



Ronald L. Tidball

R. R. TIDBALL, R. C. SEVERSON,
J. M. McNEAL, AND S. A. WILSON

PRESENTED BY
RONALD R. TIDBALL
U.S. Geological Survey
Box 25046, MS 912
Federal Center
Denver, Colorado 80225

Dr. Tidball is a soil scientist with the U.S. Geological Survey in Denver. He received his Ph.D. from the University of California, Berkeley, in 1965. He has done research in geochemical mapping of soils in numerous midcontinent and western states in studies that range from environmental geochemistry to appraisal of mineral resources.

**DISTRIBUTION OF
SELENIUM, MERCURY,
AND OTHER ELEMENTS IN
SOILS OF THE
SAN JOAQUIN VALLEY
AND PARTS OF THE SAN
LUIS DRAIN SERVICE
AREA, CALIFORNIA**

AGRICULTURAL DRAINAGE derived from the San Luis Unit of the Central Valley Project and delivered to Kesterson Reservoir in western Merced County, California, contains high concentrations of salts and trace elements (Deverall et al., 1984). Selenium in particular is believed to be responsible for excessive mortality and birth defects among waterfowl that inhabit the pond water. We have investigated the composition of solid mineral material from a part of the San Luis Drain service area by analyzing soil samples

collected on the alluvial fans of Panoche and Cantua Creeks in western Fresno County. In addition, we analyzed archival soil samples collected throughout the San Joaquin Valley to provide a background perspective against which to compare the service area. The purposes of the study were to define the natural distributions of elements in soils, to establish background values, to discover locations of unusual concentrations, and to point to possible source areas for elements of interest, particularly selenium. This paper reports on the results of chemical analyses of the soils for selected elements.

Soil samples were collected in the service area by Sherril Beard, Phillip Skoles, D. B. Hatfield, and J. C. Gray, Jr. Samples from the San Joaquin Valley were collected by Paul Sliva. All samples were analyzed in the U.S. Geological Survey laboratories in Denver, Colorado. Samples were prepared by R. E. McGregor. Analyses for selenium, arsenic, and mercury were done by D. B. Hatfield and K. R. Kennedy, and for sulfur by E. E. Engleman.

COLLECTION AND ANALYSIS TECHNIQUES

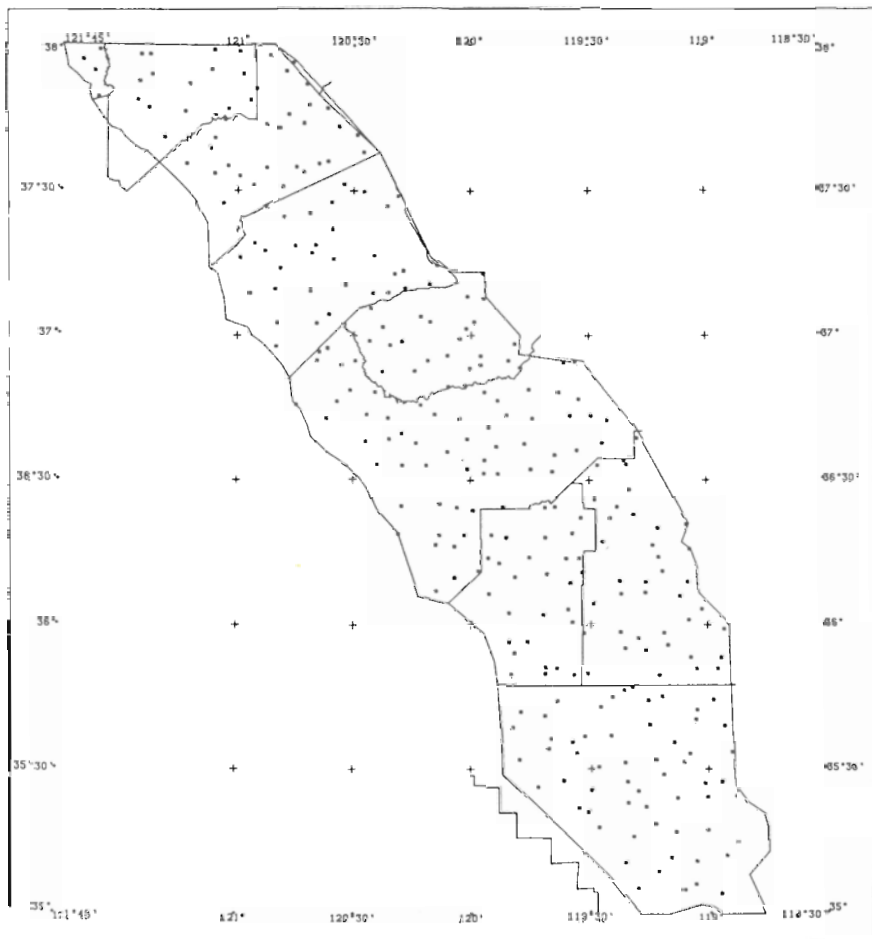
The study areas are shown in Figure 1. The U.S. Geological Survey had previously (1983) collected soil samples from 297 sites located throughout the San Joaquin Valley (Figure 2). These samples represent a stratified random sample taken at intervals that average about 10 km, and the samples are a composite of the 0-12 inch (0-30 cm) depth. I will refer to these samples as the "Valley samples." A second set of samples was collected in 1985 from 721 sites on the Panoche and Cantua Creek alluvial fans at a 1-mile (1.6 km) interval (Figure 3). I will refer to these samples as the "Panoche samples." Because we originally anticipated that higher selenium values might occur in the deeper parts of the soil profile, we analyzed a composite sample from 66-72 inches (168-183 cm) depth. A separate analysis of variance study (Sewerson et al., 1986), however, confirmed there was no significant difference in results between depths, so we feel confident in directly comparing the Panoche samples with the Valley samples.

The less-than-2-mm diameter fraction of all samples was analyzed for total amounts of thirty-five elements. I will present the results only for arsenic, mercury, selenium, and sulfur. Selenium and arsenic were determined by hydride generation and atomic absorption method (Briggs and Crock, 1986). Mercury was determined by acid digestion and cold-vapor continuous-flow atomic absorption (Koirtyhann and Khalli, 1976; Crock and Kennedy, 1986), and sulfur was determined by combustion in a Leco analyzer with infrared detection of sulfur dioxide gas (Jackson et al., 1985).

