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A regional soil and sediment geochemical study in northern California

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Abstract:

Regional-scale variations in soil geochemistry were investigated in a 20,000-km² study area in northern California that includes the western slope of the Sierra Nevada, the southern Sacramento Valley, and the northern Coast Ranges. Over 1,300 archival soil samples collected from the late 1970s to 1980 in El Dorado, Placer, Sutter, Sacramento, Yolo and Solano counties were analyzed for 42 elements by inductively coupled plasma-atomic emission spectrometry and inductively coupled plasma-mass spectrometry following a near-total dissolution. These data were supplemented by analysis of more than 500 stream-sediment samples from higher elevations in the Sierra Nevada from the same study site. The relatively high-density data (1 sample per 15 km² for much of the study area) allows the delineation of regional geochemical patterns and the identification of processes that produced these patterns. The geochemical results segregate broadly into distinct element groupings whose distribution reflects the interplay of geologic, hydrologic, geomorphic, and anthropogenic factors. One such group includes elements associated with mafic and ultramafic rocks including Cr, Ni, V, Co, Cu and Mg. Using Cr as an example, elevated concentrations occur in soils overlying ultramafic rocks in the foothills of the Sierra Nevada (median Cr = 160 mg/kg) as well as in the northern Coast Ranges. Low concentrations of these elements occur in soils located further upslope in the Sierra Nevada overlying Tertiary volcanic, metasedimentary and plutonic rocks (granodiorite and diorite). Eastern Sacramento Valley soil samples, defined as those located east of the Sacramento River, are lower in Cr (median Cr = 84 mg/kg), and are systematically lower in this suite compared to soils from the west side of the Sacramento Valley (median Cr = 130 mg/kg). A second group of elements showing a coherent pattern, including Ca, K, Sr and REE, is derived from relatively silicic rocks types. This group occurs at elevated concentrations in soils overlying volcanic and plutonic rocks at higher elevations in the Sierras (e.g. median La = 28 mg/kg) and the east side of the Sacramento Valley (median 20 mg/kg) compared to soils overlying ultramafic rocks in the Sierra Nevada foothills (median 15 mg/kg) and the western Sacramento Valley (median 14 mg/kg). The segregation of soil geochemistry into distinctive groupings across the Sacramento River arises from the former presence of a natural levee (now replaced by an artificial one) along the banks of the river. This levee has been a barrier to sediment transport. Sediment transport to the Valley by glacial outwash from higher elevations in the Sierra Nevada and, more recently, debris from placer Au mining has dominated sediment transport to the eastern Valley. High content of mafic elements (and low content of silicic elements) in surface soil in the west side of the valley is due to a combination of lack of silicic source rocks, transport of ultramafic rock

material from the Coast Ranges, and input of sediment from the late Mesozoic Great Valley Group, which is itself enriched in mafic elements. A third group of elements (Zn, Cd, As and Cu) reflect the impact of mining activity. Soil with elevated content of these elements occurs along the Sacramento River in both levee and adjacent flood basin settings. It is interpreted that transport of sediment down the Sacramento River from massive sulfide mines in the Klamath Mountains to the north has caused this pattern. The Pb, and to some extent Zn, distribution patterns are strongly impacted by anthropogenic inputs. Elevated Pb content is localized in major cities and along major highways due to inputs from leaded gasoline. Zinc has a similar distribution pattern but the source is tire wear.

1. Introduction

1.1. Overview

In 2004, the U.S. Geological Survey (USGS), the Geological Survey of Canada, and the Mexican Geological Survey (Servicio Geológico Mexicano) initiated pilot studies in preparation for a planned soil geochemical survey of North America (the North American Soil Geochemical Landscapes Project). These pilot studies were conducted at both a continental scale and a regional scale. Results of the continental-scale pilot studies are discussed elsewhere in this volume (Chiprés et al., 2009; Eberl and Smith, 2009; Garrett, 2009; Griffin et al., 2009; Woodruff et al., 2009). The regional-scale pilot study, which is the focus of this paper, was designed to represent more detailed, higher-resolution geochemical investigations in areas of interest identified from the low-sample-density continental-scale survey.

A 20,000-km² area of northern California (Fig. 1) was chosen for this regional-scale pilot study based on a number of considerations. Soils of the area contain elevated amounts of Cr and Ni in relation to the average content of soils from the conterminous U.S. (Shacklette and Boerngen, 1984; Gustavsson et al., 2001). The area also presents a wide variety of topographic, climatic, and ecoregion zones and a wide diversity of geologic units and soil types. The area supports diverse land use types including grazing and agricultural lands in the Sacramento Valley, forested areas in portions of the Sierra Nevada Mountains, and the urban/suburban centers of Sacramento, Davis, Stockton, and Lodi, among others. Also of interest is potential impact on soil geochemistry from hard rock and placer Au mining, which occurred in the foothills of the Sierra Nevada (Ashley, 2002; Alpers et al., 2005); Hg mining in the Coast Ranges (Rytuba, 1993, 2000; Rytuba and Enderlin, 1999; Domagalski et al., 2004) and base metal sulfide deposits in the Klamath Mountains to the north (Alpers et al., 2003) (Fig. 1).

This paper introduces the California pilot study and focuses, in particular, on the regional-scale distribution of selected major and trace elements in soils and stream sediments and the influence of geology, geomorphology and anthropogenic activities on this distribution.

Other papers in this volume focus on different topics addressed in the regional-scale study. McCafferty and Van Gosen (2009) describe airborne and radiometric anomaly signatures of ultramafic rocks in the study area. They describe how these tools can identify previously unrecognized serpentinite bodies. Morrison et al. (2009) focus on the transport and fate of the elements Cr and Ni derived from these ultramafic rocks. Wanty et al. (2009) discuss possible relationships between soil geochemistry and the distribution and origins of constituents in regional groundwater. Holloway et al. (2009) focus on Hg geochemistry in a portion of the study area impacted by past Hg mining.

1.2 Study Area

Much of the regional-scale pilot study area is located in the drainage basin of the Sacramento River, which flows near the center of the Sacramento Valley and is the major freshwater source to San Francisco Bay. The Sacramento Valley, the northern one-third of the Great Valley or Central Valley of California (Domagalski et al., 2000), has been transformed over the past 150 a of human settlement primarily through urbanization, agriculture, and flood control activities (Kelley, 1998). The Central Valley is one of the great agricultural regions of the world (Johnson et al., 1993) and has rapidly expanding urban and suburban population centers. The valley's importance to California and the nation is one of the reasons that the authors emphasize the processes controlling its soil composition in the study.

Headwater contributions to Sacramento River sediments include the Sierra Nevada to the east, the Coast Ranges to the west, and the Cascades, Klamath Mountains and Modoc Plateau to the north (Domagalski et al., 1998) with the dominant tributaries entering from the Klamath Mountains and Sierra Nevada. Dominant tributaries from the Sierra Nevada include the Feather, American, Cosumnes and Mokelumne Rivers and major tributaries on the western side of the valley are Cache and Putah Creeks. Cropland, pasture, and urban settings dominate land use in the Sacramento Valley portion of the study area, whereas the Sierra Nevada is heavily forested and the Coast Ranges are characterized by forest and rangeland.

The Sacramento Valley is a tectonically controlled basin bounded on the east by the Sierra Nevada and on the west by the Coast Ranges. The higher elevations of the Sierra Nevada are composed of late Mesozoic plutonic granitic rocks (largely granodiorite and tonalite) of the Sierran Batholith (Fig. 2). The steepness of the range on its eastern flank is due to uplift along normal faults that have tilted the range westward resulting in a gentle western slope. The northwestern foothills of the Sierra Nevada contain the western metamorphic belt, which is comprised of a series of accreted terranes of Paleozoic and Mesozoic age. Faults between some of these terranes host ultramafic rocks (serpentinite) (Harden, 2004).

The Coast Ranges formed by subduction and accretion along the continental margin. In the study area, the rocks include the Franciscan Complex and the Great Valley Group. The Franciscan Complex consists of fragments of oceanic crust (including serpentinite) from the Farallon Plate, which accreted to North America during Mesozoic time. The Franciscan Complex extends eastward to the Coast Range Fault, which separates Franciscan rocks from Great Valley Group rocks. The Great Valley Group comprises sandstone, shale and conglomerate formed during Jurassic, Cretaceous, and earliest Cenozoic time in an oceanic forearc sedimentary basin with approximately the same borders as the modern Great Valley. Detailed studies (Ingersoll, 1983; Linn et al., 1992; Degraaff-Surpless et al., 2002; Surpless et al., 2006) have shown that the sources for Great Valley sediments included volcanic materials from now eroded volcanic rocks to the east, evolving over time to materials eroded from Sierran granitic plutons. Quaternary uplift of the Coast Ranges led to down-cutting of Pliocene sediments and deposition of younger alluvium. The Holocene alluvial fans of Cache and Putah creeks are composed of materials derived from reworking of the Tehama Formation and Great Valley Group leading to extensive distribution of these sediments on the western flank of the Sacramento Valley. Additional inputs were from the Klamath Mountains to the north (Ojakangas, 1968; Ingersoll, 1983). The surficial sediments on the eastern side of the Great Valley consist of recent and Pleistocene alluvium derived from the Sierra Nevada. Pulses of outwash from repeated Sierra Nevada glaciations are an important component of valley sediments (James, 2003). Between glacial pulses, detritus from metamorphic rocks in the Sierra Nevada foothills became a larger component of alluvial materials entering the Great Valley (Harden, 1988). Large alluvial fans of the Riverbank Formation of Pleistocene age and Holocene alluvial and basin deposits cover much of the eastern Sacramento Valley portion of the study area (Helley and Harwood, 1985).

Olmsted and Davis (1961) mapped a series of geomorphic units in the Sacramento Valley (Fig. 3). Natural levees and flood basins that are comprised of materials transported down the Sacramento River during flood episodes occur along the Sacramento River. Low alluvial fans occur on either side of the valley and represent materials transported from adjacent highlands during the Holocene Epoch. Dissected uplands on either side of the valley also represent material transported from adjacent uplands, but these uplands in the foothills areas are older Pleistocene alluvial units formed by uplift of the Sierra Nevada and Coast Ranges over the last several Ma (Harden, 1988; White et al., 1996).

Many of the drainages to the Sacramento Valley have been impacted by historical mining resulting in the mobilization of trace metals including Hg, As, Zn, and Cu (Domagalski, 2001). Figure 1 shows the extent of mining within and adjacent to the study area. Mercury mining has had a significant impact on the headwaters of Cache Creek and Putah Creek to the west of the Sacramento Valley (Domagalski et al., 2004; Holloway et al., 2009). Mercury recovered from Coast Range mines was employed in Au recovery from hard rock (lode) Au mines of the ‘Mother Lode Belt’ as well as placer Au mining activities in the Sierra Nevada (Alpers et al., 2005). The lode Au ore contained accessory As-rich pyrite and arsenopyrite (Ashley, 2002). The headwaters of the Sacramento River were impacted by the West Shasta Mining district, which was mined for Cu, Zn, Ag and Au (Nordstrom and Alpers, 1999; Alpers et al., 2003).

The Sacramento Valley has a Mediterranean climate; hot and dry in the summer and cool and wet in the winter and spring. Predominant surface wind patterns in the summer are northerly. Climate in the Sierra Nevada varies with elevation from Mediterranean in the foothills to cool summers and snowy winters at higher elevation.

2. Methodology

2.1. Sample collection

The study utilizes archived samples supplemented by newly collected material. The basic sample set consists of more than 1300 soil samples collected on a 1-km grid spacing in the 1:250,000-scale Sacramento Quadrangle during the late 1970s and early 1980s by the U.S. Department of Energy’s National Uranium Resource Evaluation Hydrogeochemical and Stream Sediment Reconnaissance (NURE HSSR) Program (Smith, 1997) (Fig. 4). At each site, the top 5 cm of plant material and soil were removed and the sample was collected with a hand spade over a

depth interval of approximately 10-15 cm. Each sample represents a composite from at least 10 locations spaced at least 3 m apart. The soil samples were sieved into 2 fractions; 18–40 mesh (400-1000 μm) and <40-mesh (Price and Jones, 1979). In addition, the sample set includes more than 500 stream-sediment samples collected as part of the same sampling program (Fig. 4). These samples were collected from the active part of the stream and sieved on site to <40 mesh (<400 μm) (Price and Jones, 1979). Splits of the sieved soil and sediment samples were stored at the U.S. Geological Survey in Denver, Colorado. For this study, all the NURE HSSR samples collected in the Sacramento Quadrangle were chemically analyzed as described in the next section.

The locations of the soil and sediment samples were documented on topographic maps and the sample sites were photographed for reference. Most of the stream-sediment samples were collected at higher elevations in the Sierra Nevada whereas fewer were collected from the Sierra Nevada foothills (Fig. 4). This overall set of approximately 1800 soil and sediment samples represents a density of about 1 site per 15 km^2 in the 20,000 km^2 study area.

Archived samples from the El Dorado National Forest (Fig. 4) were also analyzed. Soil samples in the El Dorado National Forest were obtained from the U.S. Forest Service, and data presented here represents samples integrated over the A horizon.

