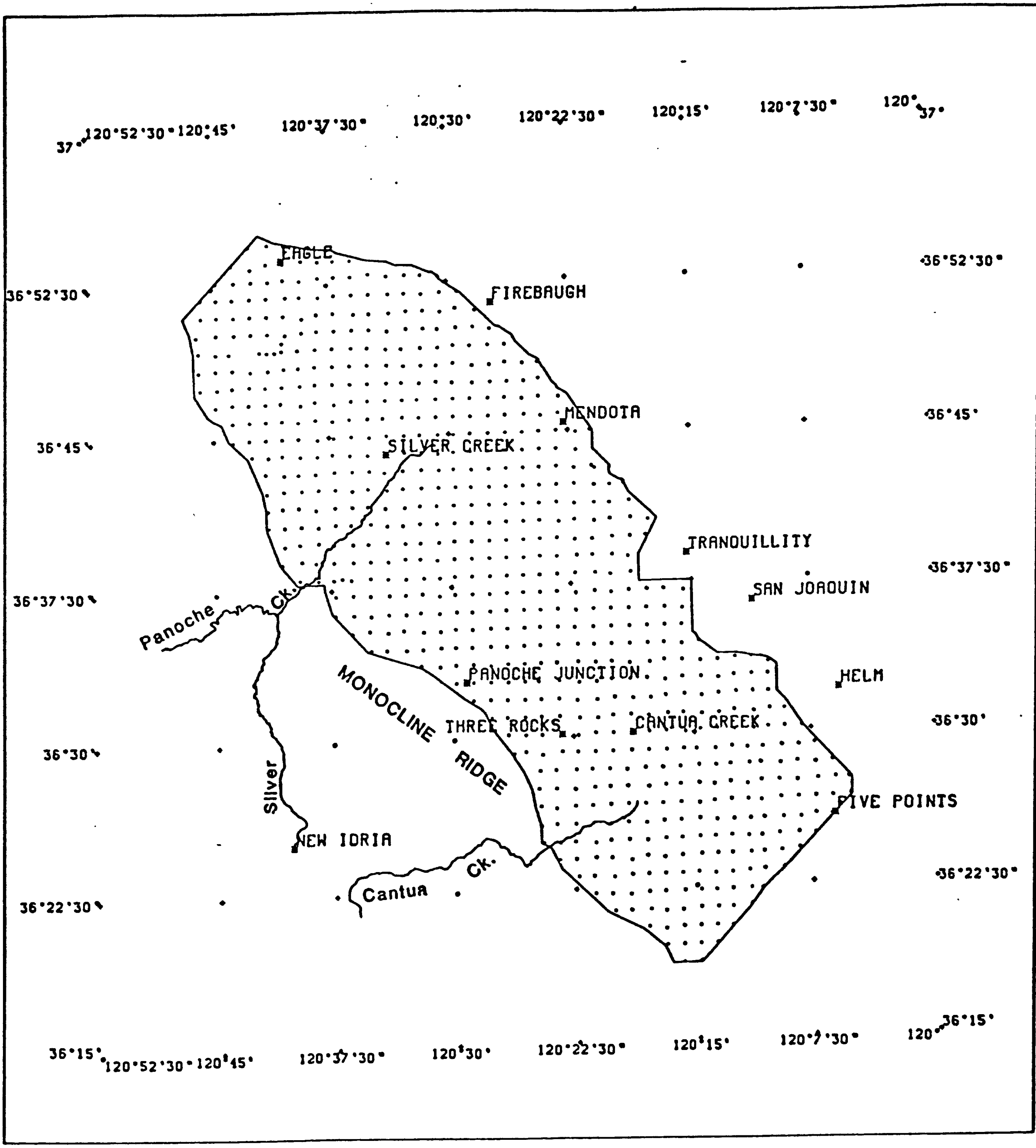

Figure 2. Map of 721 soil sampling sites in the Panoche Study Area, western Fresno County, California.

a complete data set was available for statistical computations. Elements with more than 20 percent of the data censored were eliminated from the factor analysis. Interpretations were not significantly affected by this number of replacements. If analytical variance, which is estimated by a separate analysis of variance, exceeded 50 percent of the total variance, the element was omitted from further consideration. Of the original 43 elements, 26 (indicated by the asterisk in Table 1) were used in the factor analysis.