FIGURE 1
INDEX MAP OF CALIFORNIA SHOWING
THE SAN JOAQUIN VALLEY,
THE SAN LUIS DRAIN SERVICE AREA,
AND THE PANOCHÉ STUDY AREA



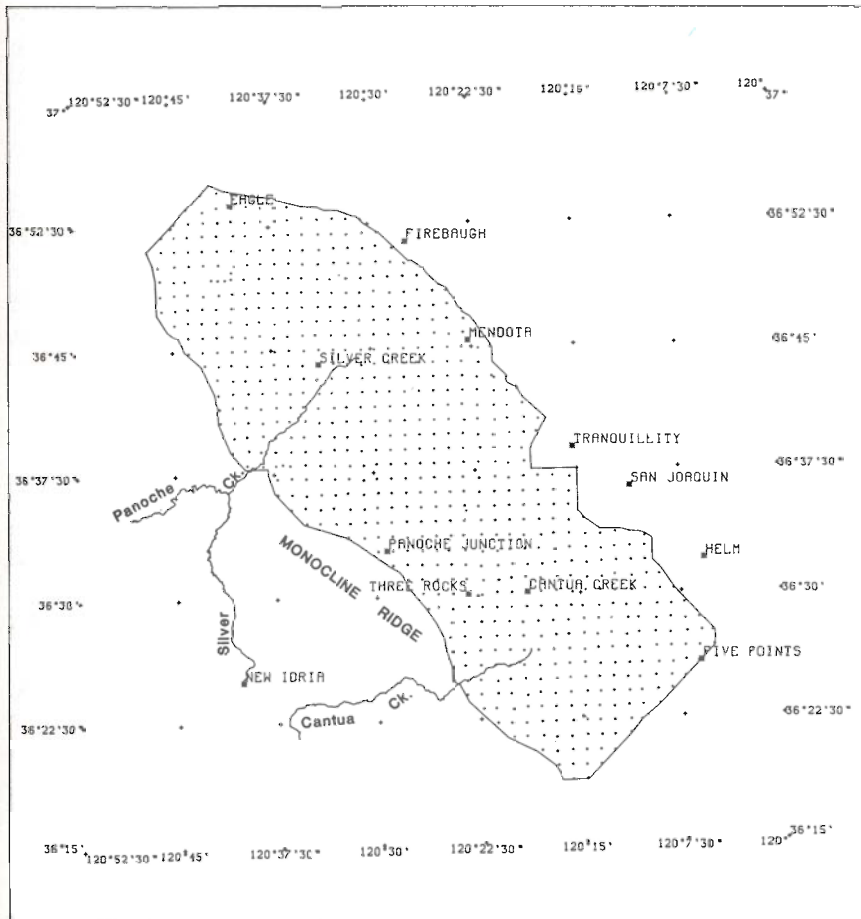
FIGURE 2
SAMPLE LOCATION MAP SHOWING SAMPLING SITES
IN THE SAN JOAQUIN VALLEY



The lower limits of determination are: arsenic, 0.1 parts per million (ppm), mercury, 0.02 ppm, selenium, 0.1 ppm, and sulfur, 0.01 percent.

The results of these analyses are illustrated by color-scale raster-format images that resemble contour maps. An automatic contouring procedure typically has two steps, gridding and contouring. We estimated the grid by universal kriging (Tidball et al., 1986). The gridding step

FIGURE 3
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computes a regular grid of data from sometimes irregularly spaced samples. The grid interval chosen is typically finer than the original sampling interval because the estimated surface of data is more continuous and the contours will be smoother. The grid for Valley soils is estimated at an interval of 2 km, and the grid for the Panoche area is estimated at 0.5-km intervals. We believe the gridding produces a faithful representation of

the original data because the mean of the kriged estimates nearly equals the mean of the original data, and the errors are randomly distributed and uncorrelated with location.

The color-scale shown on the image maps represents selected percentiles of the frequency distribution for each element. Yellow includes the median. Warmer colors (orange to red) represent areas with above average values, and cooler colors (green to blue) represent areas with below average values.

RESULTS

The kriging algorithm has a smoothing effect on the data that tends to reduce the highest peaks but changes the median value very little. For example, the geometric mean for selenium in the Panoche area is 0.68 ppm and the median for the gridded values is 0.79 ppm. This does not detract from the value of the image map for illustrating the regional distribution of an element in the soils.

The distribution of selenium in the Valley samples is shown in Figure 4. The gridded values of selenium range from 0.07 to 1.07 ppm. Above average values occur on the west side of the Valley and below average values occur on the east side. This suggests that the Coast Ranges are a more significant source of selenium than is the Sierra Nevada. There are two areas with relatively high selenium values (90th percentile or above). One is within the delineated Panoche Fan study area in western Fresno County. The other is in western Kern County in the vicinity of the Antelope Hills. The highest measured concentrations of selenium found are 1.5 ppm in the Antelope Hills area and 4.5 ppm in the Panoche area. The geometric mean for selenium is 0.14 ppm in the Valley samples and 0.68 ppm in the Panoche area; these values can be compared with 0.25 ppm for 495 soils collected extensively throughout the western United States (Shacklette et al., 1974). The distribution of selenium in the Panoche study area is shown in Figure 5. When comparing Figure 4 with Figure 5, note that the colors of the two figures represent different ranges of selenium values: The upper 10 percent of the Valley samples (greater than 0.36 ppm) are nearly equivalent to the upper 90 percent of the Panoche samples. The two sample sets both confirm the selenium distribution in the Panoche area.

Figure 5 shows that the probable source area for the selenium is located between the two major alluvial fans of Panoche Creek and Cantua Creek. Therefore, sediments from within the Diablo Range are not a major source of selenium, or, if they are, that fact is masked by deposition of more recent but barren sediments. The interfan area, where selenium is

highest, borders on a locale known as Monocline Ridge. The local sediments consist of mud-flow deposits derived from the adjacent foothills, which consist mostly of marine and nonmarine sedimentary rocks of Tertiary age. A dispersion train grades downslope toward the Valley trough. Near the lower (east) part of the fan, the gradient reverses in scattered areas, which may indicate locales where shallow groundwater has carried selenium to the surface. At present we have no data on speciation of selenium, but it appears that selenium is mostly precipitated high on the fan and more commonly dissolved in the shallow groundwater near the Valley trough (Deveral et al., 1984). Perhaps selenium is slowly dissolved into the groundwater high on the fan and is moving down through the fan to emerge at the lower end.

Figure 6 shows the distribution of mercury in the Valley soils. As with selenium, the Coast Ranges provide more mercury-enriched sediments than does the Sierra Nevada. This is not unexpected because important mercury deposits such as the New Almaden Mine in Santa Clara County about 55 miles west of Los Banos and the New Idria Mine in San Benito County about 10 miles west of Monocline Ridge were, respectively, the number one and number two producers of mercury in North America (Bailey et al., 1973). There is also mercury mineralization in the Parkfield District at the western corner of Kings County. The Valley samples, however, reflect the anomaly at New Idria most prominently.

Figure 7 shows the distribution of mercury in the Panoche samples. The dispersion trains in the alluvium from Panoche Creek and to a lesser extent from Cantua Creek are classic examples of dispersion from a mineralized area. The mineralization at New Idria is on the northeast flank of a large serpentine intrusion, which is the source for several other characteristic elements, such as nickel, chromium, cobalt, manganese, and iron.

Figure 8 shows the distribution of arsenic in the Valley samples. The Coast Ranges appear to contribute more arsenic to the sediments than the Sierra Nevada. Arsenic is often associated with sulfide mineralization, but the reasons for the patterns shown here are not known.

Figure 9 shows the distribution of arsenic in the Panoche samples. The distribution patterns are somewhat diffuse, but arsenic appears to be associated mostly with the alluvium of Panoche and Cantua Creeks. This suggests that the arsenic and mercury may be derived from a similar source.

Figure 10 shows the distribution of sulfur in the Panoche samples. Sulfur and selenium normally exhibit similar chemical behavior, and a comparison of the distribution of sulfur with that of selenium generally supports that observation. The most prominent concurrence of sulfur

with selenium is on the west side on the interfan area between Panoche and Cantua Creeks. A locale where there is no concurrence is near the southeast border adjacent to Fresno Slough. This was a former outwash channel for floodwaters from the Tulare Lake Basin. The sulfur pattern is apparently showing the trace of an old channel imprinted by sulfate-rich water.