New soil samples were collected from the Coast Ranges and Sierra Nevada foothills, along Cache Creek on the western side of the valley, and within the Sacramento Valley during the course of this study. Holloway et al. (2009) and Morrison et al. (2009) describe the locations and analyses of these samples. Fourteen rock samples from the Great Valley Group were collected from outcrops along Cache Creek. This group forms the western boundary of the Sacramento Valley and as such, is a potential source of sediment to the valley. Additional geochemical data for the Great Valley Group rocks from the study area were taken from Linn et al. (1992). Morrison et al. (2009) describe a comparison of the effect on chemical analyses of variations of sample size fractions between data sets.

2.2. Chemical analyses

The analytical methodology used for the analyses of both the new and archived samples is essentially identical to that described by Smith et al. (2005, 2009). Forty-two major, minor and trace elements were determined by a 4-acid digestion (HCl , HNO_3 , HClO_4 and HF), followed by

a combination of inductively coupled plasma—atomic emission spectrometry (ICP—AES) and inductively coupled plasma—mass spectrometry (ICP—MS) (Briggs and Meier, 2002). The samples were analyzed by the same analytical laboratory as those reported by Smith et al. (2009) who also detail the quality-control methodology and analytical precision for all these analyses. As discussed by Morrison et al. (2009), the 4-acid dissolution procedure employed in this study does not completely dissolve certain refractory minerals, notably chromite (FeCr_2O_4). Thus, the Cr values reported in this paper do not represent the total Cr content of the samples. Nonetheless, the spatial patterns exhibited by Cr are not substantially different when compared to those determined by a Li metaborate fusion that totally dissolves all Cr-bearing phases. ArcMap™ software was used for spatial analysis of the data.

3. Results

The complete analytical results from this study are available on-line (Morrison et al., 2008). An exception is the rock chemistry data from the Great Valley Sequence. These results are available as Supplementary Table 1 in the on-online version of this report. Table 1 is a summary of soil geochemical data from this study with a comparison to continental-scale data sets from North America and Europe. The European data consists of analyses from 852 topsoil samples (upper 0–25 cm) from 26 European countries (Salminen et al., 2005). The North American data set is comprised of 1323 samples collected from a depth of approximately 20 cm primarily from non-agricultural soils across the conterminous U.S.A. (Shacklette and Boerngen, 1984; Gustavsson et al., 2001). For most elements, median values of chemical data from the 3 soil surveys are within a factor of two of each other and many are much closer than that. The elements that agree within less than a factor of two include Al, As, Be, Ce, Cs, Ga, In, K, La, Li, Mo, P, Pb, Sb, Se, Th, Ti, U, Y and Zn. These elemental similarities between continental-scale data from Europe and the conterminous US and regional-scale data from California may reflect the fact that the geology of the study area is rather diverse and incorporates a range of terrestrial and marine rock types. However, several elements stand out in the California data. In particular, a subset of the elements are enriched by approximately a factor of two or more in the NURE soil samples compared to the continental US data and in most cases, the European data as well. This subset includes Co, Cr, Cu, Fe, Mg, Mn, Ni, Sc, Te and V (Cr and Fe are slightly less than a factor of two). These elements are associated with mafic and ultramafic rocks. Sodium is higher in the California data

set, but does not belong to this ultramafic suite. Rubidium, Bi, Cs, Sn and W are depleted in the California data set by a factor of about 3 compared to the European data.

The statistical summary in Table 1 provides a cursory look at the data from the California study area. Much more insight comes from analyzing spatial patterns of element distribution as shown by plotting the data geographically. This can add useful insights, but a more efficient method of comparison takes advantage of the fact that the study area is characterized by a range of rock types from ultramafic to silicic (Fig. 2), and the Sacramento Valley portion is also characterized by a range of geomorphic regions (Fig. 3). These geomorphic regions may, as noted above, receive input from distinctive source areas. In this paper, the following approach to the spatial data analysis has been adopted: Sacramento Valley data are grouped by the geomorphic units shown in Figure 3. Samples residing in the Sierra Nevada are characterized by a combination of geology and spatial position (effectively elevation) in the mountains. This hybrid approach allows comparison between potential source areas in the highlands and sediment accumulation in the valley.

In this paper, two approaches are used to portray the geochemical data. One is to show the data as a series of box plots (Figs. 5-8). The other is to plot the geochemical data in plan view maps (Fig. 9). The choice of the box plot categories requires explanation. For Sacramento Valley samples, the box plot classes were based on geomorphic units (Fig. 3) because these classes reflect sediment sources to the valley as explained previously. For samples from the Sierra Nevada, the classes are based primarily on sample location from low to high elevation. All data are from soil samples except as noted. Starting with the west, the box plot classes represent data from the following sources:

Sacramento Valley Samples (from west to east — Italicized terms are those shown in Figure 3; number of samples in each class indicated in parentheses):

1. *Low hills and dissected alluvial uplands*, west side of the Sacramento Valley (38)
2. *Low alluvial plains and fans*, west side of the valley (166)
3. *Flood basins*, west side of the Sacramento River (61)
4. *Sacramento River flood plains and natural levees* (33)
5. *Flood basins*, east side of the Sacramento River (40)

6. *Feather River flood plains and natural levees* (22)
7. *Low alluvial plains and fans, east side of the valley* (236)
8. Dissected *alluvial uplands, east side of the valley* (101)

Sierra Nevada Samples (in approximate order of increasing elevation):

9. Soil associated with (overlying and within 1 km of the edge of) ultramafic rocks of the Sierra Nevada foothills (34)
10. Soil in the Sierra Nevada not associated with ultramafic rocks (452)
11. Stream sediments from the Sierra Nevada (512)
12. Soil from the El Dorado Forest (from higher elevations in the Sierra Nevada) (50)

Soils and sediments derived from rocks of the Great Valley Group in the Coast Range are potential source materials for western Sacramento Valley alluvium; whereas, material derived from rocks of the Sierra Nevada are potential sources for alluvium on the east side of the valley. The data from the Sierra Nevada are divided into 4 broad classes; soil forming over and near (within 1 km) of mapped ultramafic rock, soil not associated with ultramafic rock, stream sediment samples, and soil from the El Dorado National Forest. The non-ultramafic soils are derived from both Paleozoic marine and Mesozoic granitic rocks (Fig. 4). Stream-sediment samples located at higher elevations of the Sierra Nevada are located over Paleozoic marine, plutonic and Tertiary volcanic rocks in sub-equal numbers, and soil within the El Dorado National Forest is derived largely from plutonic rocks.

The sample groups defined above were used to generate the box plots (Figs 5-8). The individual boxes represent the 12 subsets of the data defined above. They are arranged from west to east on the figures. The median concentration for each sample subset is shown as a horizontal bar and the mean by a dashed line within each box. The top and bottom of each box represent the 75th and 25th percentile, respectively. For each sample population, the whiskers symbolize the 10th and 90th percentiles, and the large dots represent the 5th and 95th percentiles.

3.1. *Spatial patterns of soil chemistry--major elements*

Soil and stream-sediment geochemical results show distinct spatial trends for major elements across the study area as shown by the box plots of Figures 5-8 and the geochemical maps of Figure 9. For example, in Figure 9a, it is visually apparent that Mg in soil and stream sediment is

high in association with ultramafic rocks for some areas in the western foothills of the Sierra Nevada and in the western Sacramento Valley.

Magnesium concentrations in soils located within 1 km of mapped ultramafic rocks in the foothills of the Sierra Nevada (Fig. 5b) are relatively high (median 0.94%) compared to the continental U.S.A. and European data (median for each 0.5 %, Table 1). Stream sediments in the higher elevations of the Sierra Nevada have even higher Mg concentrations (median 1.4%). This result is surprising because the ultramafic rocks might be expected to be higher in Mg than the plutons. This discrepancy may be a result of the 1-km buffer applied to the ultramafic rocks, which resulted in selecting some soil samples not derived from the ultramafic rock type (see also the discussion of Ca data below).

In the eastern Sacramento Valley, Mg content is elevated in soils adjacent to the Calaveras, Cosumnes, American and Feather Rivers (Fig. 9a), which all have ultramafic sources near their headwaters. Figures 9a and 5b also show elevated Mg in the western Sacramento valley. The median Mg concentration is 1.4 wt. % for all samples west of the Sacramento River. The median for all samples between the Sacramento River and the eastern edge of the Quaternary basin fill (including all geomorphic units on the east side of the Sacramento Valley) is 0.89 wt % and the overall median for the entire NURE soil data set is 1.03 wt % (Table 1). High Mg contents are prominent in and adjacent to the Sacramento River both in levee/flood plain (median is 1.65 wt %), and flood basin settings both west (median 1.73 wt %) and east (median 1.47 wt %) of the river. Analyses from low alluvial plain samples to the west of the river have a median Mg content of 1.31 wt %, which contrasts with substantially lower Mg contents for samples east of the river where flood plains contain 0.91 wt % Mg, low alluvial plains 0.79 wt % Mg, and dissected uplands 0.59 wt % Mg. Rock samples from the Great Valley Group (Supplementary Table 1) (1.76 wt %) are distinctly elevated in Mg compared to adjacent western Sacramento Valley soils (except for flood basin soils). The median value of Mg in soils spatially associated with ultramafic rocks (0.93 wt %) is higher than the eastern Sacramento Valley soil down slope (with the exception of eastern flood basin samples), but has a broad range extending to nearly 3 wt %. Soil and stream-sediment samples located east of the metamorphic belt are, on average, similar to or even higher in Mg than soil in and near mapped ultramafic rocks; for example, stream sediments have a median of 1.44 wt %.

Calcium content of Sacramento Valley soils shows a pattern essentially opposite to that of Mg. Calcium is more concentrated in the eastern valley (median 2.04 wt %) than in the foothills soil overlying ultramafic rocks or in the western valley (1.23 and 1.05 wt %, respectively; Fig. 9b). Figure 5c shows soils from all 3 geomorphic units on the west of the Sacramento River have lower Ca contents (range of medians 0.99-1.33 wt %) than all Sacramento Valley units to the east of the river (range of medians 1.65-2.32 wt %). As expected from their geology, soil samples associated with ultramafic rocks in the Sierra Nevada Foothills have a comparatively low Ca content (1.23 wt %), although the large range suggests potential admixture of non-ultramafic soil samples to this group. High Ca contents occur in stream sediments from upslope in the Sierra Nevada (2.34 wt %), presumably reflecting the composition of rocks weathering from higher elevation locations.

A west-to-east differentiation occurs with several other elements as well. Figure 5a illustrates that Al distribution in Sacramento Valley soil samples is approximately symmetrical about the Sacramento River. The lowest Al concentration occurs in the low alluvial hills on the west side of the valley (median 6.0 wt %). The median Al concentration in Great Valley Group rocks is 7.5 wt %, which is higher than valley alluvial soils. Samples from the levee deposits of the Sacramento River are lower in Al content (median 7.2 wt %) than soil from flood basins on either side of the river (median for both, 7.8 wt %). Soils and stream sediments from the Sierra Nevada tend to be elevated in Al compared to valley soils. For example, soils in the Sierra Nevada have a median value of 10.1 wt %; however, the median Al-content for all NURE soil samples is 7.5 wt %. Potential source materials in the Sierra Nevada, with the exception of El Dorado National Forest A-horizon soils, are all elevated in Al compared to valley soils and rocks from the Great Valley Group. This observation suggests that soil derived from plutonic rocks of the Sierra that underlie the El Dorado forest soils may be a significant source of material to the valley.

Potassium does not vary dramatically across the sample transect (Fig. 5d). Median values for all data groupings range from 1.1 to 1.4 wt % K. The highest values occur in low alluvial plain samples from the west side of the Sacramento Valley (1.4 wt %) and the lowest values occur in flood basins on the east side of the Sacramento Valley (1.07 wt %) and soil associated with ultramafic rock (1.1 wt %). The median for Great Valley rocks falls in this same range. Sodium is conspicuously higher in Great Valley rocks (2.1 wt %) compared to the other data sets

and is elevated in low alluvial plains from the west Sacramento Valley (1.7 wt %) compared to all other soil samples. The marine origin of the Great Valley rocks probably explains their elevated Na content and sediments derived from these high-Na rocks are a likely component of the high-Na soil in the western valley. Sodium concentrations in stream-sediment samples from higher elevations in the Sierra Nevada (1.6 wt %) are similar to eastern Sacramento Valley soil samples that range between 1.3 and 1.6 wt %.

In summary, higher Mg and Na concentrations in soil characterize the western Sacramento Valley compared to the eastern valley. These data indicate a more mafic and marine source for the western valley soils. Marine rocks of the Great Valley Group are a likely component of these western valley soils. In contrast, eastern valley soil composition is characterized by higher Ca. These contrasting west to east relationships are illustrated in Online Figure 1, which is a color plot of the ratio of Mg/Ca. This ratio is systematically higher in the western Sacramento Valley (0.65-51.1) than the eastern valley (0.05-0.65). The eastern valley soil is similar to stream sediment and soil from higher elevations in the Sierra.