The data were transformed to logarithms because the frequency distributions are more nearly normal on a log scale than on an arithmetic scale. The data were analyzed by R-mode factor analysis (A. T. Miesch, U.S. Geological Survey, unpublished computer program). The model used was an oblique solution using extreme variables as the reference axes. Two distinct variables computed by factor analysis are a factor score and a correlation coefficient.

A factor score is an index computed for each sample that expresses the degree of similarity between the factor composition and the association of elements (composition) in the sample. Each sample has as many scores as there are factors (axes), and these scores define the mixture of end-member compositions that make up the sample. The scores are dimensionless numbers with a mean of zero and a standard deviation of one. A sample with a large positive score for a particular factor has a composition like that factor. A large negative score indicates the sample composition is opposite to the factor; that is, if the factor contains an element the sample will definitely not contain that element. A small score indicates the sample composition is entirely different than the factor.

The correlation coefficients quantify the relationship of individual elements with each of the factors. The coefficient is computed between the sample score and the concentration of each element, respectively, in the sample. A coefficient may be either positive or negative indicating that an element is commonly enriched in an association or commonly depleted, respectively. The largest coefficient indicates the most dominant element. Some elements may be associated with two or more factors.

Each of the factor scores was plotted on a map as a continuous surface of values on a 0.5 km square grid interpolated by kriging the original 721 factor scores (Tidball, Grundy, and Sawatzky, 1986). The magnitude of the factor scores, classed by selected percentiles of the frequency distribution of gridded values, is shown in shades of gray. The darkest shade represents the class with the largest positive scores and delineates the area where samples are most similar to the factor composition.

Results

The optimum model derived from the factor analysis has five factors. The principal elements that correlate with each of the factors are listed in Table 2 in order of descending correlation coefficients.

Factor 1 includes aluminum, titanium, gallium, yttrium, and cerium. The distribution pattern of the factor scores, Figure 3, shows large scores south of Mendota. Soil samples from this area contain micaceous sediments probably derived from granitic rocks in the Sierra Nevada. The composition and the distribution of scores are interpreted as felsic sediments.

Factor 2 includes nickel, magnesium, chromium, and cobalt (Table 2) and probably represents sediments from serpentine rock. The distribution of the factor scores, Figure 4, outlines the alluvium derived from Cantua Creek but is weak in the alluvium from Panoche Creek. A large intrusive of serpentine is located near the headwaters of both Silver Creek and Cantua Creek; the