POSSIBLE SOURCES

The distribution of mercury and arsenic on the alluvial fans of Panoche Creek and Cantua Creek suggests these elements were both derived at least in part from a mineralized zone. Mercury most certainly came from New Idria and perhaps arsenic did also. The dispersion patterns for selenium and sulfur, however, radiate from a more local source area in the vicinity of Monocline Ridge. The foothills in this area are composed of dipping sedimentary beds of marine and nonmarine origin that range from Pleistocene age near the Valley edge to Cretaceous age near the serpentine intrusion of New Idria. The strata at the Valley edge are in the Tulare Formation of Tertiary age.

Selenium has been found elsewhere in a number of different geologic materials including sulfide minerals such as pyrite in sedimentary rocks, black shales, phosphorites, coals, brimstones, sedimentary metal deposits, tuffaceous rocks, and mercury and antimony deposits (Lakin and Davidson, 1973). In the Northern Great Plains, seleniferous soils occur particularly over the Pierre Shale and the Niobrara Formation, both fine-grained marine sediments of Cretaceous age (Lakin, 1941). The cross-section of strata between the Valley edge and New Idria contains marine shales of both Tertiary and Cretaceous ages, and scattered measurements of selenium in these shales indicate values ranging from 4 to 10 ppm. Thus there is some evidence that selenium in the Valley sediments could be derived from one or more sedimentary strata that border the Valley. Certainly the proximity of the selenium anomaly to the locale of the mud-flow deposits that come from sedimentary rock materials lends some credence to that notion. That is hypothesis number one.

Recall that Figure 4 shows selenium to be higher on the west side of the Valley than on the east side. There are marine sediments all along the west side of the Valley that may be a potential host for selenium. There are isolated anomalies along the Valley margin, but the most prominent one is near Monocline Ridge. Is it only coincidence that the Monocline Ridge anomaly is close to the New Idria mineralization? The evidence for a halo effect is circumstantial at this time, but such an effect is offered as hypothesis number two.

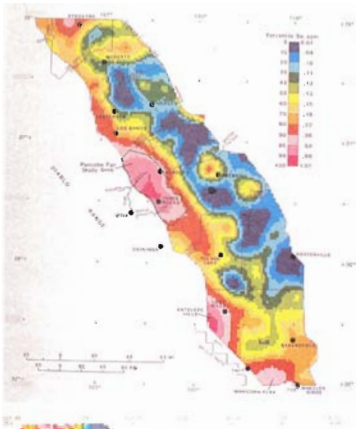


FIGURE 4

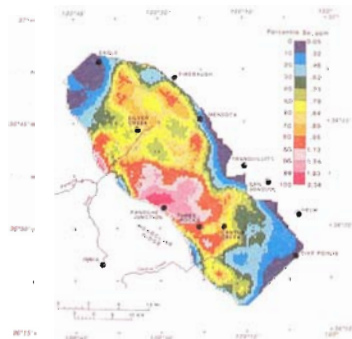


FIGURE 5

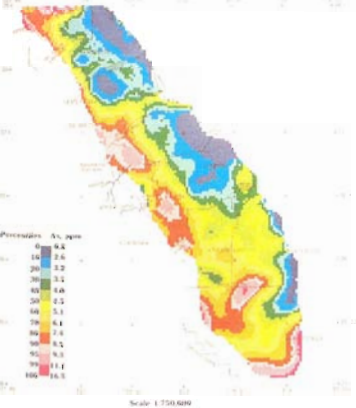


FIGURE 6

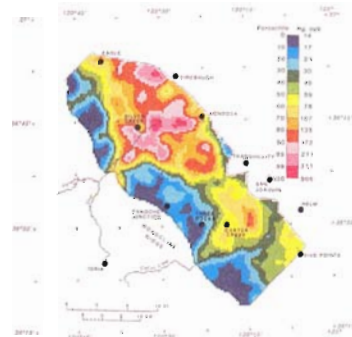


FIGURE 7

PLATE 1. Refer to Tidball et al., *Distribution of Selenium, Mercury, and Other Elements in Soils of the San Joaquin Valley and Parts of the San Luis Drain Service Area, California*, pages 71-82.

FIGURE 4. Map of total selenium at 0-12 inch (0-30 cm) depth in soils of the San Joaquin Valley, California. Color scale identifies percentiles of the frequency distribution of gridded values in each 2-km cell.

FIGURE 5. Map of total selenium at 66-72 inch (168-183 cm) depth in soils of the Panoche study area, California. Color scale identifies percentiles of the frequency distribution of gridded values in each 0.5-km cell.

FIGURE 6. Map of total mercury at 0-12 inch (0-20 cm) depth in soils of the San Joaquin Valley, California. Color scale identifies percentiles of the frequency distribution of gridded values in each 2-km cell.