An overall tendency exhibited for all major elements is that lower concentrations occur in older alluvium comprised of the dissected uplands (data groupings 1 and 8) on both the west and east sides of the valley, compared to younger alluvium (data groupings 2 and 7). This trend occurs for Al, Mg, K and Na on both sides of the valley, but only on the eastern side for Ca.

3.2. Spatial patterns of soil chemistry -- minor elements

Minor element box plots are grouped by those that are typically enriched in mafic or ultramafic rocks (Fig. 6), those that tend to be enriched in more silicic or intermediate rock types (Fig. 7), and a group of elements that are associated with the specific types of mineralization occurring in the Sacramento Valley drainage basin (Fig. 8). Chromium, Ni, and Co are enriched in mafic rock types and, therefore, exhibit conspicuously high values in soil overlying and adjacent to ultramafic rock bodies (Fig. 6). The highest median values for both Cr (160 mg/kg), and Co (32 mg/kg) occur in these ultramafic soils. For Ni, the median value of 93 mg/kg in ultramafic-associated soil is lower than flood basin (147 mg/kg) and alluvial plain samples (130 mg/kg) from the west side of the valley. However, the range of Ni concentrations is much higher in ultramafic-associated soil than soil from other settings. Like Mg, which also is enriched in mafic rocks, Ni, Cr and Co are more concentrated in soil and stream sediment on the west side of the

Sacramento River than on the east side. Analogous to the trend recognized in the major elements, these minor elements have lower concentrations in older dissected upland soil (data categories 1 and 8) than in adjacent younger alluvium (data categories 2 and 7). This pattern occurs on both sides of the valley for Ni and Cr, but only on the west side for Co. Spatial distribution patterns for V and Sc (not plotted) are similar to those for Ni, Cr, and Co.

Elements that typically are higher in silicic and intermediate rocks types than in ultramafic rocks include La, Sr, Li, and Pb. Lanthanum content is distinctly higher on the east side of the Sacramento River than the west side (Fig. 7a). This includes samples from both the eastern Sacramento Valley and the Sierra Nevada. The highest median La concentration occurs in soil and stream sediment from the Sierra Nevada sample sets exclusive of ultramafic-associated soil (data categories 10, 11 and 12). Soil associated with ultramafic rock in the Sierra Nevada Foothills (median 15 mg/kg) has approximately the same content of La as soil from the west Sacramento Valley (median 14 mg/kg) and Great Valley Group rock samples (median 16 mg/kg – data from Supplementary Table 1). The overall trends for Ce (not plotted) are similar to those for La.

The pattern for Sr across the study area is similar to that for La in that soil and stream sediment from the east side of the Sacramento Valley have distinctly higher median Sr concentrations than samples from west of the Sacramento River (Fig. 7b). Also similar to La, soil samples spatially associated with ultramafic rocks are lower in Sr than eastern Sacramento Valley soils. Strontium in soil associated with ultramafic rocks also has comparable median values to western Sacramento Valley soil samples. Strontium differs from La in that Sierra Nevada soil samples, not including stream sediment data (data category 11), have lower Sr concentrations than eastern Sacramento Valley soils located further down slope. In this regard, the pattern of Sr distribution is similar to that of Ca described above. This similarity is not unexpected. Strontium is known to substitute for Ca in minerals such as feldspars and carbonates (Fig. 5c).

A prominent enrichment of Li is evident in soil of the western and central Sacramento Valley compared to both eastern valley soil and Sierra Nevada soil and stream-sediment samples. The highest median value, 49 mg/kg, occurs in western flood basin soil, followed by western alluvial basin soil with 38 mg/kg, levee deposits, 29 mg/kg, and eastern flood basin soil, 24 mg/kg. This pattern indicates that the source of the Li enrichment occurs both upstream from the

study area based on the high values in levee and flood basin deposits, and to the west in the Coast Ranges based on high values in western alluvial basin soil samples. The source of the Li enrichment is likely the Great Valley Group. These rocks occur along the entire margin of the Sacramento valley, and based on data from the study area, contain an average of 91 mg/kg Li (dashed line in Fig. 7c). Additional analysis of the source of Li in western Sacramento Valley soil based on characterization of sediment sources in the coast ranges is in Morrison et al. (2009). In contrast, with the exception of eastern flood basin soil (median 24 mg/kg), median values for eastern valley soil samples only range between 11-15 mg/kg and the Sierra Nevada hosted soil and stream sediment sample populations between 14-18 mg/kg.

Lead concentration is elevated in the eastern Sacramento Valley as demonstrated by both the median and 75th percentile relative to Pb values in all other geomorphic units (Fig 7d). This eastern enrichment is especially prominent for the sample set from the eastern alluvial basin, but flood basin and dissected alluvial uplands also stand out with a wide range and elevated median compared to western Sacramento Valley soil and Sierra Nevada samples. Potential source areas in the Sierra Nevada and Coast Ranges have low Pb concentrations compared to these eastern valley soil samples. The origin of this Pb distribution is tied to anthropogenic inputs, as will be shown below.

Other trace elements of interest in the study area are Zn, Cu, Cd and As. Zinc and Cu are major constituents of ore deposits in the Sacramento Valley drainage basin, and Cd and As are accessory elements that accompany this mineralization. Box plots for these elements (Fig. 8 a, b, c, d) show elevated concentrations in Sacramento River levee deposits and adjacent flood basin soils in the center of the valley compared to valley soil samples situated both east and west of the central valley units. The highest median values for Zn are in flood basin samples located on the west and east sides of the river (111 and 98 mg/kg, respectively), whereas alluvial basin sediments further from the river contain less Zn on the east and west sides (median 87 and 76 mg/kg, respectively). The median Zn concentrations of Sierra Nevada sample categories, which range from 65 to 96 mg/kg, are also somewhat elevated compared to alluvial basin sites located down slope. The distribution pattern for Zn is shown in map view in Supplementary Figure 2.

The general pattern for Cu is similar to Zn (Fig 8b and Supplementary Fig. 3). The flood basin sample categories both have a median of 53 mg/kg Cu, whereas lower values occur in low alluvial plain soil (34 and 27 mg/kg on the west and east sides, respectively). Median Cu

concentrations in flood basin samples are greater than or equal to those from soil derived from ultramafic rocks in the Sierra Nevada foothills, which have a median content of 51 mg/kg. Although Cu is grouped with the ore suite here, it could have been presented as a mafic/ultramafic-associated element, and indeed, Cu values are higher on the west side of the valley compared to the east, as is the case for Cr, Ni and Co. Also, note the elevated value for Cu in Great Valley Group rocks (83 mg/kg) (Supplementary Table 1).

The highest Cd values (Fig. 8c and Online Fig. 4) are associated with Sacramento River deposits and adjacent flood basins. The same is true for As (Fig. 8d and Supplementary Fig. 5), although some elevated values occur in the foothills of the Sierra Nevada.

For all the elements plotted in Figure 8, median soil concentrations from the natural levee sites along the Sacramento River are lower than the adjacent flood basin. This may reflect a grain size effect. The natural levees are dominated by sand and silt sized material, whereas the adjacent flood basins are composed of fine clay soils (Bryan, 1923). The clay fraction of sediments is commonly enriched in trace elements compared to the more coarse fractions.

4. Discussion

The element distribution patterns described above reflect the interaction of hydrologic, geomorphic, geologic, pedologic, and anthropogenic processes. These processes combine to determine the dominant sources and transport pathways for alluvial materials and their subsequent fate during weathering. There are 3 major transport pathways for surficial materials residing in the southern Sacramento Valley soil: (1) transport along the Sacramento River from the northern headwaters region, (2) transport from rivers and streams draining the Sierra Nevada on the east, and (3) transport from rivers and streams draining the Coast Ranges on the west.

The mixing of materials derived from these major sources explains the difference in abundance for a number of elements between the eastern and western Sacramento Valley. This differentiation implies maintenance of at least partial physical separation of eastern and western sediment sources. These west-east differences are attributed to the existence of natural (Bryan, 1923) and more recent artificial levees (Kelley, 1998) along the Sacramento River which have acted to maintain spatial segregation of west versus east sediment sources.

4.1. *Origin of soil geochemical trends on the east side of the Sacramento Valley*

Elements enriched on the east side of the valley, including Ca, Sr, LREE (typified by La and Ce), and Pb as well as Ti, Th and U, which are not plotted, tend to be associated with silicic to intermediate rock types. The prominence of these silicic elements in the eastern Sacramento Valley is, at first glance, surprising given the presence of a belt of ultramafic rocks (western metamorphic belt) in the Sierra Nevada foothills (Fig. 2), which contains relatively high concentrations of the elements Mg, Cr, Ni and V. The overall dominance of more silicic alluvium in the eastern Sacramento Valley is attributed to the influence of two factors: the introduction of large amounts of sediment derived from Sierra Nevada glaciation to the valley and the influence of hydraulic mining for Au on sediment transport to the valley.

The Sierra Nevada Mountains were glaciated during the Pleistocene with multiple glacial advances and retreats (Guyton, 2000). The glacial advances occurred in the northern portion of the Sierra Nevada within the study area. James (2003) emphasized that glaciation at high elevations in the NW Sierra Nevada generated a tremendous volume of sediment, but that the landscape at high elevations is now dominated by bare rock. James (2003) concluded that erosion of glacio-fluvial sediment transported this material to low-gradient reaches of the rivers in the Sacramento Valley and beyond. Plutonic rocks comprised largely of granodiorite with subordinate amounts of more mafic rock types dominate the glaciated portion of the Sierra Nevada (Ague and Brimhall, 1988; Wiebe et al., 2002). Glacial outwash is assumed to be the source of the older sedimentary terraces that make up the low alluvial hills and terraces on the east side of the northern San Joaquin Valley (Marchand and Allwardt, 1981; Harden, 1988). The alluvial uplands mapped in the study area (Fig. 3) are the same geomorphic units that were studied in detail in the northern San Joaquin Valley (Helly and Harwood, 1985). The geochemical data are consistent with the finding of these previous studies that glacial outwash is a major component of surface materials in the eastern Sacramento Valley.

A second major source of sediment within the study area is historical placer Au mining. This activity imposed a large anthropogenic impact on the sedimentary environment of the southern Sacramento Valley (Kelley, 1998). Gilbert (1917) documented the interplay between mining debris merging with debris released to streams through agriculture and grazing in the Sierra Nevada foothills. Hydraulic mining in the northern Sierra Nevada generated more than 3.5 billion metric tons of tailings between 1853 and 1884 with specific sediment production of up to 15,000 metric t/km²/a, much of which is stored in the upland of Sacramento tributary watersheds

(James, 2004). Mobilization of a minimum of 24 million m³ of additional sediment occurred from 1893 to 1953 during a period of licensed mining (James, 1999). The maximum aggradation of hydraulic mine sediment occurred by the 1880s. Reworking of material through flood events continues to mobilize the sediment well over a century after the cessation of hydraulic mining (James, 1999). The host for placer Au deposits was Tertiary gravels associated with ancient riverbeds flowing from an older Sierra Nevada mountain range. These gravels reflect the composition of material derived from higher elevations. It is concluded that the dominant intermediate to silicic geochemical signature in the eastern Sacramento Valley is a result of combined inputs of material from glacial and hydraulic mining sources that have contributed a much greater volume of material than that derived from the foothills ultramafic belt.

4.2. Origin of soil geochemical trends on the west side of the Sacramento Valley

The elements Mg, Cr, Co, Ni and V (not plotted) that are enriched on the west side of the Sacramento Valley, are those with affinities to mafic or ultramafic rock types. The Coast Ranges are the major sediment source to the western valley. Cache and Putah Creeks are the largest tributaries to the Sacramento River system in the study area. Marine rocks of the Franciscan Complex and Great Valley Group dominate in these catchments. Ultramafic rocks (e.g. serpentinites) also occur in the drainages of Cache and Putah Creeks.

Holloway et al.(2009) and Morrison (2009) have analyzed the sources of sediments in Cache Creek and its tributaries from its headwaters to the Sacramento Valley based on sampling of stream sediment and associated bedrock. They argue that marine sedimentary rocks of the Great Valley Group and the Franciscan Complex weather more rapidly than serpentinite under natural conditions. This relationship is easily observed in the field because serpentinite soils are thin and poorly developed (Meadows et al., 1988; Oze et al., 2004). In contrast, soil developed on marine sedimentary rock is much thicker with better developed soil horizons (Andrews, 1972). Despite this difference in weathering rate between serpentinite and other rock types in the Coast Ranges, historic Hg mining in Cache Creek headwaters has resulted in the mobilization of large volumes of mineralized serpentinite which was the host for the Hg ores (Domagalski et al., 2004). This mobilization, in turn, has increased the proportion of serpentinite-derived materials transported along Cache Creek during historic times as reflected in slightly elevated Hg and Ni

content in Cache Creek sediments above that which characterizes the marine sedimentary units (Holloway et al., 2009).