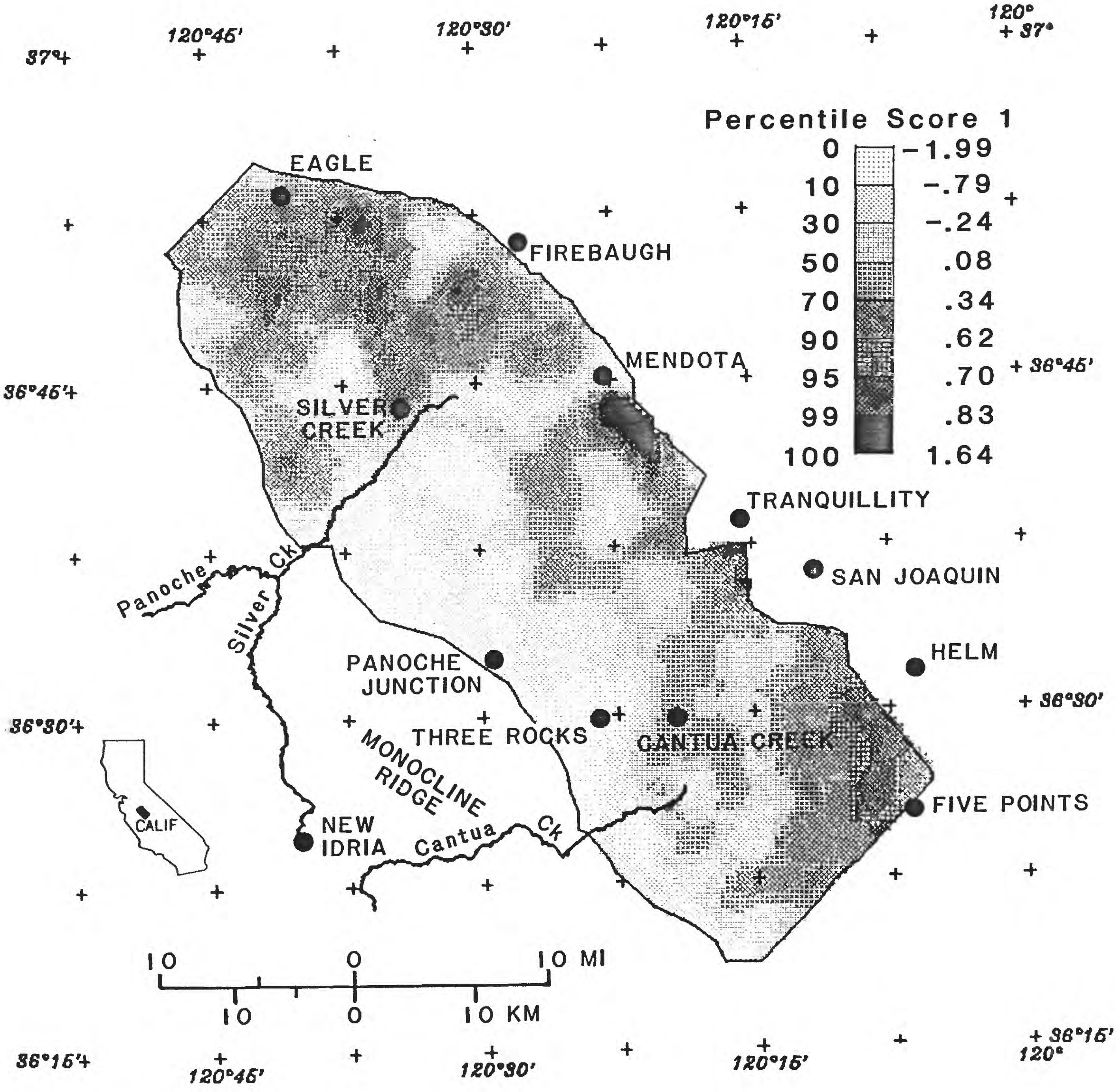

Figure 3. Map of factor-1 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

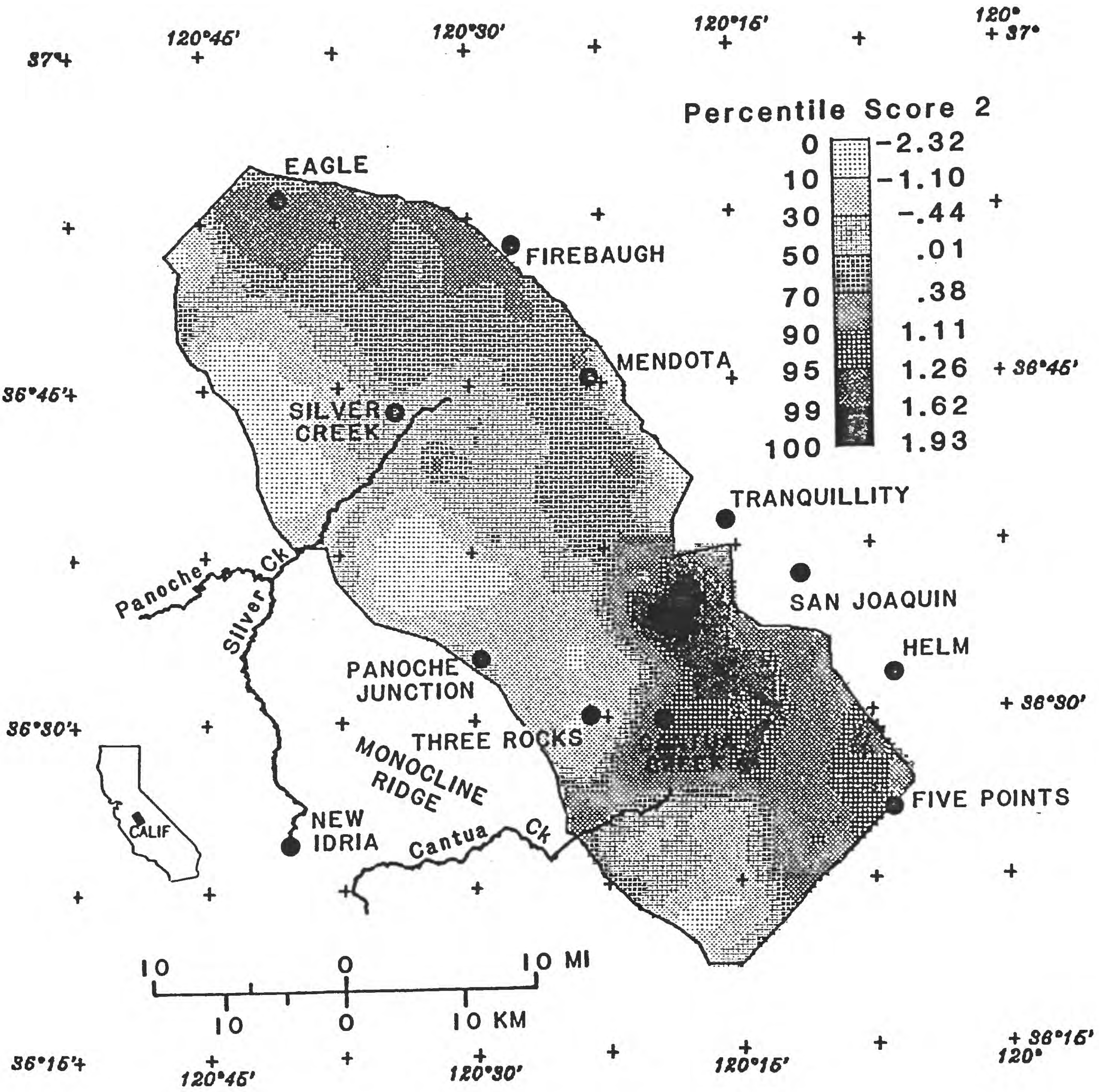

Figure 4. Map of factor-2 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

latter feeds sediment directly to the valley. The influence of serpentine in the sediments from Silver Creek is evidently so diluted by sediments from the much larger Panoche Creek watershed that the Panoche fan only moderately exhibits the composition of the factor. Sediments derived from serpentine may also enter the area from the south. The valley of Los Gatos Creek, just south of the study area, drains the southern margin of the serpentine body.

Factor 3 is predominantly a selenium factor with sulfur as a minor constituent. Sodium is negatively associated with this factor which indicates an antithetic relation between sodium and selenium in the sediments. The association of selenium with sulfur reflects the similar chemical behavior of these two elements. The distribution of factor-3 scores, Figure 5, shows maxima between the major alluvial fans near Panoche Junction and near the valley edge just north of Panoche Creek. Soils on the principal alluvial fans are dissimilar to this factor.

Factor 4 is interpreted as an alkaline-earth factor with major amounts of calcium and strontium and minor amounts of carbon and sulfur. The latter elements probably occur as the anions, carbonate and sulfate. The soils are commonly effervescent in HCl, and gypsum is abundant. The distribution of factor-4 scores shown in Figure 6 suggests that the principal