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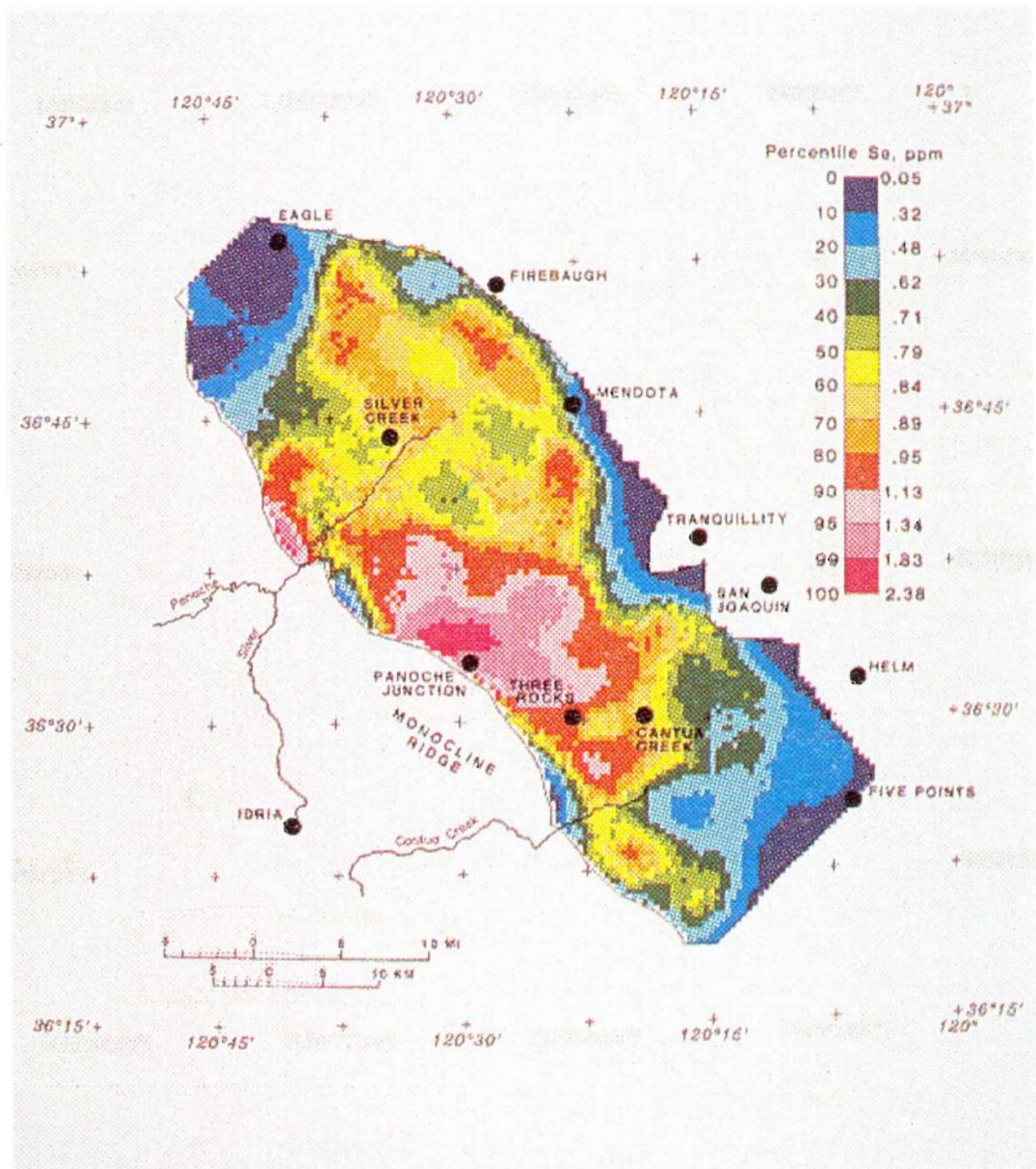
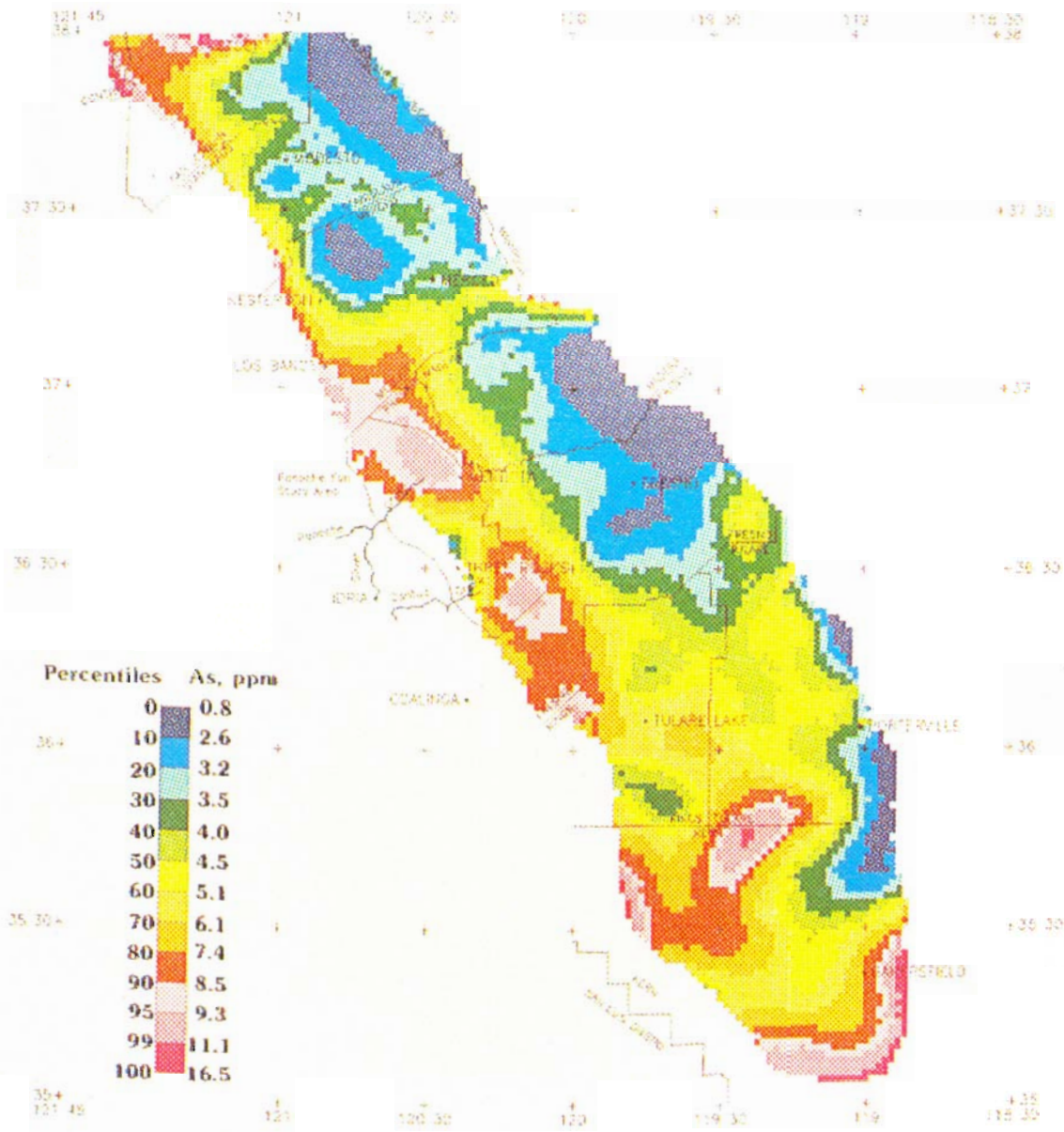