In addition, a prominent contribution to Cache Creek sediment is the Great Valley Group (Holloway et al., 2009; Morrison et al., 2009). This input is evident from Li concentrations, which are higher in Great Valley Group rocks compared to all soils and sediments analyzed, and compared to all sources that have been characterized in the Sierra Nevada (Fig. 7c). This enrichment in the Great Valley rocks is not surprising because marine sedimentary rocks are enriched in Li compared to other rock types. Horstman (1957) reported mean Li values for ultramafic rocks (26 mg/kg), diorite (24 mg/kg), granite (40 mg/kg), and marine shale (66 mg/kg). The concentration of Li in marine shale is the result of its diagenetic incorporation into clay minerals. Lithium is released from marine sediments upon hydrothermal heating (Chan et al., 1994). High concentrations of Li occur in hydrothermal springs sourced in Great Valley Group sediments as well as Cache Creek water impacted by these springs (Domagalski et al., 2004). The prominence of Great Valley Group material in the Cache and Putah Creek drainages is thus the likely explanation of the high Li concentration in soil samples from the west side of the Sacramento Valley relative to the east side. The results demonstrate that a mixture of alluvium from Great Valley Group and ultramafic sources of the Coast Ranges dominates the sediments contributed to the western Sacramento Valley. It is noteworthy that both Sacramento Valley levee samples and adjacent flood basins are also elevated in Li compared to Sierra Nevada and eastern Sacramento Valley soils (Fig. 7c). This pattern is interpreted as reflecting the transport of Li down the Sacramento River and its deposition in the adjacent flood basins. The Great Valley Group crops out over the entire western extent of the Sacramento Valley and is, thus, a potential Li source to the north of the study area as well.

4.3. Soil geochemistry in levee and flood basin environments

Magnesium and other elements associated with ultramafic rocks, including Ni, Cr, Cu and Co (Figs 5, 6, 8, 9A), are all more concentrated in levee and adjacent flood basin sediments than in alluvial deposits closer to the highlands on either side of these deposits. The formation of these levee and flood-basin deposits occurs during floods along the Sacramento River and, thus, represents material transported down the river during these flood events. The northern source area of the Sacramento River includes the Klamath Mountains. Comparable to the metamorphic

belts in the foothills of the Sierra Nevada, the Klamath Mountains are comprised of accreted oceanic terranes (Harden, 2004) that contain extensive exposures of ultramafic rocks. It is hypothesized that the levee and flood basin deposits contain a component of materials derived from this northern source area in addition to the contribution from Cache and Putah Creeks. The occurrence of elevated concentrations of the metallic elements Zn, Cu and Cd in these levee/flood-basin soils (Fig. 8) is also associated with a source area in the Klamath Mountains as further discussed below.

4.4. Role of weathering processes

Weathering processes may significantly modify soil composition. In the Sacramento Valley, however, it appears that weathering processes have not altered the geochemical signature of surface soils sufficiently to mask the signature of their original source material. This conclusion is based both on previous studies in the area and the present results. The effect of depositional age on weathering of Sacramento Valley soils with granitic source materials has been characterized by study of soils comprising the Merced Chronosequence. This chronosequence consists of a series of alluvial terraces in the northern San Joaquin Valley foothills of the Sierra Nevada. Terraces at progressively higher elevation are progressively older. The Merced Chronosequence has an age span of 3 Ma between the youngest and oldest sediments (Marchand and Allwardt, 1981; Harden, 1988; White et al., 1996; Bullen et al., 1997). The sequence lies just 50 km south of the southern edge of the study area. Terraces which correlate with the Merced Sequence are present to the north of the study area in the Sacramento Valley (Busacca and Singer, 1989) and similar terraces are mapped in the Sierra Nevada foothills in the study area. Chemical analyses of the Merced sequence by Harden (1988) showed that both sand and finer fractions have lost Ca, Mg, Na, and K, whereas Al is lost from the sand fraction and added to the finer fractions. Compatible results were found by White et al. (1996) who showed that mineralogical losses with time occur in the order of hornblende>plagioclase>K-feldspar.

Although the soil geochemistry data generated in this study has not been categorized by location within specific quaternary geologic units, the geomorphic units described earlier and shown in Figure 3 provide a crude approximation. The alluvial uplands on either side of the Sacramento Valley (units 1 and 8) correspond to the alluvial terraces that comprise the older portions of the chronosequence. In contrast, the low alluvial plains on either side of the valley

(units 2 and 7) are comprised of geologically younger (Holocene) alluvium. Figure 5 shows that the older surface soil in the upland terraces is systematically depleted in Al, Mg, Ca, K and Na compared to the soil in the plains. The trend in element depletion between older low hills and dissected alluvial uplands on either side of the valley and adjacent low alluvial plains and fans in Figure 5 indicate this trend of depletion in older soil. Although the trends identified in Figure 5 are consistent with loss of these major elements from older surface material, they are not so dramatic as to obscure the overall geochemical signature of the source areas despite exposure of the older alluvial terraces to weathering for times as long as 3 Ma.

4.5. Anthropogenic impacts

Elevated concentrations of Pb are localized in the eastern Sacramento Valley compared to the western valley (Fig. 7d), but Pb distribution is controlled largely by anthropogenic inputs. This conclusion is illustrated in Figure 10 that shows the spatial distribution of Pb in the NURE soil samples in map view. Grey shaded areas show the location of urban areas, which are delineated on the basis of percent impervious surface (Yang, 2002). The greater Sacramento area, together with the cities of Stockton and Lodi, have significantly higher soil Pb concentrations compared to adjacent, less populated areas. Increased Pb concentration is also evident along major highways. Figure 11 summarizes the Pb data, as a series of box plots with the data segregated by location into categories for cities, highways, and samples that are not associated with either of the two previous groupings. For this plot, location in cities was defined as coinciding with a value of impervious surface >20%. Lead spatially associated with roads was estimated by selecting soil Pb analyses for samples lying within a 500-m buffer zone of major federal and state highways. The mean and median Pb concentrations for cities (125 and 47 mg/kg, respectively) and highways (65 and 31 mg/kg) are both greater than mean and median values for all remaining samples (31 and 21 mg/kg). This trend is also evident in Figure 8 in which Pb concentrations are highest in the eastern Sacramento Valley groupings – where the preponderance of the major cities and highways are located.

Combustion of leaded gasoline and, secondarily, the use of leaded paint are the dominant anthropogenic Pb sources in urban areas. Use of leaded gasoline peaked in the mid 1970s and Pb in the environment from this source has been declining ever since (Callender, 2005).

Nonetheless, in some urban settings Pb is still present in high concentrations (Filippelli et al.,

2005). The collection of the NURE soil and stream sediment samples took place in the late 1970s and early 1980s, not long after peak usage of leaded gasoline. The original high Pb sites in cities have not been resampled, but there are indications that gasoline-derived Pb is still affecting the environment. Dunlap et al. (2000) used Pb isotope data to estimate that, in the period 1995-1998, more than 50% of the Pb contained in river water at the confluence of the Sacramento and San Joaquin rivers, where they enter San Francisco Bay, was derived from gasoline combustion. Material transported down the Sacramento River dominates the sediments in the San Francisco Bay. Core samples from the bay show that Pb increases above background levels beginning about 1910 and has not returned to these background levels in young sediments near the sediment-water interface (Hornberger et al., 1999).

Automobiles may also contribute to the abundance of Zn in soils. Tire tread material has a Zn content of about 1 % by weight (Callender, 2005). Callender (2005) showed that tire wear releases large amounts of Zn along roadways and accounts for a significant fraction of the flux of Zn to urban reservoir sediments. His data showed Zn flux increasing over the period 1950 to 2000 in amounts proportional to the average annual daily traffic near the reservoirs. A discernable impact of tire wear on Zn distribution is inferred in the California study area from Figure 11, which shows a box plot of Zn abundance, partitioned using the same criteria as for Pb. Zinc associated with cities (median 91 mg/kg, mean 144 mg/kg) and roads (median 98 mg/kg, mean 111 mg/kg) are both higher than the remaining data exclusive of cities and roads (median and mean 86 and 96 mg/kg, respectively).

Zinc likely has another important anthropogenic source to Sacramento River levee deposits and flood basins relative to other geographic areas (Fig. 8). The association of Zn with sediment transported down the Sacramento River is interpreted as being due in large part to mining activity in the Klamath mining district north of the study area. There were numerous mines in the Klamath Mountains (Fig. 1); however, the Iron Mountain Group of mines in Shasta County was the largest. Mining for Ag and Au occurred from the 1860s onward, with Cu and Zn recovered through World War II. Open-pit mining was active from 1955 to 1962 with an estimated 300 tons of dissolved Cu, Zn and Cd draining annually into the Sacramento River prior to remediation (Nordstrom and Alpers, 1999). The Iron Mountain Group of mines was the sixth largest producer of Cu in the US during the first quarter of the 20th century and mining continued intermittently from the 1860s until 1962. During these mining and smelting activities, acid mine

drainage from Iron Mountain discharged directly to Spring Creek, a tributary to the Sacramento River upstream of Redding, CA (Alpers et al., 2000). In 1983, Iron Mountain was listed on the U.S. Environmental Protection Agency's National Priorities List, ranking as the third-largest polluter in the state of California

Alpers et al. (2000) studied metal loads in dissolved and colloidal form as well as bed sediments in the Sacramento River during the period 1996-1997 and found that, during low flow conditions, Cu and Zn added as agricultural amendments might be important as sources of these elements to the Sacramento River system. However, during flood conditions, which would contribute to overbank and adjacent flood basin sediments of this study, Cd, Cu and Zn were derived from upstream of the main agricultural regions. Significantly, collection of the NURE soil samples occurred prior to major remediation efforts at the Iron Mountain Superfund site. It is therefore not surprising that some impacts from the input of metals from this source are recognizable in the data. The ore-related elements that are enriched in levee and flood basin sediments along the Sacramento River (Fig. 8) are those which were released to the river during mining activity; notably Zn, Cu and Cd.

5. Conclusions

The results of this study provide insight into the controls on surface soil and stream-sediment composition in a portion of the Sierra Nevada, Sacramento Valley and Coast Ranges of northern California. A statistical summary of median values for the entire data set show that the elements Al, As, Be, Ce, Cs, Ga, In, K, La, Li, Mo, P, Pb, Sb, Se, Th, Ti, U, Y and Zn are within a factor of two of the elemental abundance in continental data sets for soil from Europe and the conterminous U.S.A. This similarity likely results from the broad range of rock types that occur in the California study area, which permits an approximation of the geochemistry of geographically larger areas. However, there are some chemical elements in the California data set, specifically Co, Cr, Cu, Fe, Mg, Mn, Ni, Sc and Te that are enriched by approximately a factor of two compared to European and conterminous U.S.A. data. The enrichment in these elements is directly and indirectly due to the abundance of ultramafic rocks (largely serpentinites) in the study area compared to the continental-scale studies. The direct impact from ultramafic rocks arises from their input during weathering in both the Coast Ranges and Sierra Nevada foothills, as well as mobilization by disturbance during Hg mining in the Coast Ranges.

The indirect influence is due to the weathering of a component of ultramafic materials that was incorporated into the Great Valley Group during its formation.

Spatial distribution patterns of element concentrations in the study area reflect geologic controls on soil and sediment source materials. The Coast Ranges predominantly consist of marine sedimentary rocks and upper marine crust. In contrast, the Sierra Nevada in the study area contains a more complex mix of rock types; the foothills metamorphic belt is comprised of a number of marine accreted terrains and ultramafic rocks, and the higher elevations are dominated by volcanic and plutonic rocks of intermediate to silicic composition. The contrasting geology on either side of the Sacramento Valley has left an imprint on the composition of alluvial plain material on the valley floor adjacent to these highlands. The predominant geologic sources for much of the surface soil in the western Sacramento Valley are marine rocks in the Coast Ranges comprised of both the Great Valley Group and the Franciscan Complex. These natural sources have been combined in historic times with inputs from Hg mining. Mercury deposits occurred in ultramafic rock and this mining enhanced the transport of ultramafic rock to the valley (Holloway et al., 2009; Morrison et al., 2009). The net effect of these sources has been to impart the signature of elements associated with mafic rock types in the western valley. In contrast, glacial outwash from multiple episodes of glacial retreat and huge volumes of sediment mobilized by hydraulic mining are dominant sources for surface soil in the eastern valley. This has resulted in an overall silicic character to the surface soils in the eastern Sacramento Valley. Natural levees along the river form a barrier, which maintains the separation of sedimentary sources across the Sacramento Valley.

In contrast to these inputs from the adjacent mountain ranges, levees and flood basins along and adjacent to the Sacramento River have received significant sedimentary debris from further north in the Valley. Sacramento River levees and flood basins (Fig. 3) formed by downriver transport of sediments during flood events. Compared to adjacent alluvial deposits, these two depositional environments contain higher contents of elements associated with weathering of ultramafic rocks (Figs 5, 6 and 9A). This contrast is probably due to the abundance of ultramafic rocks in the Klamath Mountains at the north end of the valley. Data showing elevated concentrations of Cd, Cu and Zn (Fig. 8) reinforce the hypothesis that a source of levee and flood basin sediment is the Klamath Mountains. It is believed that mining activities in the

West Shasta Mining District at the north end of the valley supplied detritus enriched in these elements.