occurrence of soils with this composition is at the western edge of the valley downstream from Monocline Ridge. Elements from this source appear either to accumulate in the central part of the valley perhaps as evaporites or to derive from the east side of the valley.

Factor 5 is primarily a carbon factor with mercury as a minor constituent. The distribution of factor-5 scores is shown in Figure 7. Carbon is partitioned into two associations which suggests two distinct forms of carbon. In factor 4 carbon probably occurs as the carbonate anion with calcium and strontium. In factor 5 carbon is more likely to be organic. The map pattern outlines the alluvial fan of Panoche Creek and to a lesser extent Cantua Creek. The mercury originates from mercury deposits in the vicinity of the New Idria mine at the head of Silver Creek.

Discussion

The five-factor model defines the optimum number of element associations to classify the soils geochemically. Most of the soils are a mixture of two or more associations. Sediments from the coast ranges have predominant control over the composition of the soils as indicated by factors 2, 3, and 5. The influence of alluvium from the east side of the valley is evident in factor 1. Factor 4 may exhibit an influence from both sides of the valley.

Factors 2 and 5 are controlled by alluvium transported by one or both of the major streams on the west side. Factor 2 reflects the serpentine body exposed at the head of Silver Creek and Cantua Creek. Soils that best express the composition of factor 2 are located near the outer perimeter of the Cantua Creek fan.

