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Geochemical Characterization of Mining Districts and Mining-related Contamination in the Prescott National Forest area, Yavapai County, Arizona: a preliminary assessment of environmental effects

by

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SUMMARY

Many natural and mining-related sources contribute heavy metals to the surficial environment in the Prescott National Forest area, Yavapai County, AZ. Our geochemical studies show that mining and related mineral processing activities, which were widespread in the area of the Prescott National Forest in the period 1860 to 1955, produced local contamination of moderate to severe magnitude, chiefly on private lands. However, unmined mineralized rocks also contribute the same suite of heavy metals to the environment. Most of the 39 mining districts in the area show moderate to high heavy metal contamination at local (deposit) to district scale from one of more sources (mine workings, waste dumps, mill tailings, smelter slag or smoke, or unmined mineralized outcrops). Six important watersheds in the area show a range of indications of contamination, with the Lynx and Hassayampa watersheds having the most widespread transport of heavy metals in waters because natural buffering capacity of rocks in these basins is low. The widespread occurrence of both primary and secondary carbonate minerals (chiefly calcite) in sedimentary rocks, alluvium and altered igneous rocks neutralize and naturally mitigate the heavy-metal contamination of most drainages that otherwise would have severe environmental impact by metals. Despite some local drainage problems (at the scale of acres to hundreds of acres), the general geochemical condition of the environment is good, and better than might be expected for a region having more than a century of widespread mining activity.

This study provides chemical data and geologic information that characterize metallic mining districts and the products of mining, including waste dumps, mill tailings, smelter slag, soils, and stream alluvium contaminated by mining activities. Geochemical characteristics of five mineral deposit types that have been mined in the area are reviewed and the environmental impact of districts are ranked. Heavy metal contamination is visible and measurable in most mining districts, but dispersal is generally only over short distances (less than a mile). The bioavailable portion of the contaminants has not been established, and further work is needed to determine aspects such as degree of pollution and toxicity. Our reconnaissance studies suggest that effects are local in scale and generally do not have impact beyond private property boundaries. Highest geochemical mobility is in districts at high elevation that receive in excess of 25 inches of precipitation. However, at drier lower elevations brief pulses of degraded water quality can be produced when storm events dissolve efflorescent crusts that form on mine dumps and tailings impoundments during dry periods.

INTRODUCTION

The Prescott National Forest and adjacent areas in Yavapai County, north-central Arizona (fig. 1), has had a productive history of mining for more than 125 years. As in other parts of industrialized society, there are adverse consequences to economic activities and it should come as no surprise that the legacy of past mining--abandoned and neglected mines, dumps, mills, and smelters--remains as a possible threat to the natural environment. Assessment of the impact of past mining is a complex task that requires collecting many kinds of information and interpreting dynamic surficial processes. No systematic regional studies have been attempted for this area previously, and this reconnaissance study is only a modest start toward the understanding of some of the issues. The goal of this study is to identify the kinds of problems that may exist, their character, and distribution. As in most scientific studies, this work raises many questions and answers few: numerous topics that are briefly described need more systematic study and rigorous analysis.

Geo-environmental conditions in the Prescott National Forest area must be considered in the context of both geologic and industrial conditions. Mother Nature created many natural geochemical anomalies (mineral deposits and rock alteration) in the area that contaminate the surficial environment when exposed to weathering processes. Miners, chiefly in the period 1875-1925, caused moderate to severe contamination through mining, milling, and smelting practices that were expedient at the time but which would not be permitted today. Health and environmental regulations did not exist in the 19th Century, or early 20th Century, and of course never did apply to Mother Nature. The conditions that we observe today cannot be corrected retroactively, but we must attempt to distinguish many situations, such as 1) conditions that we cannot control (Mother Nature), 2) contamination that is anthropogenic but mitigated by nature, 3) contamination that is anthropogenic and in need of mitigation by owners or the public, and 4) natural and mining-related contamination that is exacerbated by residential and recreational uses today. This geochemical reconnaissance is a first step in the environmental assessment of these and other complex issues.