Finally, anthropogenic sources, in addition to mining, can also be recognized in the data. Most obvious is the close correlation of Pb abundance to cities and highways (Figs 10 and 11). This positive correlation has been observed frequently and is due to Pb released by leaded gasoline and Pb-bearing paint (Callender, 2005). Zinc also shows the same correlation with cities and highways (Fig. 11), with the source of this Zn being tire wear.

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Figure Captions

Figure 1. Map of northern California showing mining areas and the location of the study area (rectangle). Mine symbols at the north end of the Sacramento Valley are massive sulfide (Zn, Cu, Fe) deposits. The Hg symbols on the west side of the valley are Hg mines with past production. The Au symbols on the east side of the valley are lode Au deposits with past production. Mine data is from USGS (2005).

Figure 2. Geology of the study area (rectangle) and vicinity. Map data from Saucedo et al. (2000).

Figure 3. Geomorphology of the Sacramento Valley in the study area. The rectangle shows the western, northern and southern boundaries of the study area. Geomorphology data from (Helly and Harwood, 1985)

Figure 4. Locations of soil and stream-sediment samples from the study area. The shaded portions are urban areas.

Figure 5. Box plots showing the concentrations of Al (a), Mg (b), Ca (c), K (d) and Na (e) in soils and sediments of the study area. The box plots are arranged from west to east (left to right). For each box plot the solid line within the box is the median value, the dashed line is the mean value. The bottom of each box is the 25th percentile, the top line is the 75th percentile. The whiskers are the 10th and 90th percentiles and dots are the 5th and 95th percentile values. A long horizontal dashed line represents the median value for data from rocks of the Great Valley Group on the west side of the Sacramento Valley. The abbreviations are: WSV- western Sacramento Valley soils, SR - Sacramento River levee material, ESV – eastern Sacramento Valley soils, UM – soil overlying ultramafic rocks, SN – soil and stream sediment from Sierra Nevada. Numbers along the horizontal axes represent geomorphic units described in text.

Figure 6. Box plots showing the concentrations of Ni (a), Cr (b) and Co (c) in soils and sediments of the study area. The box plots are arranged from west to east (left to right). Box plots and abbreviations as in Fig. 5.

Figure 7. Box plots showing the concentrations of La (a), Sr (b), Li (c) and Pb (d) in soils and sediments of the study area. Box plots and abbreviations as in Fig. 5.

Figure 8. Box plots showing the concentrations of Zn (a), Cu (b), Cd (c) and As (d) in the study area. Box plots and abbreviations as in Fig. 5.

Figure 9. Map showing the concentrations of Mg (a) and Ca (b) in study area soil and sediment. The size of the circle is proportional to the abundance of the element. Darker circles represent soil samples, lighter ones are stream-sediment samples. The shaded portions are urban areas. Concentration classes based on quartiles of the data.

Figure 10. Map showing the distribution of Pb in the study area. The size of each circle is proportional to the concentration of Pb. The shaded regions are urban areas. The dark lines are major state and federal highways. Concentration classes are based on percentiles of the data.

Figure 11. Box plots showing the concentrations of Pb (a) and Zn (b) in the study area. The data have been grouped and plotted on the basis of their spatial association with cities, highways and all other sites (see text for details).

Captions for Supplementary Figures (to appear in the on-line version):

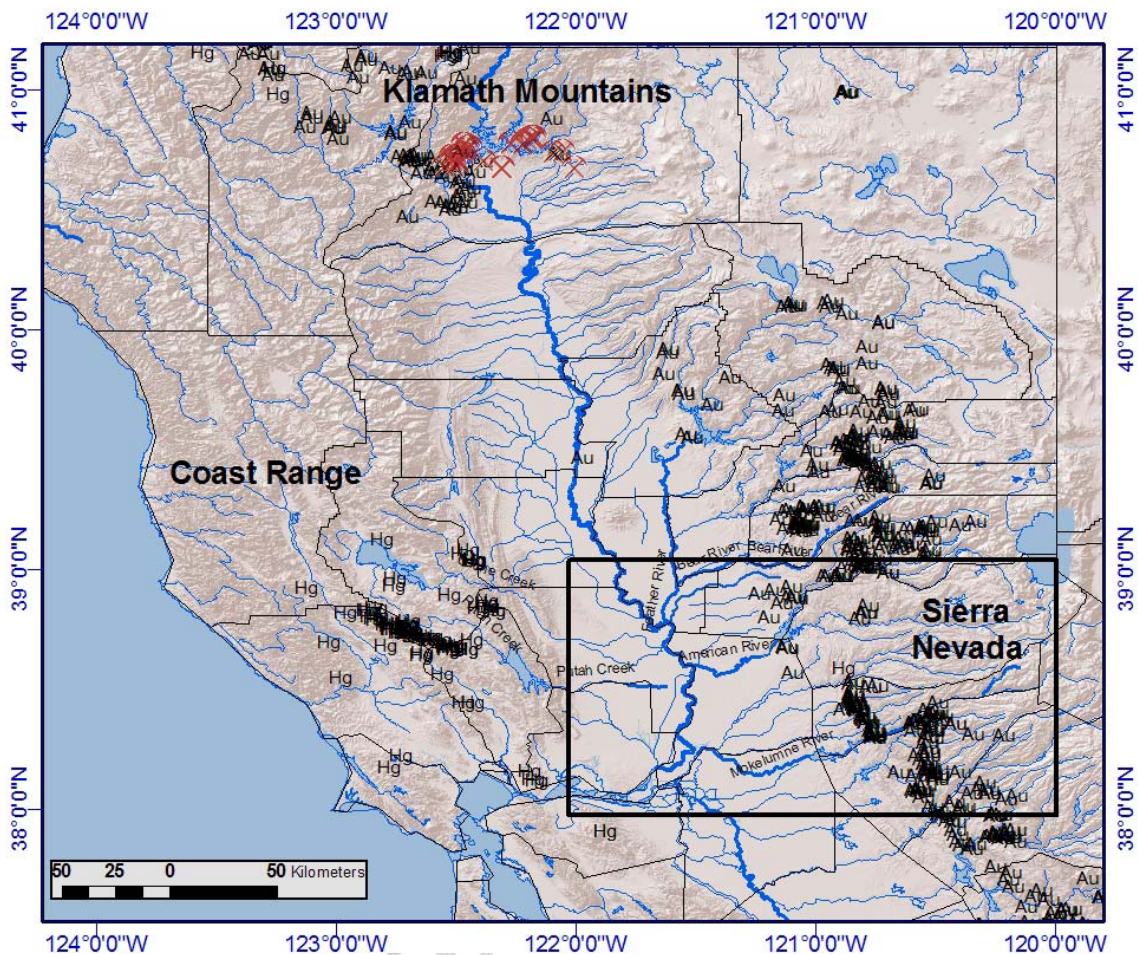
Supplementary Figure 1. Map showing the ratio of Mg/Ca in soil and stream-sediment samples. Soil samples are circles, stream-sediment samples are squares with the same relative proportions as for the soil samples.

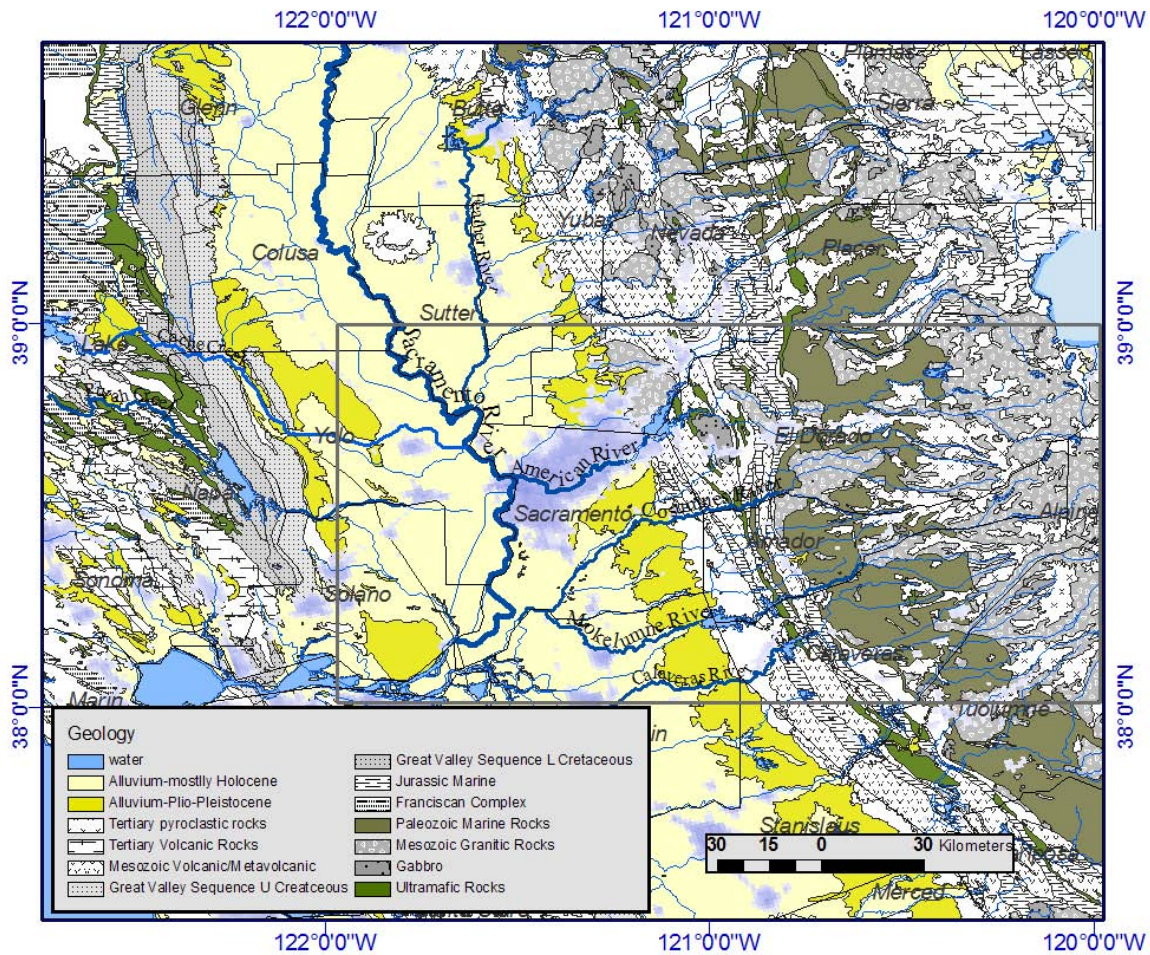
Supplementary Figure 2. Map showing the distribution of Zn as a series of proportionally sized symbols. Soil samples are circles, stream-sediment samples are squares with the same relative proportions as for the soil samples.

Supplementary Figure 3. Map showing the distribution of Cu as a series of proportionally sized symbols. Soil samples are circles, stream-sediment samples are squares with the same relative proportions as for the soil samples.

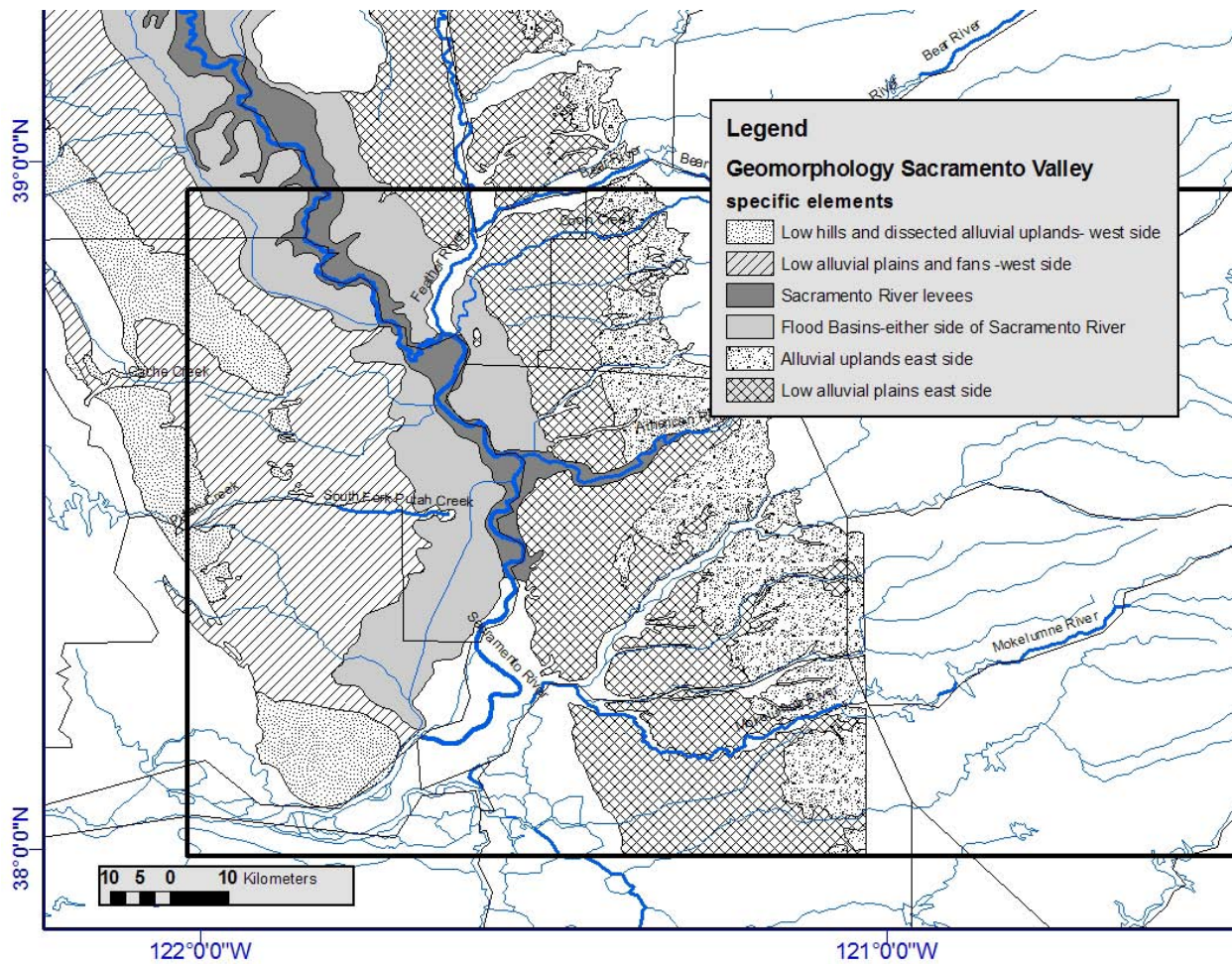
Supplementary Figure 4. Map showing the distribution of Cd as a series of proportionally sized symbols. Soil samples are circles, stream-sediment samples are squares with the same relative proportions as for the soil samples.