FIGURE 5

FIGURE 6



Scale 1:750,000

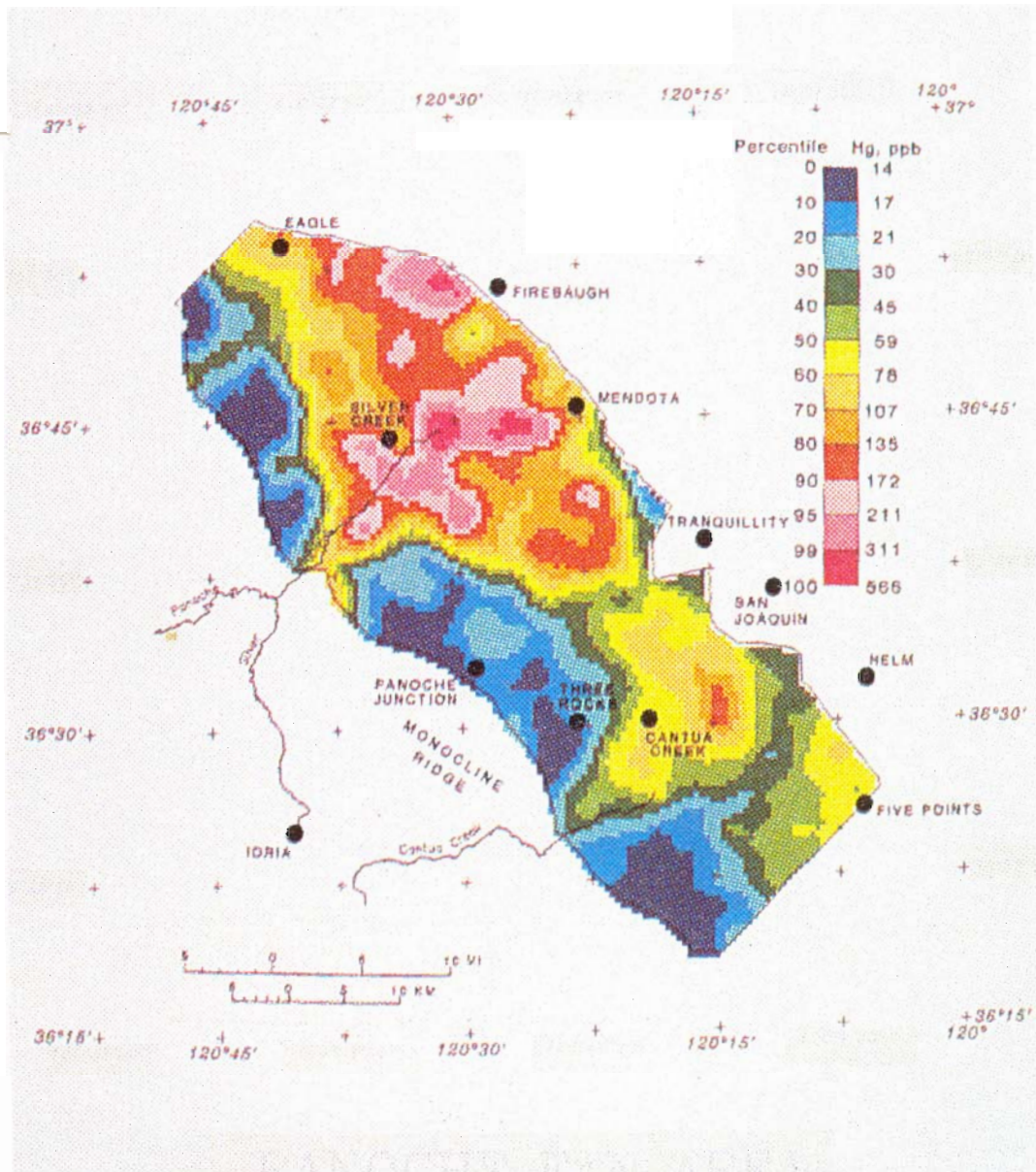


FIGURE 7

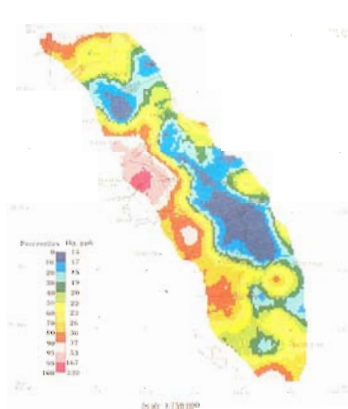


FIGURE 8

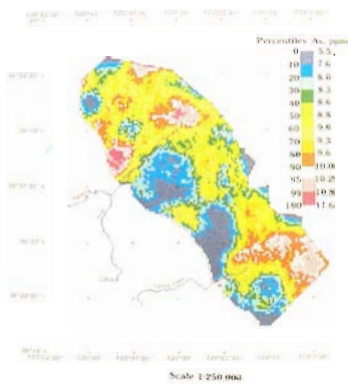


FIGURE 9

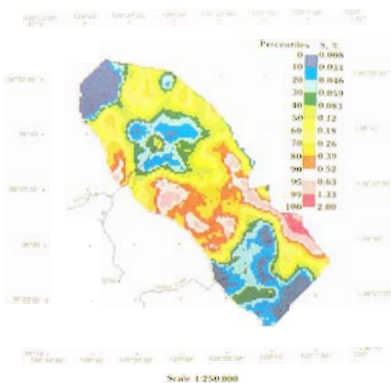


FIGURE 10

PLATE 2. Refer to Tidball et al., *Distribution of Selenium, Mercury, and Other Elements in Soils of the San Joaquin Valley and Parts of the San Luis Drain Service Area, California*, pages 71-82.

FIGURE 8. Map of total arsenic at 0-12 inch (0-20 cm) depth in soils of the San Joaquin Valley, California. Color scale identifies percentiles of the frequency distribution of gridded values in each 2-km cell.

FIGURE 9. Map of total arsenic at 66-72 inch (168-183 cm) depth in soils of the Panoche study area, California. Color scale identifies percentiles of the frequency distribution of gridded values in each 2-km cell.

FIGURE 10. Map of total sulfur at 66-72 inch (168-183 cm) depth in soils of the Panoche study area. Color scale identifies percentiles of the frequency distribution of gridded values in each 0.5-km cell.