This study focuses on two features associated with metallic mineral deposits that can have toxic effects on the biosphere (Moore and Ramamoorthy, 1984): acid drainage[1] and heavy metal[2] contamination. Sulfuric acid, created by the action of atmospheric oxygen and water with sulfur in sulfide minerals, is a potent solvent that dissolves and transports heavy metals. Of particular concern is possible degradation of water quality and consequent impact on the health of wildlife and people. Many natural and mining-related sources contribute heavy metals to the surficial environment in the Prescott National

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[1] The term "drainage" is grammatically questionable, but is widely used by environmental scientists in the 1990's in the sense of water or waters (collective). Mine drainage refers to waters draining from mine workings, underground or pit. Rock drainage refers to waters that have percolated through mineralized rocks, in situ or on dumps.

[2] In this report the term "heavy metal" will be applied somewhat loosely to include arsenic, which is technically not a metallic element.

Forest area. Studies elsewhere have shown that anthropogenic sources around the world are the major contributors of heavy metal contaminants to the environment (Nriagu, 1980b; Davies, 1983). Our study shows that mining and related mineral processing activities which were widespread in the area of the Prescott National Forest in the period 1860 to 1955, produced local contamination of moderate to severe magnitude, chiefly on private lands. However, unmined mineralized rocks also contribute the same suite of heavy metals to the environment. Fortunately, the widespread carbonate minerals (chiefly calcite) in sedimentary rocks, alluvium, and altered igneous rocks neutralize and naturally mediate drainages that otherwise would have a much greater environmental impact. Despite some local drainage problems (at the scale of acres to hundreds of acres), the general geochemical condition of the environment is good.

Heavy metal contamination of the environment has been studied by scientists, and reported in abundant and diverse literature that cannot be reviewed here. Fortunately there are several reviews (Nriagu, 1979; Nriagu, 1980a; Moore and Ramamoorthy, 1984; Davies, 1983; Nriagu, 1984). Some of the environmental contaminants in the Prescott National Forest area have been studied by various State or Federal agencies, but many others may remain unidentified. The environmental impacts of heavy metals are complex scientifically and politically. For instance, the toxicity of arsenic is highly dependent on oxidation state, which has not been determined in our work, and toxicity of copper is high for plants and invertebrates, but not acute for humans. Toxicity and contamination are discussed elsewhere (Moore and Ramamoorthy, 1984; EPA, 1986; ADEQ, 1995), but impacts and regulatory issues will not be addressed here. A report assessing Arizona Water Quality (ADEQ, 1994) reports "violations" of arsenic, beryllium, cadmium, copper, lead, mercury, and other metals at several of the mines and river segments discussed in this report. The results of our work are generally in agreement with the ADEQ summary, but ADEQ uses more specific criteria (and in many cases lower analytical levels) than we employ here.

In an attempt to promote clarity and to focus on priority issues, magnitude and geographic scale of geochemical features described here will use terms in a *relative* rather than absolute sense. The magnitude of chemical concentrations in solids are generally expressed in parts per million, and for emphasis the terms "anomalous", "high", and "very high" will be used. Anomalous is a term commonly used by geochemists (Rose and others, 1979) to describe concentrations that are distinctly higher than normal; in statistical terms, this generally equates to approximately the 75th to 90th percentile interval. High is used to describe the next higher anomalous values, approximately 90th to 95th percentile. Very high is the highest range observed *in this study*, equivalent to 95th to 100th percentile (top 5 percentile). For geographic size, the term "local" will be used to describe features characteristic of small areas approximately the size of a mine site on several mining claims (each approximately 20 acres, and most sites being less than 1 square mile). The term district (taken from mining district) is used to describe intermediate-scale features, approximately 3 to 10 square miles or 2,000-6,000 acres. Watershed is the next larger scale, describing headwater areas of roughly 10 to 100 square miles, or approximately 6,000 to 60,000 acres. For comparison, the Prescott National Forest comprises approximately 1.25 million acres.