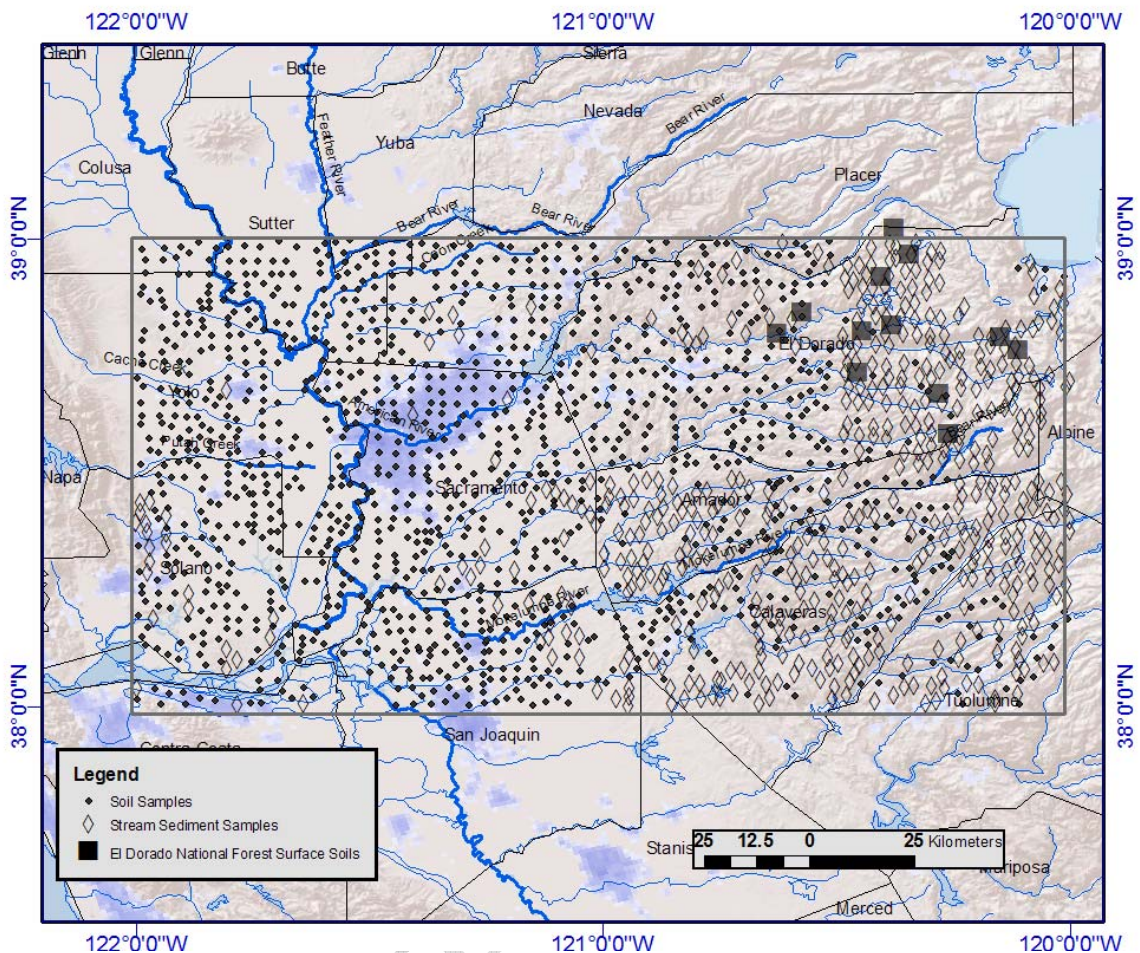
Supplementary Figure 5. Map showing the distribution of As as a series of proportionally sized symbols. Soil samples are circles, stream-sediment samples are squares with the same relative proportions as for the soil samples.