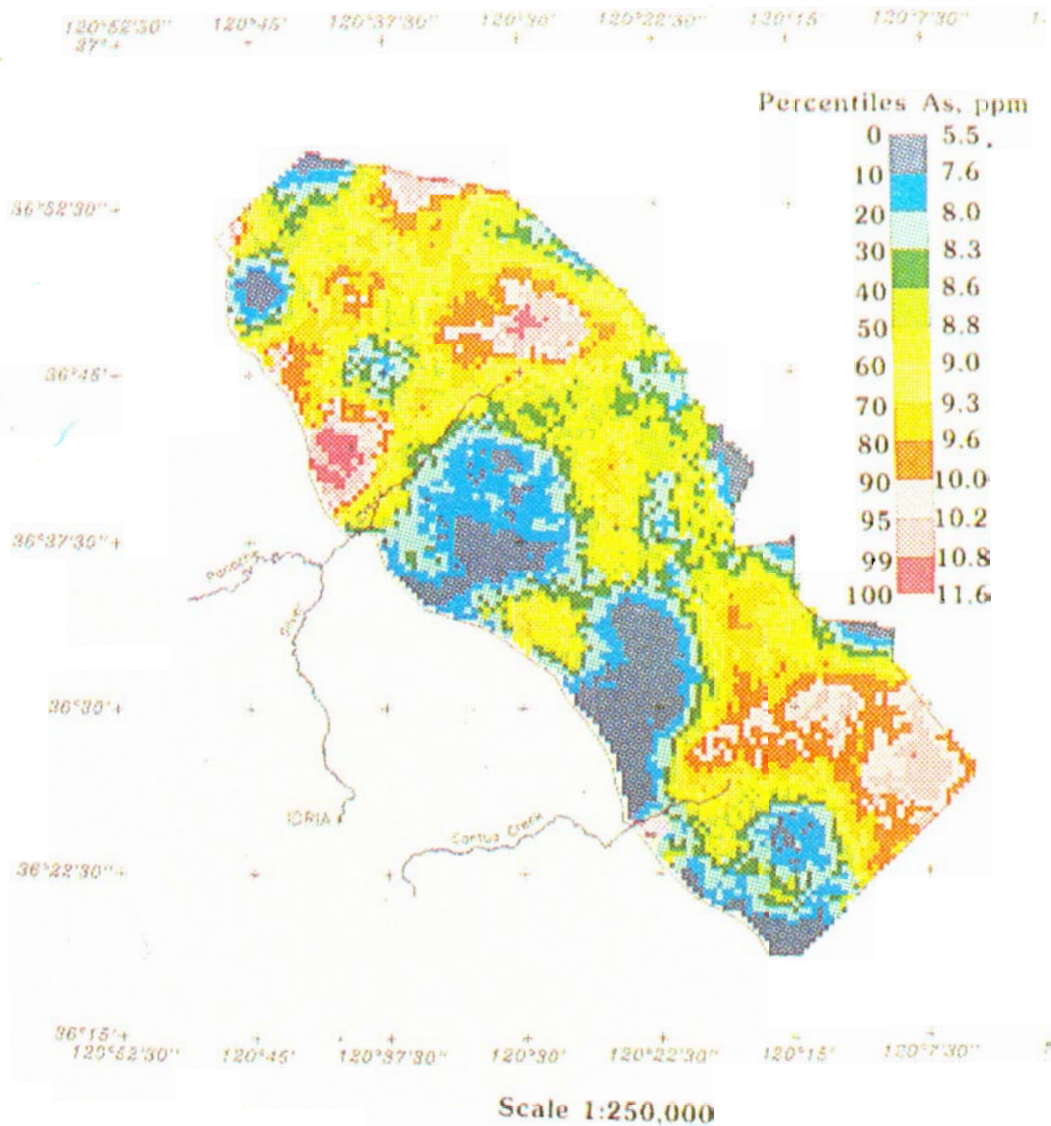


FIGURE 9

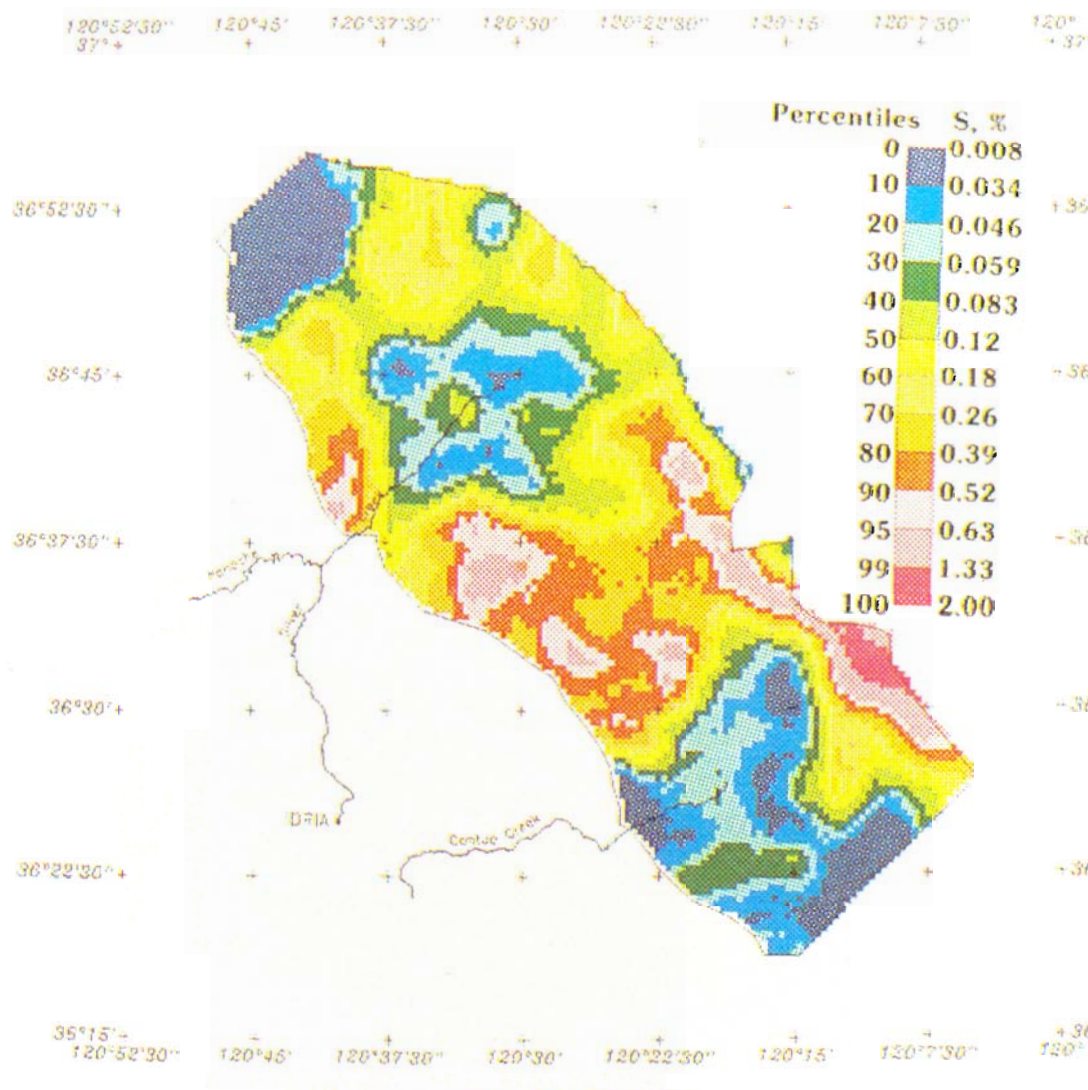


FIGURE 10

If we speculate that selenium was originally more generally dispersed in the several alluvial fans, it is troublesome that selenium occurs mainly in the interfan area and is not more widely dispersed over the alluvial fans (like mercury), as one might expect of sediments derived from the Silver Creek and Cantua Creek watersheds. This speculation would require that such dispersion does not appear because of a transport mechanism where selenium in the alluvium is carried in solution through to the water table and fails to appear in the surface sediments. The selenium in the mud-flow deposits would not have been leached and therefore appears as a lag deposit.

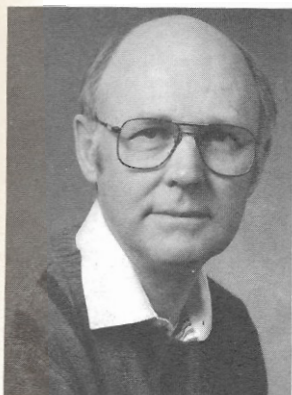
SELENIUM PROBLEMS LIKELY ELSEWHERE

Whatever the explanation may be, it is evident that selenium in the Panoche area is a natural geologic condition. The circumstances at Kesterson Reservoir were aggravated by human activity. The selenium occurrence in the Panoche area is not unique even in the San Joaquin Valley. The Antelope Hills area in western Kern County appears to offer a destiny similar to that of the Panoche area and Kesterson. Other problem areas are known in the central and northern Great Plains of the U.S. (Miller et al., 1981); Rosenfeld and Beath, 1964), as well as in various parts of the western U.S. (Harris and Morris, 1985). Even Marco Polo wrote in 1295 about animal diseases in western China that we now attribute to selenium toxicity (Rosenfeld and Beath, 1964). Although selenium is the current issue in the San Luis Drain service area, the larger concern is that of soil salinity. The San Luis Drain was an engineering solution for the removal of excess salts in the soils and groundwater, but it merely transferred salt from one problem area to another one.