This study was initiated in May of 1994 as part of the USGS Mineral Resource Surveys Program of mineral-resource and mineral-environmental assessments. This work was done at the request of the U.S. Forest Service and helpful suggestions were made by local and regional Forest Service staff. The primary goal of this study is to provide geochemical descriptions of mineral deposits and related topics for use in ecosystem management by the U.S. Forest Service and other public lands agencies. Secondary goals are description and interpretation of processes that disperse contaminants in the environment and identification of natural geologic processes that mitigate contamination.

THE STUDY AREA

The focus of this study is the Prescott National Forest, but nearby areas also have been sampled and considered. The land status is complex and has changed in numerous ways over the past 125 years. There are substantial blocks of private land inside the broad outline of the Prescott National Forest, carved out as homesteads and as patented mining claims. The broad intermountain valleys adjacent to the Forest include public lands administered by the U.S. Bureau of Land Management and the State of Arizona, as well as private lands. To simplify subsequent discussions, land status generally will not be mentioned. The broad area under discussion (fig. 2) will be called the Prescott National Forest area. Many of the mines, prospects, mills, and smelters under discussion were established long before the Forest was established in 1898 (technically as Prescott National Forest Reserve, prior to becoming Prescott National Forest in 1905).

Climate, mentioned many times in this report for its important role in geochemical processes, needs to be reviewed briefly using descriptions and tabulations in Sellers (1960). This rugged area of mountains and broad valleys is characterized by a generally semi-arid climate, but there are large local variations produced chiefly by differences in elevation. Elevations range from 7,971 feet at Mount Union in the Bradshaw Mountains south of Prescott, and 7,743 feet at Mingus Mountain in the Black Hills west of Jerome, to less than 2,500 feet in Black Canyon at the southeastern edge of the study area near Bumble Bee. Four major vegetation zones are represented in this span of more than 5,000 feet. The mountains, at elevations above about 6,000 feet, tend to be pine forests of ponderosa pine, spruce, several varieties of firs, and aspen (Elwood, 1976). A lower mountain zone is characterized by juniper, pinyon pine, and Gambel oak. Somewhat lower, from about 6,000 to 4,000 feet, the foothills are characterized by chaparral with manzanita, mesquite, mountain mahogany, and numerous other shrubs. The Lowest elevations, below about 4,000 feet, are characterized by desert vegetation such as cholla, saguaro, and sparse shrubs. Riparian zones, characterized by willows and similar shrubs, are well developed along the larger creeks and rivers and represent a unique and important life zone that transcends the general life zones that are related to elevation and precipitation.

Precipitation data are available for seven stations in or near the Prescott National Forest area (table 1), but do not document the more extreme locales. Mean annual precipitation at elevations of 6,000 feet or more (as at the Crown King station) is 27 inches or more (fig. 3). The valleys, such as the Montezuma Castle station, receive less than 12 inches of precipitation. Winter snow is common at high elevations, but rare in the valleys. Precipitation across the area tends to be highest in winter and late summer months. Summer storms during the monsoon can dump 0.2 to 0.5 inches or more of rain in a few hours. Local differences can be pronounced both in individual storms and in long-term trends. Residents living in the mountains above Walker (at approximately 7,500 feet) told us they receive about 120 inches of snow in winter and about 25 inches of rain in the summer. The thick stands of alpine fir thrive in this moist microclimate. The valleys near Cleator and Bumble Bee contain healthy desert flora and appear to get considerably less than 12 inches of precipitation, but the discrepancy probably is caused by higher evaporation in the valleys as compared with adjacent mountains. The maps of annual precipitation (Sellers, 1960; fig. 3) show in general how precipitation varies in the area, but are not as faithful to local differences as the distribution patterns of flora.