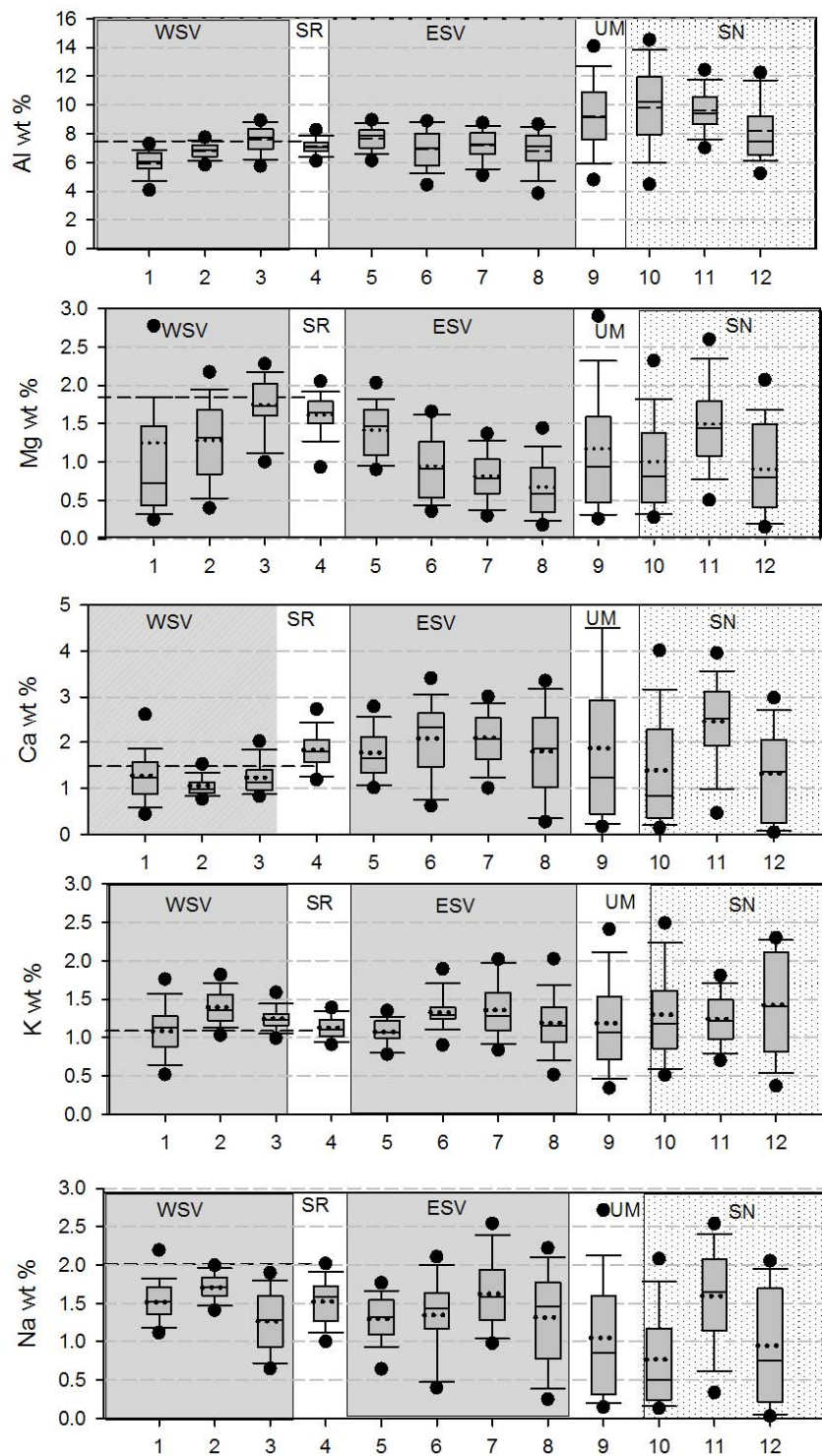


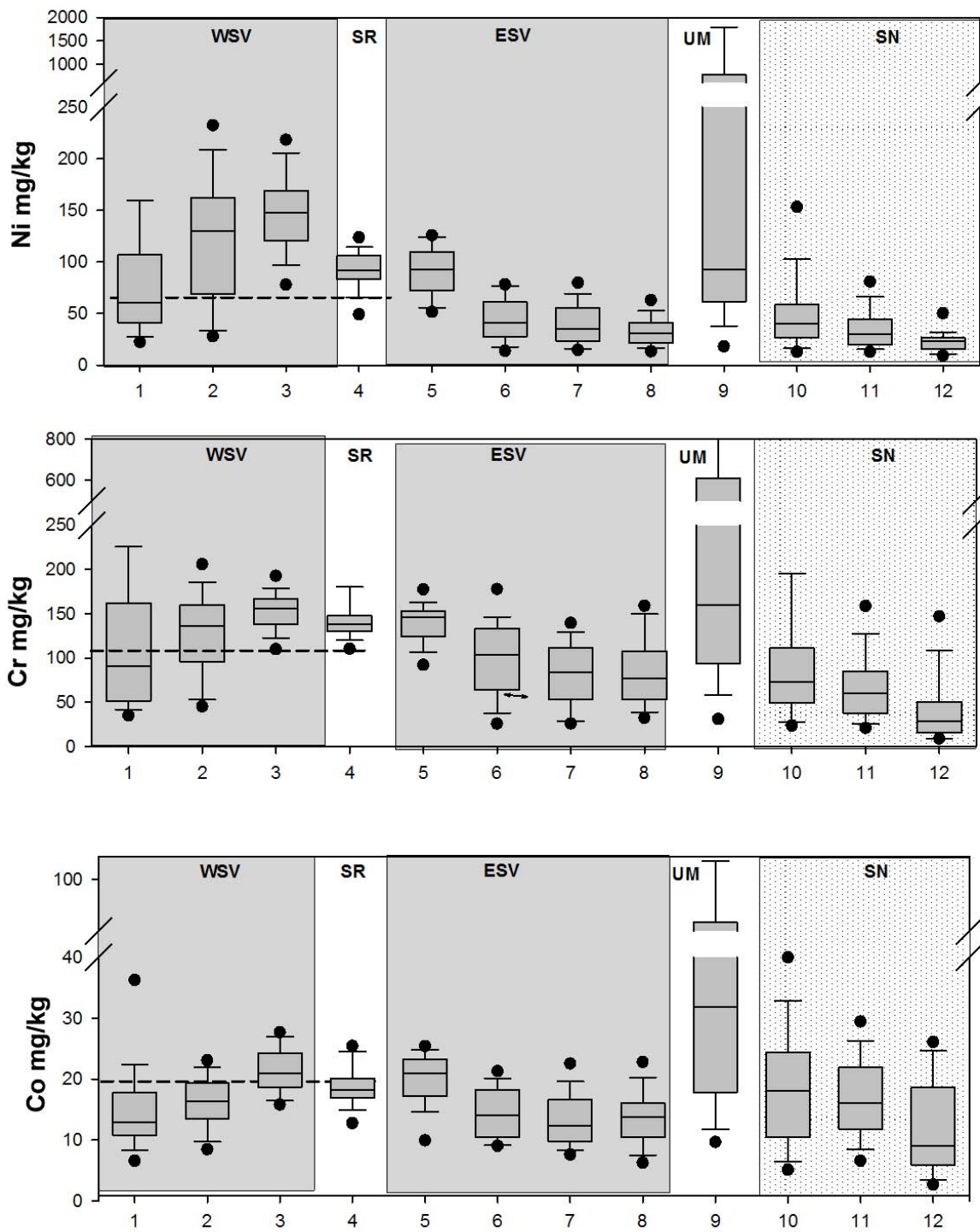


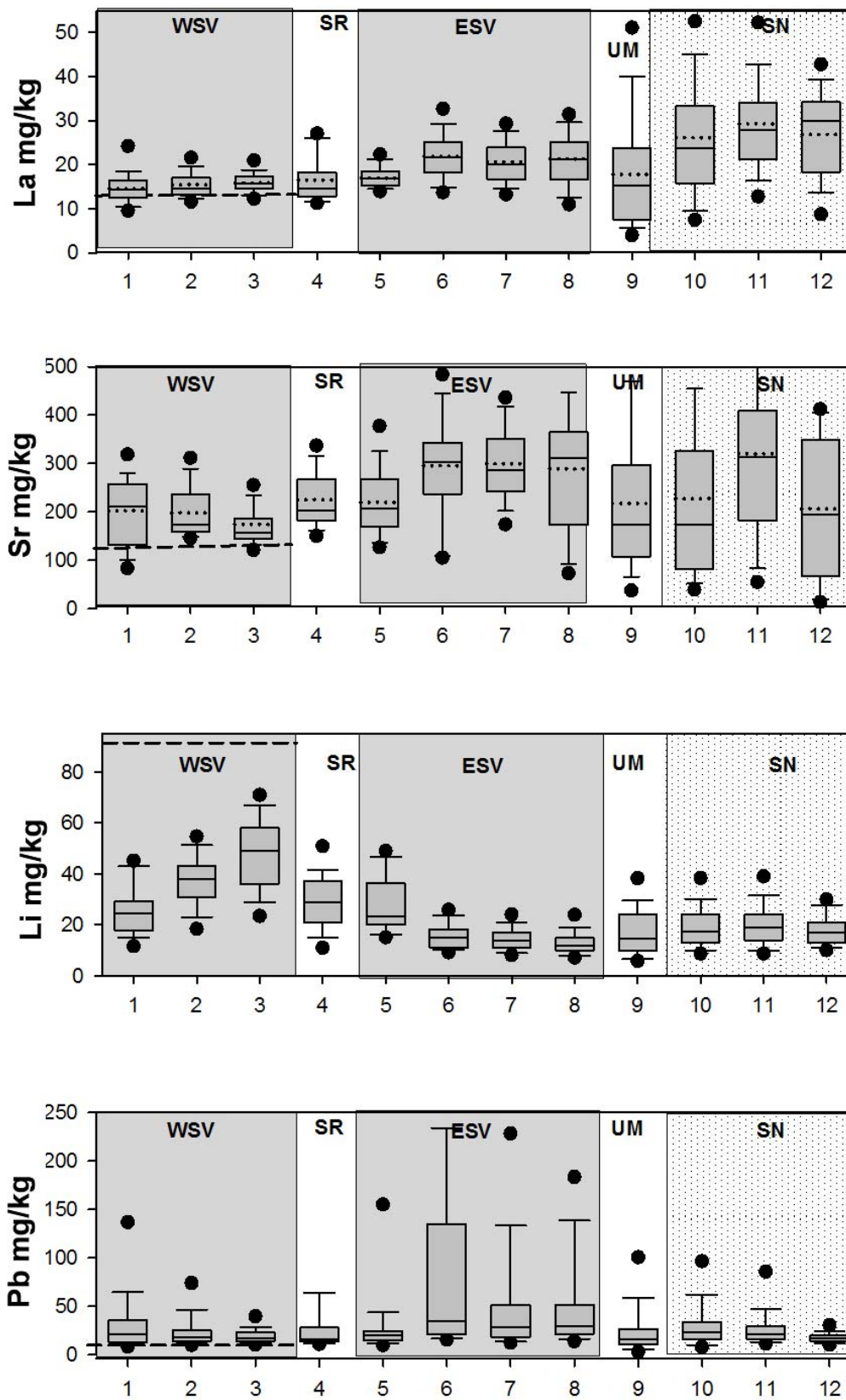
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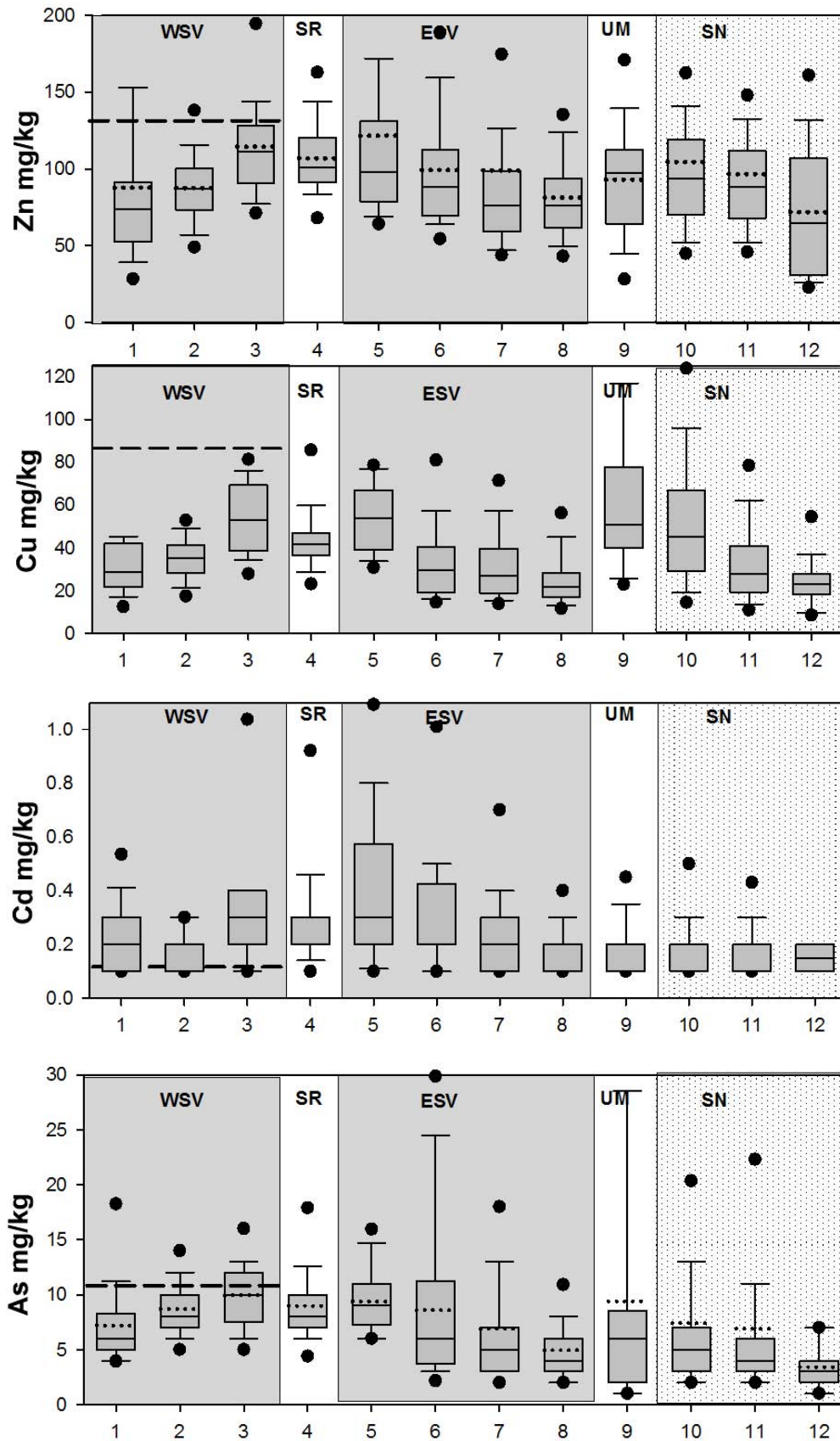