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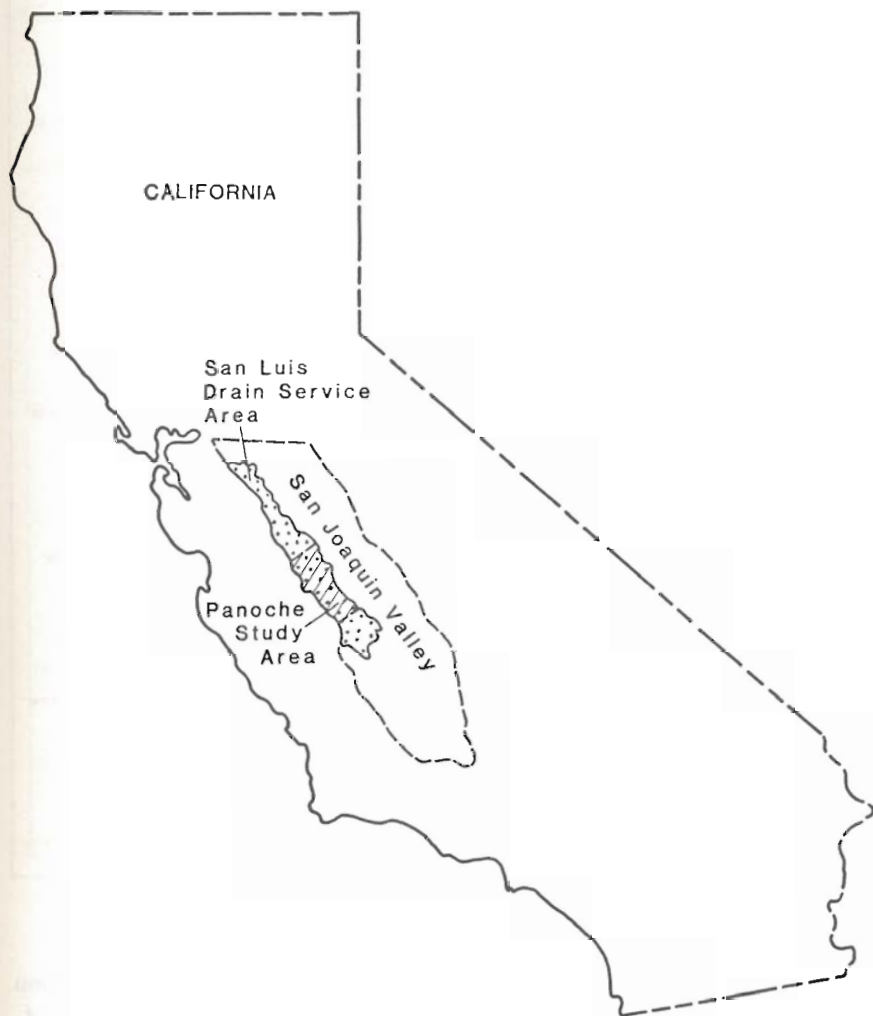
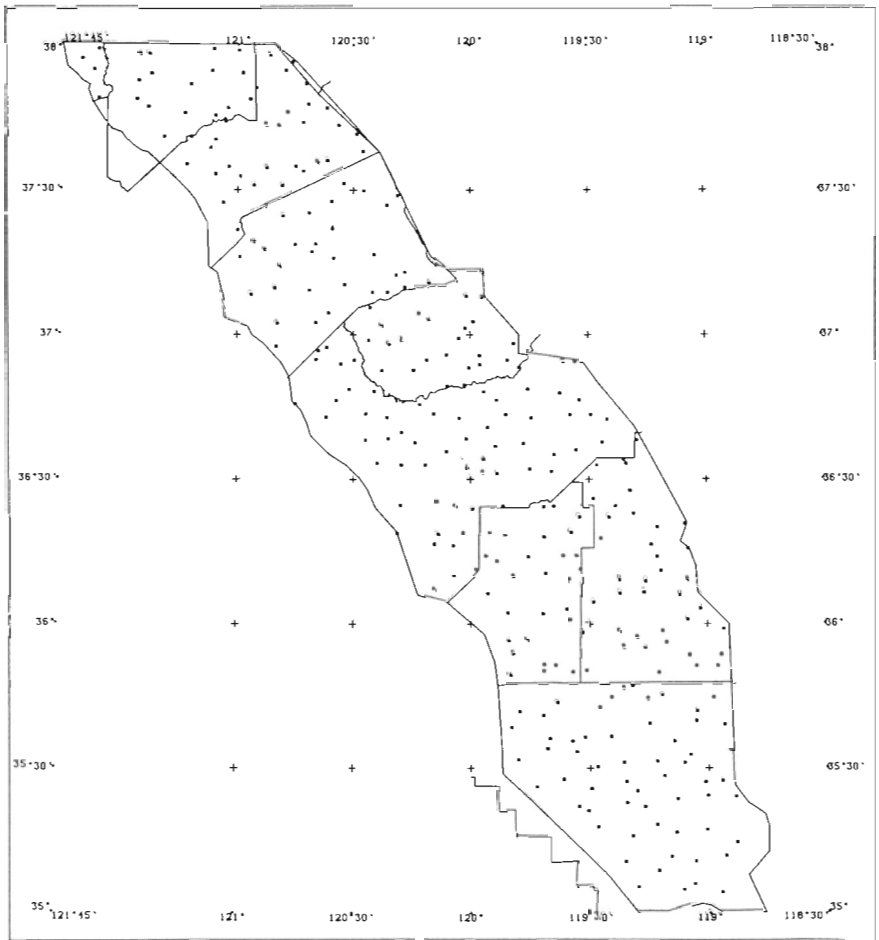


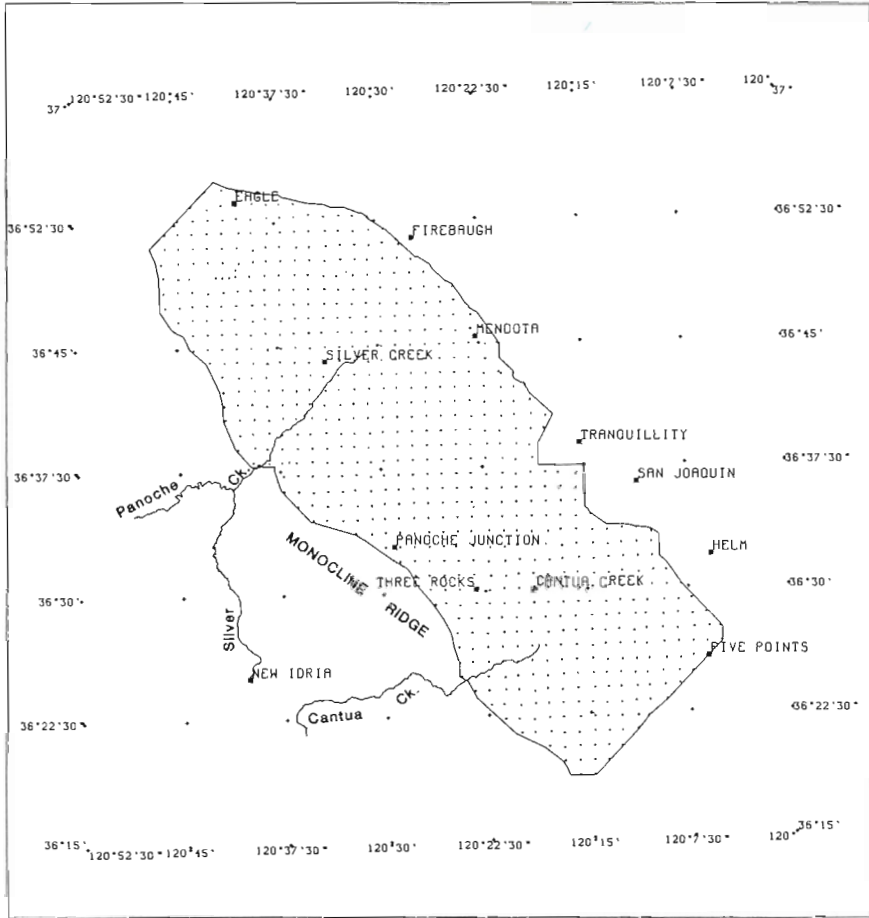
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RESULTS

The kriging algorithm has a smoothing effect on the data that tends to reduce the highest peaks but changes the median value very little. For example, the geometric mean for selenium in the Panoche area is 0.68 ppm and the median for the gridded values is 0.79 ppm. This does not detract from the value of the image map for illustrating the regional distribution of an element in the soils.