GEOCHEMICAL METHODS

Sample collection

We have utilized 5 media to characterize the environment and aspects of geochemical mobility: 1). altered and mineralized rock samples from outcrops and from mine spoil dumps; 2) stream sediment from active stream channels, both randomly and specifically located; 3) soil and the uppermost 0-5 cm of decomposed rock (soils are not well developed in this arid climate); 4) water from streams, seeps, or flowing wells; and 5) specifically collected grab samples of mineralized rock, tailings, or slag. Also included in this study are new multi-element analyses of more than 1,000 stream-sediment samples retrieved from USGS-maintained archives of the NURE (National Uranium Resource Evaluation) program (Clark, 1979). Rock, stream-sediment, and soil samples were processed and analyzed by standard USGS methods, including pulverizing to -100 mesh in alumina-faced grinders, drying if necessary at 105 °C, and analysis by USGS chemists in Lakewood, CO. Inductively coupled plasma, atomic emission spectroscopy (ICP) was utilized for the determination of 40 major and trace elements. Additional analyses for 10 heavy and precious metals were made using a partial extraction technique, followed by ICP analysis, that yields improved lower limits of determination for many elements of interest (Ag, As, Au, Bi, Cd, Cu, Mo, Pb, Sb, and Zn). Gold also was determined by graphite-furnace atomic absorption spectroscopy in a method that has a lower limit of determination of 0.002 parts per million (2 parts per billion). These analytical methods are described by Arbogast (1990). Water samples were filtered through a 0.4 micrometer filter, acidified with 1:1 HNO_3 in the field, and analyzed by ion chromatography for anions. Unfiltered water samples were analyzed by ICP-mass spectrometry (ICP-MS) for trace elements (Meier, unpublished research method).

Geochemical Analyses

All chemical analyses, unless otherwise reported, were determined by chemists of the USGS, Branch of Geochemistry, in Lakewood, CO. In most cases the methods are standard ones that are routinely applied to thousands of sample per year, and monitored by an in-house quality assurance program. The methods and their limits of determination are summarized in table 2. The complete database of analytical results are reported in digital form by Nash and others (1996a, 1996b). Pertinent results are summarized in tables 4 to 10 in this report.

MINING DISTRICTS AND MINERAL DEPOSIT TYPES

The framework for these geochemical descriptions will be mining districts, as described by Keith and others (1983), and a simplified classification of mineral deposit types. (We will use the term 'mineral deposit' to cover both ore deposits and prospects with no inference of economic value). The districts (fig. 4) defined by Keith and others (1983) are useful for this study because they are based on geologic criteria with the intent of geographically portraying areas having metallic mineral deposits of similar age and style of mineralization (deposit type). Because experience elsewhere has shown environmental signatures of mineral deposits to be strongly dependent on geology and deposit type (Plumlee and Nash, 1995), it is likely that mines and prospects in a district (as defined by Keith and others, 1983) will have similar signatures, allowing discussion by district or deposit type rather than by individual mine or prospect.

Pertinent geologic and deposit information for the districts is summarized in table 3. Production figures are given to suggest the composition of ores and the amount of disturbance; one can assume that a district with a record of large production will have also created more waste dumps and mill tailings than a small or unproductive district. The Verde district had by far the largest production (and value), followed by much smaller amounts at Walker, Mt. Union, Peck, and Copper Basin. Most of the larger mines had their own processing facility, but some mills and smelters served one or more districts. Also, from about 1900 to 1930, local railroads carried ores from several districts to the Valverde mill and smelter at Humboldt.

Five general types of metallic mineral deposits are known in the Prescott National Forest area (table 4); this classification is similar to, but simpler than that used by Keith and others (1983). The deposit types considered here include: 1). massive sulfide deposits of base and precious metals (as at United Verde near Jerome); 2) porphyry-copper deposits of copper, molybdenum and minor precious metals (as at Copper Basin); 3) polymetallic vein deposits of base and precious metals (as near Walker); 4) vein deposits of gold (as near Cherry); and 5) placer deposits of gold (Lynx Creek). A few other types of ores are known but occur at only a few localities and will not be discussed here. The distribution of 296 known mines and prospects, classified by these five types, is shown on fig. 5; the names and locations of major mines mentioned in this study are shown on figure

2. Because of fundamental geologic controls in the formation of these ore deposits and prospects, they tend to form in belts or clusters that have geologic rock types, ages, or structures in common.