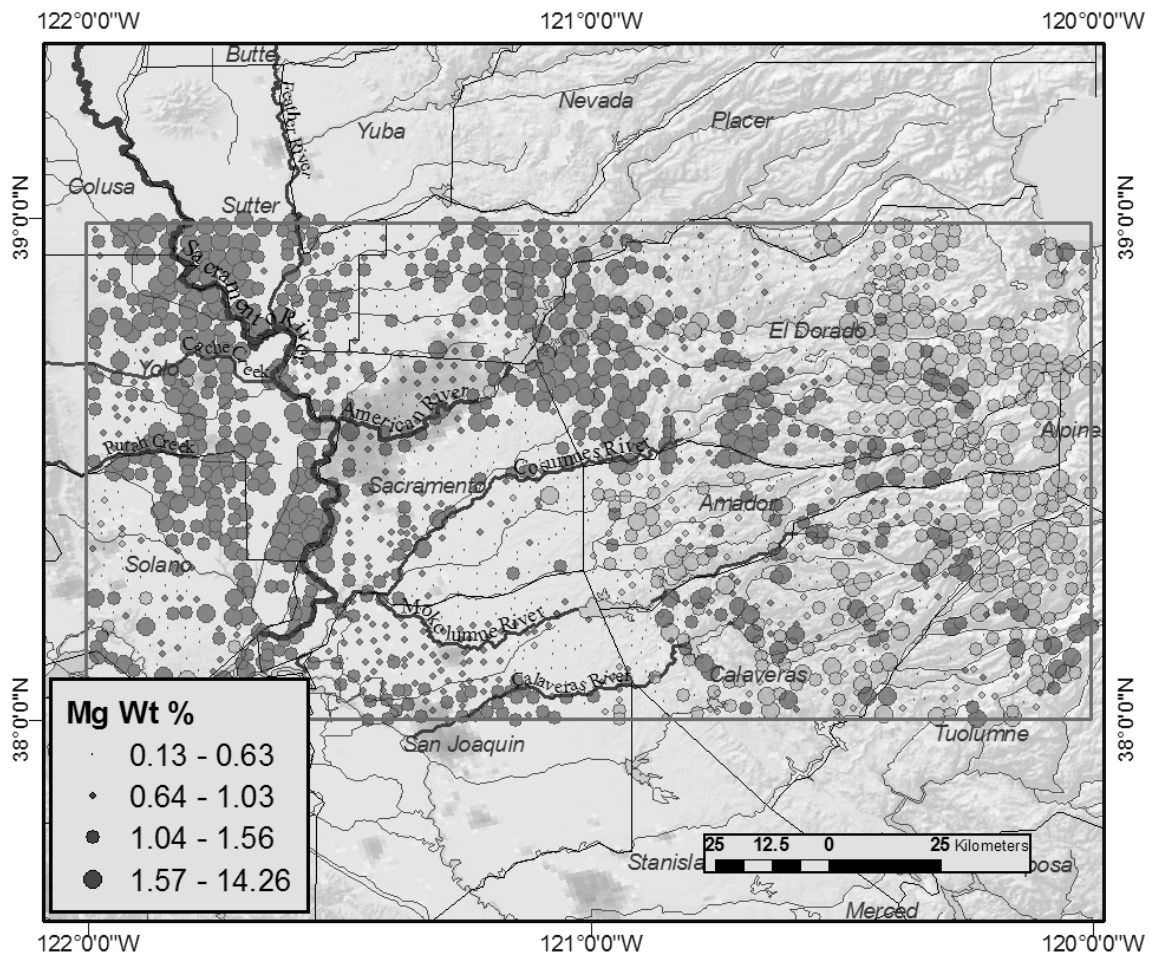


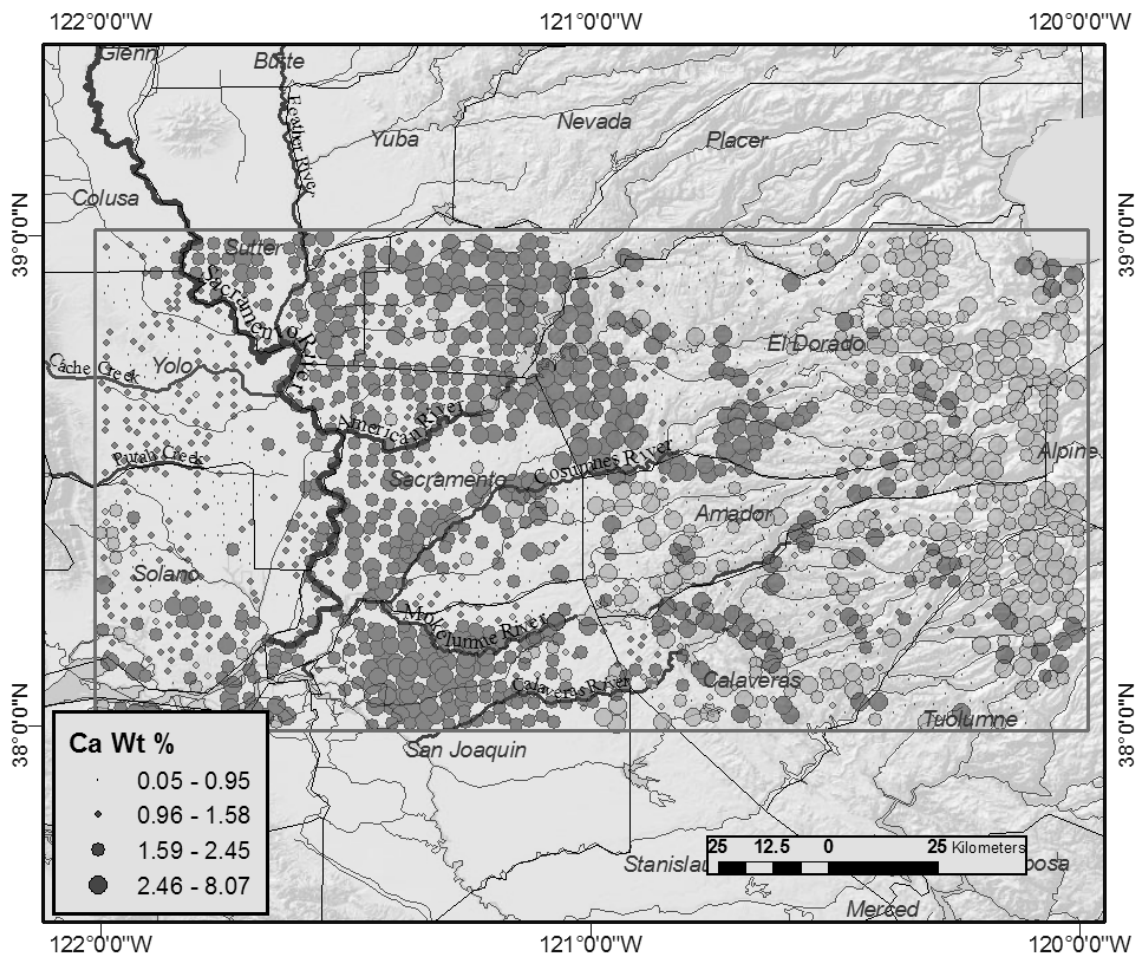




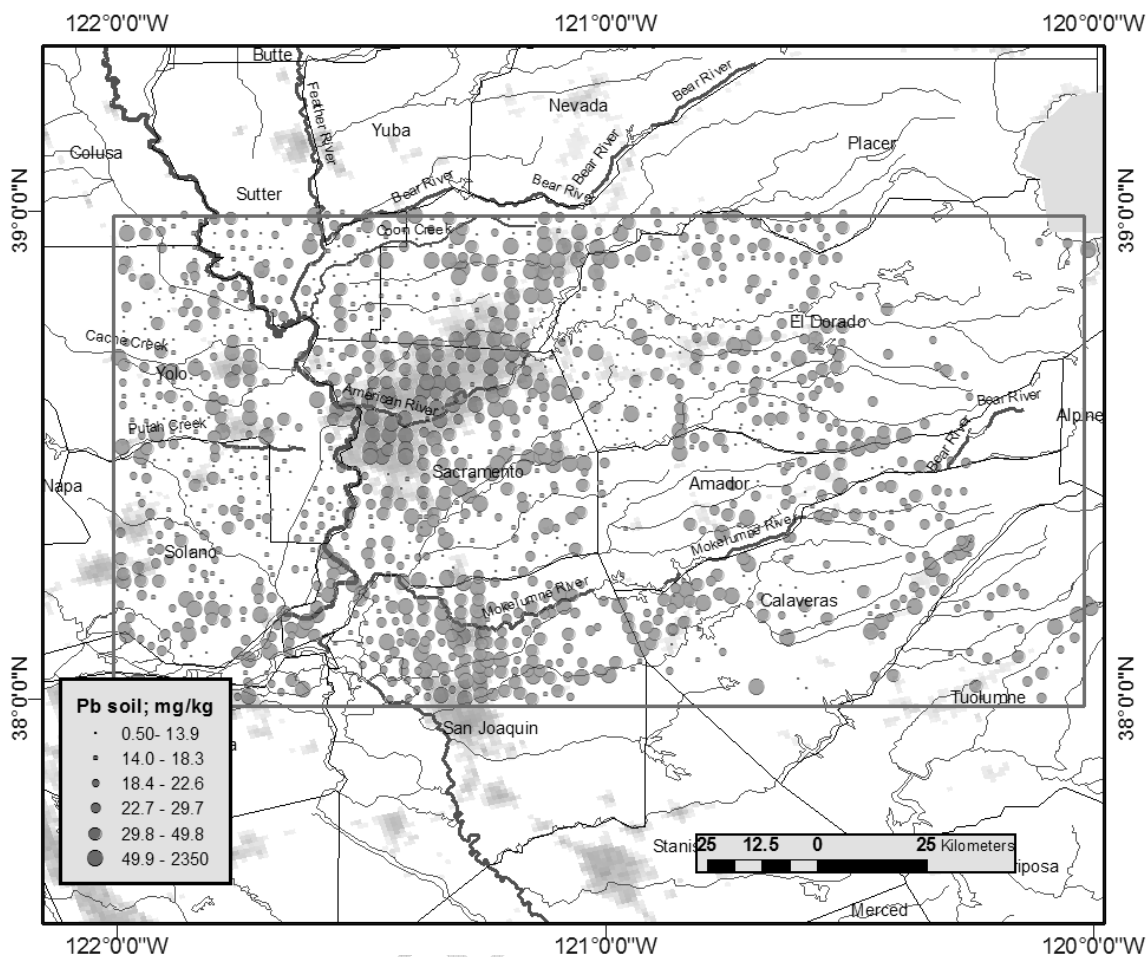


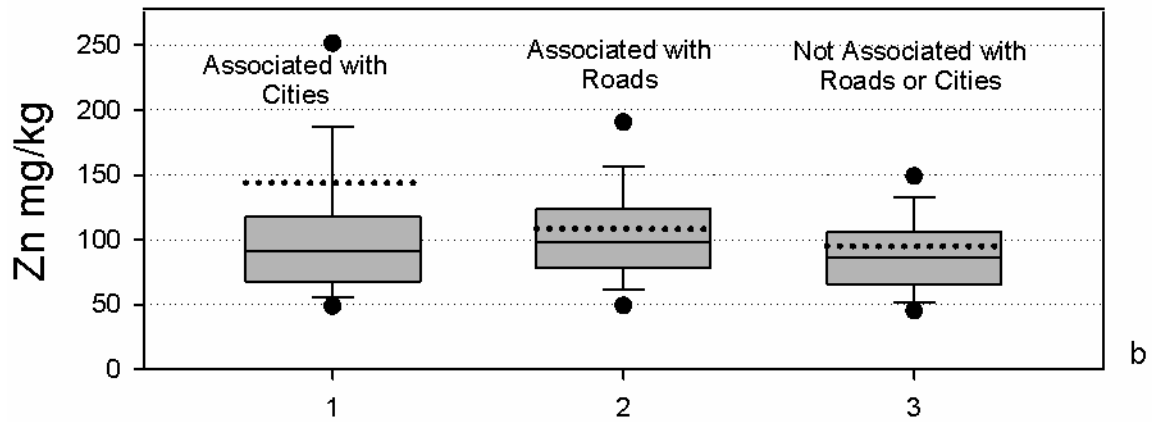
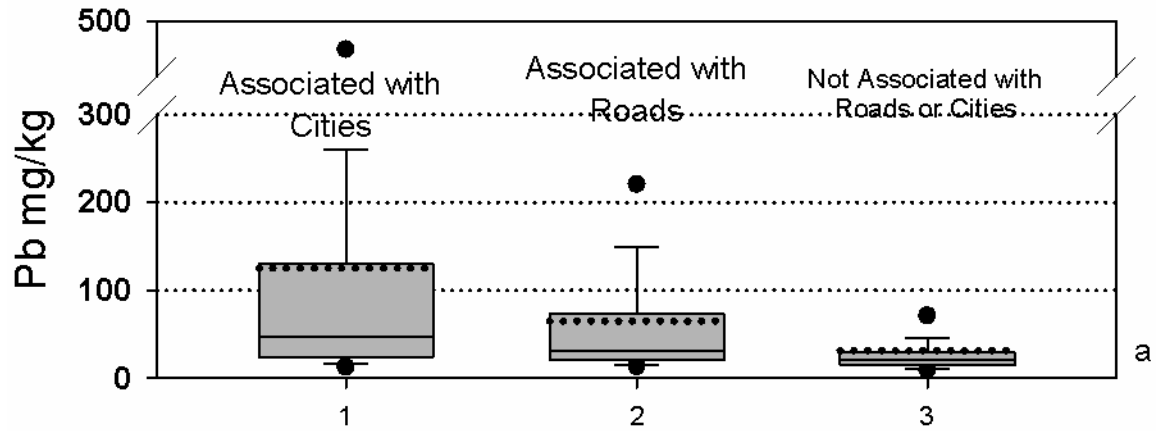






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Table 1.

Statistical comparison of California data set (this study) with continental-scale data sets.

This Study					European Data ¹				Conterminous US Data ²			
Element	Mean	Max	Min	Median	Mean	Max	Min	Median	Mean	Max	Min	Median
Al (wt %)	7.9	16.0	0.0	7.5	5.6	14.1	0.2	5.8	5.6	12.0	<0.07	5.0
As (mg/kg)	7.9	106.0	1.0	6.0	11.6	282.0	0.3	7.0	6.8	97.0	<0.01	5.8
Ba (mg/kg)	640	7610	28	601	399	1870	5	375	546	5000	<10	500
Be (mg/kg)	1.2	5.8	0.1	1.1	1.0	2.0	0.3	1.0	1.6	15.0	<0.5	1.5
Bi (mg/kg)	0.1	2.2	0.0	0.1	0.4	9.6	0.3	0.3				
Ca (wt %)	1.81	8.07	0.05	1.56	2.53	34.07	0.02	0.66	2.25	32.00	0.01	0.90
Cd (mg/kg)	0.3	11.2	0.1	0.2	0.3	14.1	0.0	0.1				
Ce (mg/kg)	43	289	0	38	52	267	2	48	169	300	<150	150
Co (mg/kg)	18	166	0.1	16	2	3	2	2	10	70	<3	7
Cr (mg/kg)	119	5910	12	96	95	6234	2	60	54	2000	<1	50
Cs (mg/kg)	3	25	0.1	2	6	69	0.01	4				
Cu (mg/kg)	49	3088	5	37	17	256	1	13	25	700	<1	20
Fe (wt %)	4.25	12.43	1.20	3.92	2.70	15.78	0.11	2.49	2.36	>10	0.01	2.00
Ga (mg/kg)	15.765	36.5	0.05	14.9	13.141	34.3	0.54	13.5	17	70	<5	15
In (mg/kg)	0.0496	0.15	0.02	0.05	0.0499	0.41	0.005	0.05				
K (wt %)	1.25	3.67	0.07	1.23	1.67	5.09	0.02	1.59	1.53	6.3	0.005	1.57
La (mg/kg)	21	128	1	19	26	143	1	24				
Li (mg/kg)	23	77	3	19					22	136	<5	20
Mg (mg/kg)	1.19	14.26	0.13	1.03	0.71	14.85	0.00	0.46	0.7	>10	0.005	0.5
Mn (mg/kg)	823	4430	48	752	624	6030	31	503	487	7000	<2	300

Mo (mg/kg)	0.988	10	0.05	0.71	0.943	21.3	0.05	0.62				
Na (wt %)	1.36	4.27	0.04	1.45	0.86	3.30	0.03	0.59	0.93	10.00	0.03	0.70
Nb (mg/kg)	7	51	0	6	11	134	0	10	10	100	<10	10
Ni (mg/kg)	84	4955	6	50	37	2690	1	18	20	700	<5	15
P (mg/kg)	619	4790	50	554	653	5770	48	559	416	6800	10	300
Pb (mg/kg)	45	2354	1	23	33	970	5	23	22	700	<10	15
Rb (mg/kg)	51	168	0	49	87	390	1	80	65	210	<20	65
S (mg/kg)	0.03	1.32	0.01	0.02								
Sb (mg/kg)	0.8	6.9	0.1	0.7	1.0	31.1	0.0	0.6	1.7	8.8	<1	1.3
Sc (mg/kg)	17.1	72.3	0.2	15.7	9.1	54	0.3	8.2	10	50	<5	10
Se (mg/kg)	0.272	2	0.2	0.2					0.37	4.32	<.1	0.30
Sn (mg/kg)	2	110	0	1	4	106	1	3				
Sr (mg/kg)	245	1717	11	226	130	3125	2	89	200	3000	<5	150
Te (mg/kg)	0.1	1.1	0.1	0.1	0.0	0.9	0.01	0.03				
Th (mg/kg)	7.4	145.6	0.2	6.0	8.2	75.9	0.3	7.2				
Ti (wt %)	0.456	2.08	0.07	0.4	0.365	3.265	0.0126	0.343	0.29	2.00	0.01	0.30
Tl (mg/kg)	0.33	1.5	0.1	0.3	0.821	24	0.05	0.66				
U (mg/kg)	2.1	11.4	0.1	1.8	2.4	53.2	0.2	2.0	2.7	10.7	0.3	2.7
V (mg/kg)	149	490	35	135	68	537	3	60	76	500	3.5	70
W (mg/kg)	0.884	18	0.1	0.8	2.642	14	2.5	2.5				
Y (mg/kg)	15	153	0	15	23	267	2	21	26	200	5	20
Zn (mg/kg)	102	3350	18	88	68	2904	2	52	63	2890	5	50

Data in bold with shading are median values that are approximately a factor of two higher in the California data set than in the Conterminous US data set.

¹ Salminen et al. (2005)

² Boerngen and Shacklette (1981)