The dominant element in factor 5 is carbon with minor mercury. Carbon is partitioned between factor 4 and factor 5, a fact that might not be evident from a single-element map. Carbon probably occurs in two forms that have different distributions; factor 4 is located between the major alluvial fans, and factor 5 is located on those fans. The carbon of factor 4 is probably inorganic calcium and strontium carbonate. The carbon of factor 5 is interpreted as organic. Some carbon was probably transported onto the fans by the streams, but the supply of water also stimulated the production of vegetation on the fans. The dispersion of mercury is confined to the alluvial

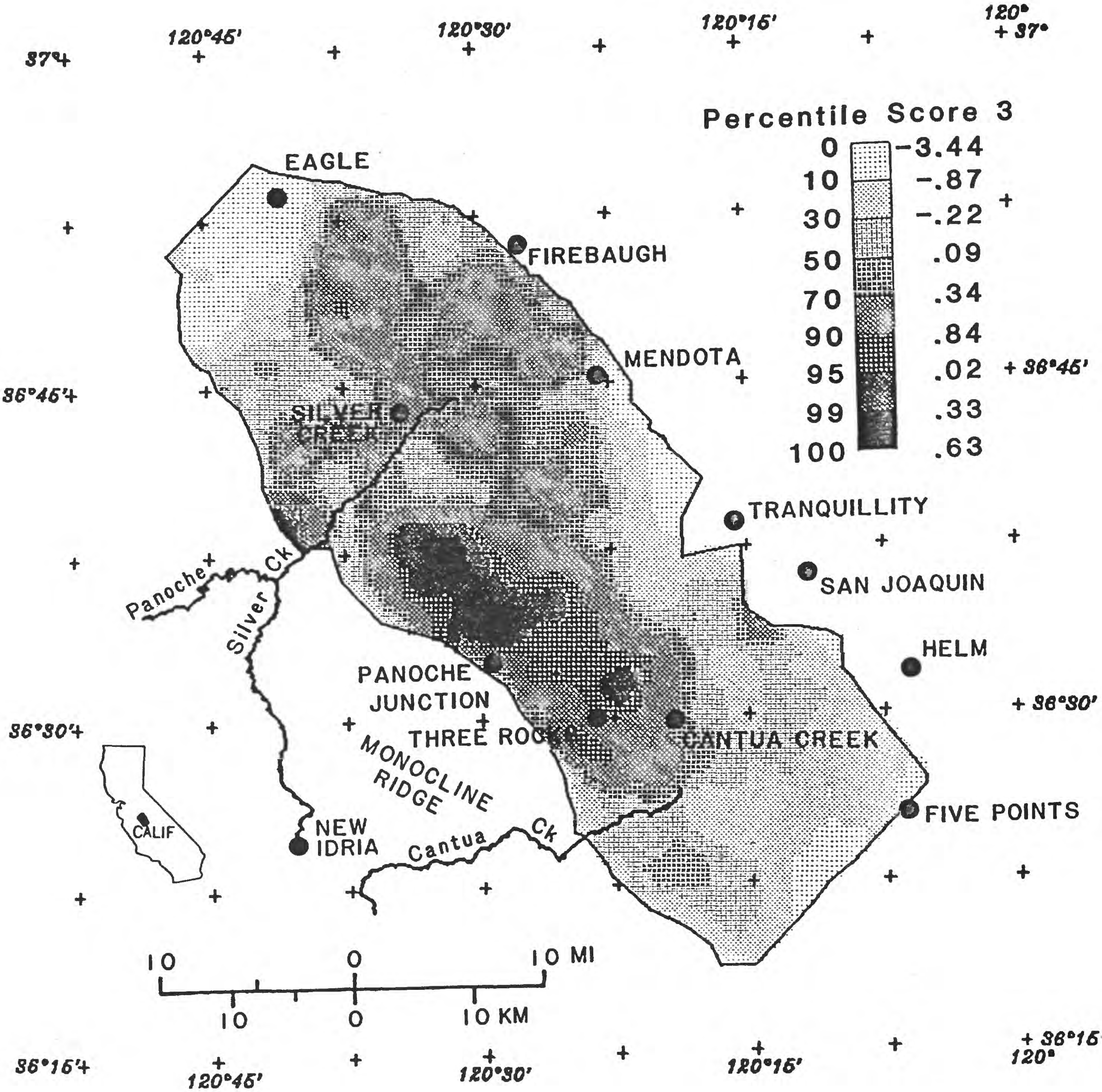

Figure 5. Map of factor-3 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

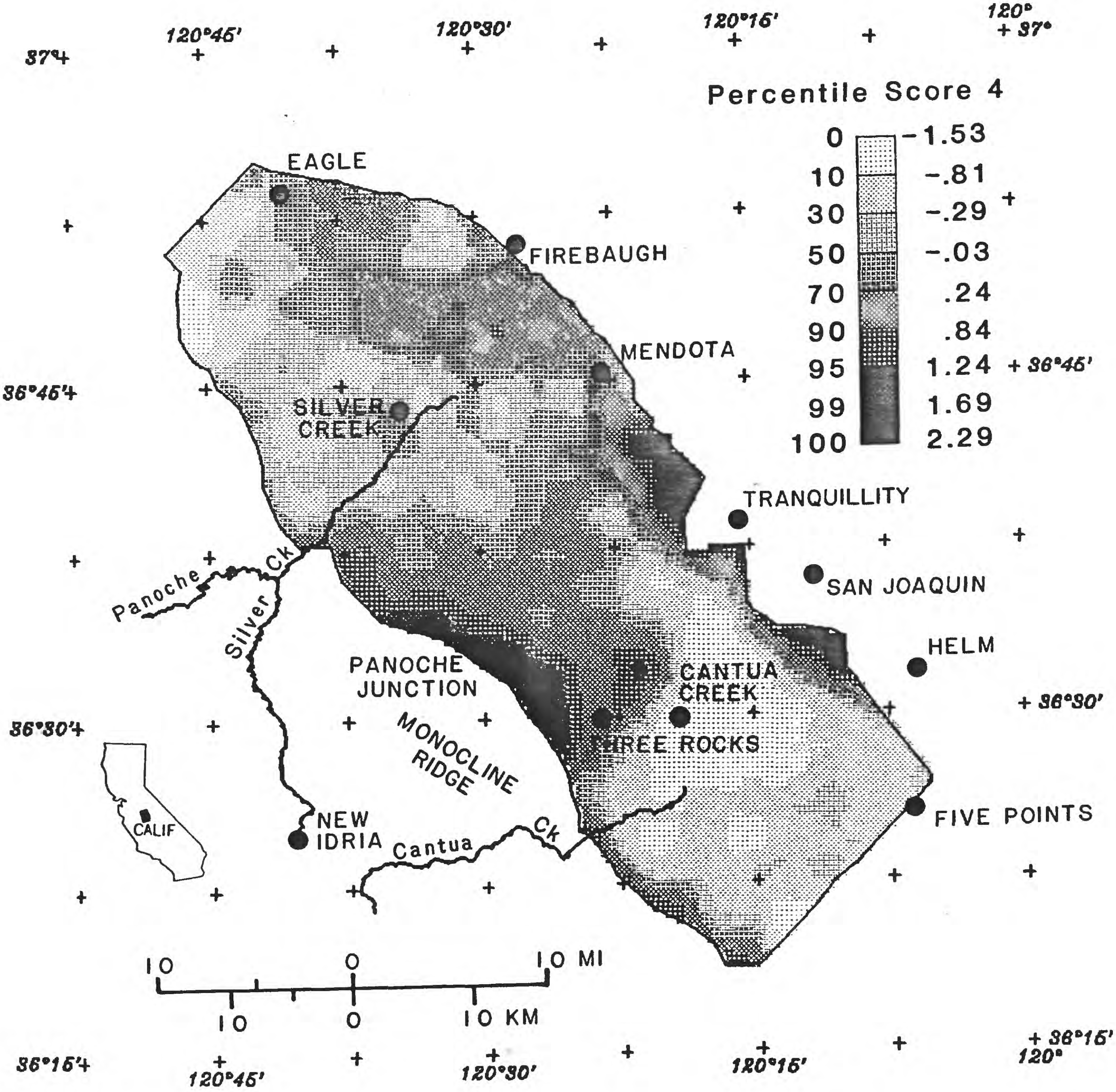

Figure 6. Map of factor-4 scores for soils of the Panoche Study Area. Gray scales delineate percetiles of the frequency distribution of gridded values estimated from sample scores.