EVOLUTION OF THE MINING INDUSTRY

Mining History

The chronology of mining in the region is important because ore-recovery technology changed substantially during period of about 1875 to 1953, when the last major mine (Iron King) closed. There were no environmental regulations during the early years. Many procedures that were convenient and inexpensive would not be allowed by regulations and industry practices of the 1990's. Even brief inspections of the mines, mill sites, and smelters leads any observer to conclude that much of the contamination recognized today could have been avoided or minimized if the original practices had given more consideration to long term effects. For example, placement of waste dumps, tailings, and slag in stable sites rather than in the arroyos and streams that were typically selected because they were downslope from the mine or mill, would have greatly reduced contamination.

The first mining was in about 1863 when placer miners from California found gold in several of the streams draining the Bradshaw Mountains (Lindgren, 1926). Mining of significance started in about 1875 with the location of oxidized silver-gold lodes in the Bradshaw Mountains, as in the Crown King district. Mining of the oxidized, silver-rich lodes was largely finished by about 1885, but some mining continued into deeper, unoxidized sulfide-bearing ores. The world-class United Verde massive sulfide deposit was discovered in 1894, and the extremely rich United Verde Extension copper deposit was discovered nearby in 1914. In the 20th Century, mining evolved toward a few large operations, notably at United Verde, United Verde Extension, and Iron King. These large copper mines ceased operation in the 1950's and there has been only minor, small-scale mining since then (except at the re-opened McCabe mine). Essentially all of the mining was underground, but some of the mines also had a stage that developed glory holes that extended to the surface. The underground mining created smaller waste dumps of altered and weakly mineralized rocks than if open-pit methods had been used, but the dumps are nonetheless a legacy that will continue to be an environmental factor in the future. The mined waste is broken, porous rock that is highly reactive to percolating surface water, especially if sulfide minerals are abundant. In the presence of water and oxygen, sulfide minerals will decompose and create sulfuric acid.

Milling and Smelting History

Any ore that was mined had to be beneficiated before it could be sold, and those processes were either done at the mine site or at a distant site, depending upon transportation costs and available technology. In the earliest years of mining, before 1881, ore and concentrates were hauled to the Colorado River and eventually carried by ships to San Francisco, CA or to Wales (Lindgren, 1926). Railroads helped greatly in the latter part of the 19th Century, but there always was the incentive to concentrate the valuable metals near the mines. To that end, two general technologies were employed: milling and smelting. Mills, located at the mines or central to several mines in a district, processed the ores through several stages of grinding, riffling, amalgamation, or cyanide-extraction to produce a metal-rich concentrate and a tail of fine sand having relatively low metal content--but still much higher in sulfide minerals and heavy metals than normal rocks. The tails were typically a slurry that was poured down the hillside or into a gully, and at several sites poured over a cliff into a river such as the Hassayampa. Milling technology evolved over the years, with significant advances known as floatation (that allowed selective concentration of various sulfide minerals such as galena (PbS), sphalerite (ZnS), and chalcopyrite ($CuFeS_2$) and cyanidation (that allowed selective dissolution of minerals containing gold or other metals), with improved metal recoveries and decreased heavy metal concentrations in tailings.