The distribution of selenium in the Valley samples is shown in Figure 4. The gridded values of selenium range from 0.07 to 1.07 ppm. Above average values occur on the west side of the Valley and below average values occur on the east side. This suggests that the Coast Ranges are a more significant source of selenium than is the Sierra Nevada. There are two areas with relatively high selenium values (90th percentile or above). One is within the delineated Panoche Fan study area in western Fresno County. The other is in western Kern County in the vicinity of the Antelope Hills. The highest measured concentrations of selenium found are 1.5 ppm in the Antelope Hills area and 4.5 ppm in the Panoche area. The geometric mean for selenium is 0.14 ppm in the Valley samples and 0.68 ppm in the Panoche area; these values can be compared with 0.25 ppm for 495 soils collected extensively throughout the western United States (Shacklette et al., 1974). The distribution of selenium in the Panoche study area is shown in Figure 5. When comparing Figure 4 with Figure 5, note that the colors of the two figures represent different ranges of selenium values: The upper 10 percent of the Valley samples (greater than 0.36 ppm) are nearly equivalent to the upper 90 percent of the Panoche samples. The two sample sets both confirm the selenium distribution in the Panoche area.

Figure 5 shows that the probable source area for the selenium is located between the two major alluvial fans of Panoche Creek and Cantua Creek. Therefore, sediments from within the Diablo Range are not a major source of selenium, or, if they are, that fact is masked by deposition of more recent but barren sediments. The interfan area, where selenium is

highest, borders on a locale known as Monocline Ridge. The local sediments consist of mud-flow deposits derived from the adjacent foothills, which consist mostly of marine and nonmarine sedimentary rocks of Tertiary age. A dispersion train grades downslope toward the Valley trough. Near the lower (east) part of the fan, the gradient reverses in scattered areas, which may indicate locales where shallow groundwater has carried selenium to the surface. At present we have no data on speciation of selenium, but it appears that selenium is mostly precipitated high on the fan and more commonly dissolved in the shallow groundwater near the Valley trough (Deveral et al., 1984). Perhaps selenium is slowly dissolved into the groundwater high on the fan and is moving down through the fan to emerge at the lower end.

Figure 6 shows the distribution of mercury in the Valley soils. As with selenium, the Coast Ranges provide more mercury-enriched sediments than does the Sierra Nevada. This is not unexpected because important mercury deposits such as the New Almaden Mine in Santa Clara County about 55 miles west of Los Banos and the New Idria Mine in San Benito County about 10 miles west of Monocline Ridge were, respectively, the number one and number two producers of mercury in North America (Bailey et al., 1973). There is also mercury mineralization in the Parkfield District at the western corner of Kings County. The Valley samples, however, reflect the anomaly at New Idria most prominently.

Figure 7 shows the distribution of mercury in the Panoche samples. The dispersion trains in the alluvium from Panoche Creek and to a lesser extent from Cantua Creek are classic examples of dispersion from a mineralized area. The mineralization at New Idria is on the northeast flank of a large serpentine intrusion, which is the source for several other characteristic elements, such as nickel, chromium, cobalt, manganese, and iron.

Figure 8 shows the distribution of arsenic in the Valley samples. The Coast Ranges appear to contribute more arsenic to the sediments than the Sierra Nevada. Arsenic is often associated with sulfide mineralization, but the reasons for the patterns shown here are not known.

Figure 9 shows the distribution of arsenic in the Panoche samples. The distribution patterns are somewhat diffuse, but arsenic appears to be associated mostly with the alluvium of Panoche and Cantua Creeks. This suggests that the arsenic and mercury may be derived from a similar source.

Figure 10 shows the distribution of sulfur in the Panoche samples. Sulfur and selenium normally exhibit similar chemical behavior, and a comparison of the distribution of sulfur with that of selenium generally supports that observation. The most prominent concurrence of sulfur

with selenium is on the west side on the interfan area between Panoche and Cantua Creeks. A locale where there is no concurrence is near the southeast border adjacent to Fresno Slough. This was a former outwash channel for floodwaters from the Tulare Lake Basin. The sulfur pattern is apparently showing the trace of an old channel imprinted by sulfate-rich water.

POSSIBLE SOURCES

The distribution of mercury and arsenic on the alluvial fans of Panoche Creek and Cantua Creek suggests these elements were both derived at least in part from a mineralized zone. Mercury most certainly came from New Idria and perhaps arsenic did also. The dispersion patterns for selenium and sulfur, however, radiate from a more local source area in the vicinity of Monocline Ridge. The foothills in this area are composed of dipping sedimentary beds of marine and nonmarine origin that range from Pleistocene age near the Valley edge to Cretaceous age near the serpentine intrusion of New Idria. The strata at the Valley edge are in the Tulare Formation of Tertiary age.

Selenium has been found elsewhere in a number of different geologic materials including sulfide minerals such as pyrite in sedimentary rocks, black shales, phosphorites, coals, brimstones, sedimentary metal deposits, tuffaceous rocks, and mercury and antimony deposits (Lakin and Davidson, 1973). In the Northern Great Plains, seleniferous soils occur particularly over the Pierre Shale and the Niobrara Formation, both fine-grained marine sediments of Cretaceous age (Lakin, 1941). The cross-section of strata between the Valley edge and New Idria contains marine shales of both Tertiary and Cretaceous ages, and scattered measurements of selenium in these shales indicate values ranging from 4 to 10 ppm. Thus there is some evidence that selenium in the Valley sediments could be derived from one or more sedimentary strata that border the Valley. Certainly the proximity of the selenium anomaly to the locale of the mud-flow deposits that come from sedimentary rock materials lends some credence to that notion. That is hypothesis number one.

Recall that Figure 4 shows selenium to be higher on the west side of the Valley than on the east side. There are marine sediments all along the west side of the Valley that may be a potential host for selenium. There are isolated anomalies along the Valley margin, but the most prominent one is near Monocline Ridge. Is it only coincidence that the Monocline Ridge anomaly is close to the New Idria mineralization? The evidence for a halo effect is circumstantial at this time, but such an effect is offered as hypothesis number two.

If we speculate that selenium was originally more generally dispersed in the several alluvial fans, it is troublesome that selenium occurs mainly in the interfan area and is not more widely dispersed over the alluvial fans (like mercury), as one might expect of sediments derived from the Silver Creek and Cantua Creek watersheds. This speculation would require that such dispersion does not appear because of a transport mechanism where selenium in the alluvium is carried in solution through to the water table and fails to appear in the surface sediments. The selenium in the mud-flow deposits would not have been leached and therefore appears as a lag deposit.

SELENIUM PROBLEMS LIKELY ELSEWHERE

Whatever the explanation may be, it is evident that selenium in the Panoche area is a natural geologic condition. The circumstances at Kesterson Reservoir were aggravated by human activity. The selenium occurrence in the Panoche area is not unique even in the San Joaquin Valley. The Antelope Hills area in western Kern County appears to offer a destiny similar to that of the Panoche area and Kesterson. Other problem areas are known in the central and northern Great Plains of the U.S. (Miller et al., 1981); Rosenfeld and Beath, 1964), as well as in various parts of the western U.S. (Harris and Morris, 1985). Even Marco Polo wrote in 1295 about animal diseases in western China that we now attribute to selenium toxicity (Rosenfeld and Beath, 1964). Although selenium is the current issue in the San Luis Drain service area, the larger concern is that of soil salinity. The San Luis Drain was an engineering solution for the removal of excess salts in the soils and groundwater, but it merely transferred salt from one problem area to another one.

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