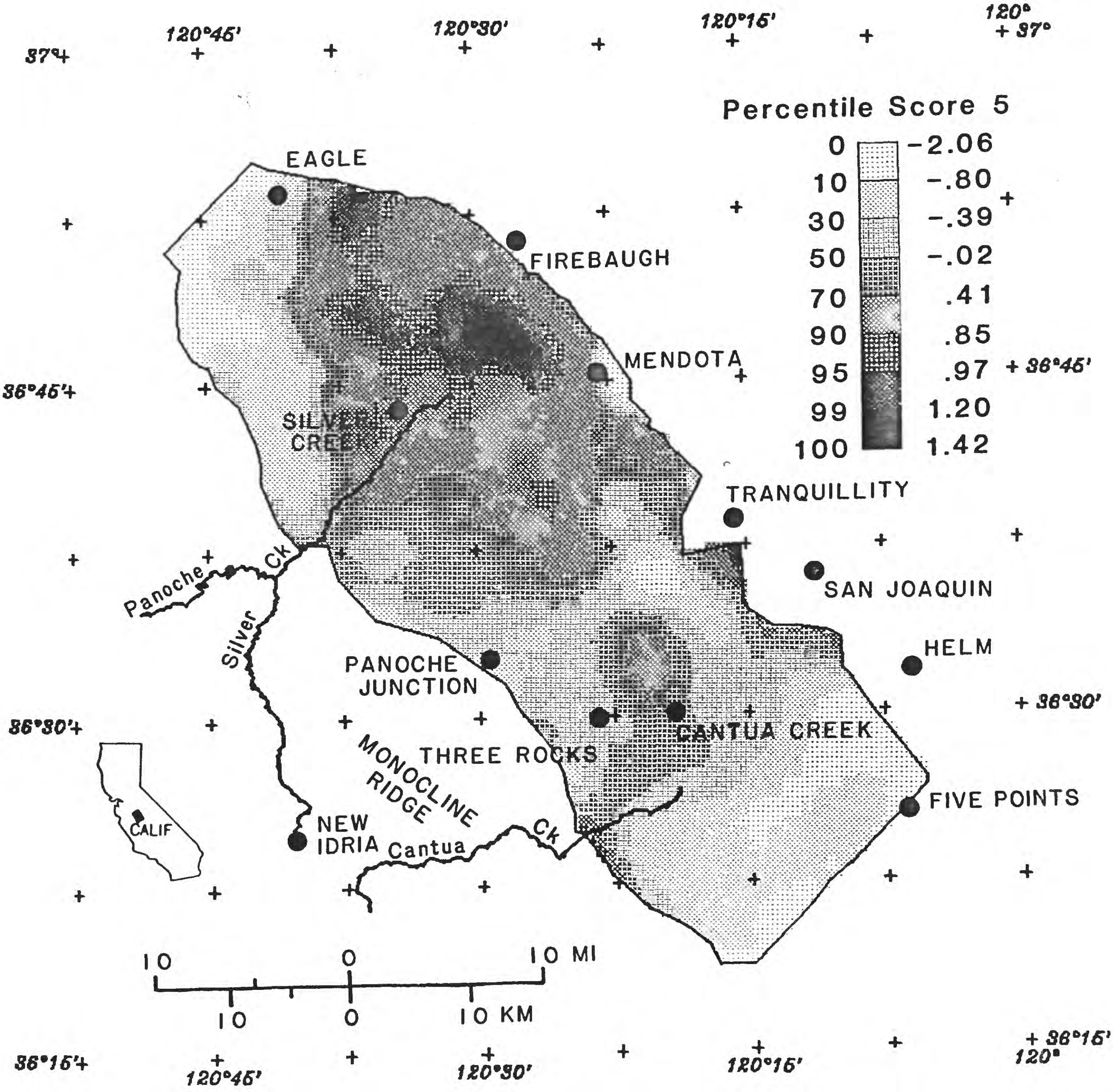

Figure 7. Map of factor-5 scores for soils of the Panoche Study Area. Gray scales delineate percentiles of the frequency distribution of gridded values estimated from sample scores.

fan of Panoche Creek and to a lesser extent the fan of Cantua Creek because the source is near the New Idria mercury mine at the head of Silver Creek. Mercury probably occurs mostly as either mercuric sulfide or elemental mercury. The organic carbon may also produce a reducing environment favoring the preservation of mercury. The common occurrence of carbon and mercury in the same location suggests a common controlling process but it does not necessarily imply a chemical bond between the two.

Factors 3 and 4 when considered together exhibit two features: (1) at the west side of the study area near Panoche Junction calcium, strontium, carbon, sulfur, and selenium are abundant, and sodium is impoverished and (2) at the east side of the study area calcium, strontium, carbon, and sulfur are also abundant, sodium is moderately high, but selenium is absent. The inverse relation between selenium and sodium indicates the two elements do not share the same spatial distribution. Sulfur is partitioned between factor 3 and 4 with a greater abundance along the east side where it probably occurs as a sulfate in an evaporite. On the west side most of the sulfur is more likely to be detrital sulfate (gypsum). Lakin and Davidson (1973, p.574) state that "In weathering, selenium and sulfur tend to be separated, in large part because selenium becomes fixed in insoluble basic ferric selenites. Only in an alkaline oxidizing environment is selenium oxidized to the soluble selenate form; sulfur, however, is even more readily oxidized to highly soluble sulfate and is carried away in surface and ground waters. As a result, selenium is present neither in sulfate deposits nor in sedimentary sulfur deposits." This might explain the absence of selenium in the east side evaporites and also suggests that selenium in the west side detritus occurs in a form independent of the sulfur.

Selenium is added to the valley sediments in moderate amounts all along the west side of the San Joaquin Valley (unpublished data) probably as detritus from shales (Lakin and Byers, 1941). In the fan areas selenium may be diluted by barren sediments as well as be more readily dissolved and removed in a well watered system. In the interfan areas the solution of selenium would be diminished by the lack of a solvent, ineffective removal, and possible excess evaporation. Superimposed on this scenario is an anomalous occurrence of selenium near Monocline Ridge. It appears that sedimentary rocks, perhaps marine shales, that border the valley are a host for the selenium. The ultimate source of that selenium is yet another question. Perhaps selenium in a broad halo around the mercury deposit at New Idria migrated into the adjacent sedimentary materials.

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Table 1.--Elements measured in soils, methods of determination, lower limits of detection, detection ratio, and percent error variance.

Element	Method[1]	Lower limit of detection[2]	Detection ratio[3]	Error variance, percent[4]
Al*	ICP	0.05%	721/721	12
As	HG	.1	721/721	54
Ba	ICP	1	721/721	54
Be	ICP	1	669/721	0
C*	LA	.1%	719/721	3
Ca*	ICP	.05%	721/721	2
Cd	ICP	2	2/721	--
Ce*	ICP	4	721/721	16
Co*	ICP	1	721/721	7
Cr*	ICP	1	721/721	11
Cu*	ICP	1	721/721	6
Fe*	ICP	.05%	721/721	4
Ga*	ICP	4	721/721	18
Hg*	CV	.02	579/721	17
K*	ICP	.05%	721/721	4
La	ICP	2	721/721	24
Li*	ICP	2	721/721	5
Mg*	ICP	.005%	721/721	3
Mn*	ICP	4	721/721	4
Mo	ICP	2	89/721	--
Na*	ICP	.005%	721/721	9
Nd	ICP	4	721/721	38
Ni*	ICP	2	721/721	2
P*	ICP	.005%	721/721	9
Pb	ICP	4	721/721	60
S*	LA	.01%	679/721	3
Sc*	ICP	2	721/721	7
Se*	HG	.1	713/721	21
Sr*	ICP	2	721/721	6
Th*	ICP	4	716/721	24
Ti*	ICP	.005%	721/721	13
V*	ICP	1	721/721	7
Y*	ICP	2	721/721	11
Yb	ICP	1	713/721	55
Zn*	ICP	4	721/721	8

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[1] ICP, induction coupled plasma. HG, hydride generation. LA, Leco analyzer. CV, cold vapor atomic absorption.

[2] Values in mg/kg (ppm) except as noted percent.

[3] Number of values reported above lower limit/total number samples analyzed.

[4] Laboratory-error variance as percentage of total variance.

Table 2. Factor compositions. Elements are arranged in descending order of correlation coefficient, which indicates relative importance of the element.

Factors				
1	2	3	4	5
Al .95	Ni .95	Se .84	Ca .90	C .87
Ti .94	Mg .92	S .50	Sr .78	Hg .51
Ga .94	Cr .91		C .42	
Y .91	Co .89		S .40	
Ce .90	Mn .64			
Sc .89	Fe .64			
Fe .88	Cu .61			
Li .88				
Zn .84				
V .84				
Cu .83				
Th .72				
Mn .65		Na -.79		