Smelting and roasting of ores have been used since antiquity to recover metals of value to society. At least 10 small smelters operated in various districts in the area before about 1900 and three large smelters operated from about 1900 to the 1950's. The very earliest operations employed open beds for roasting (burning) sulfide minerals (Rickard, 1987). The open bed roasters created noxious plumes of smoke laden with metals that killed vegetation and livestock, according to reports on other similar roasting operations in Montana and Ontario (Hutchinson, 1979; Fell, 1979; Jeffries, 1984). In about 1890, closed smelters were developed with somewhat better control on metal recovery and emissions. The smelters used several stages of roasting, melting, mixing with fluxes, oxidation and reduction to produce a matte that was rich in a metal of value, chiefly copper (Howe, 1885; Fell, 1979). Deleterious elements were removed in two ways: volatile elements such as sulfur and arsenic were deliberately oxidized and sent up a short flue into the atmosphere, whereas heavy elements such as iron and zinc were concentrated into a molten slag. The early smelters employed short stacks with no equipment for collection or condensation of hazardous materials, whereas by 1918 the Clemenceau smelter boasted the tallest stack in the world at 425 feet (Rickard, 1987) with design improvements to reduce emissions. The slag was poured into vessels or onto the ground as waste. For most base metal ores, iron and zinc were concentrated into the slag, whereas the valued copper sank as a copper-sulfur melt. Depending upon parameters such as the sulfur:arsenic ratio, arsenic would be driven off as a vapor by oxidizing the mix, or it could move into the matte with copper. Most sulfur was driven off as a vapor, but some was desired for the liquid matte. Analyses of slag (Howe, 1885) show as much as 12 percent zinc (zinc was not a desired metal in the 19th century), and 0.5 percent copper (an inefficient recovery of copper). Details on the behavior of mercury, cadmium, lead, and other heavy metals are not given by Howe (1885), but we now know that substantial amounts of these metals are released in fine particulate matter in smelter smoke (Jeffries, 1984; Pagenkopf and Maughan, 1984). Smoke contamination must have been especially abundant in the early days of open roasting, improving somewhat in later closed smelters with short stacks but no dust collectors.

The sites of historic mills and smelters are poorly recorded in the published literature and modern electronic databases. Some early writers, such as Lindgren (1926) mentions them in descriptions of mining districts, and a few historians such as Rickard (1987) have tracked old records to compile helpful reviews. Collections of old photographs, as at Sharlot Hall in Prescott and the Jerome State Historic Park provide excellent factual records. Databases such as the MILS system of U.S. Bureau of Mines are very complete for many aspects of the U. S. mining industry, but have very few entries for old mills and smelters (N. J. Niemuth, AZ Dept. of Mines and Mineral Resources, written commun.,1994) We have located 11 smelter sites (fig. 6) and collected samples from 8 of them for chemical analyses.

CONTAMINATION RELATED TO SMELTERS

Many studies have documented the nature and spatial extent of contamination related to smelters. One of the earliest observations was sick or dead trees within several miles of smelters in the late 19th Century (Fell, 1979; Hutchinson, 1979). At least as early as 1907 chemists were called upon to determine what was killing vegetation and livestock, as in the vicinity of the smelters at Anaconda, MT and other locations in the western U.S. (Haywood, 1907). Pioneering studies by Harkins and Swain (1907) demonstrated that arsenic was killing cattle (despite findings of only small amounts of arsenic in organs of dead cattle). The effects of 19th and 20th Century smelters have been described in many reports (Nriagu, 1979; Hutchinson, 1979; Pagenkopf and Maughan, 1984; Jeffries, 1984). A study in 1906 noted injury to trees over a radius of 13 to 15 miles from the Anaconda smelter in Montana (Haywood, 1907). Biologists have documented the effects through studies of soils and vegetation (Buchauer, 1973; Wood and Nash, 1976; and others). Geochemists have mapped the distribution of pollution from smelters, in part to distinguish it from exploration targets; Canney (1959) documented a plume of contamination extending more than 7 miles from a smelter at Coeur d'Alene, Idaho. Similar findings of pollution related to old or modern smelters raises the question: what is the effect of smelter smoke and slag around the numerous smelters in the Prescott National Forest area? For an introductory study of smelters we sampled slag on slag piles, slag from alluvium, and soils from uppermost horizons that might reflect deposition from smoke.

The locations of 11 smelters identified in this study and mentioned in the literature (Lindgren, 1926; Rickard, 1987) are shown on figure 6. Several of these sites were occupied by more than one generation of smelter (Rickard, 1987) if replaced by newer technology or rebuilt after a fire. Stacks remain at Humboldt and Mayer, buildings remain at Clarkdale, and concrete foundations are visible at most sites. Slag piles are evident at all sites, and range in size from huge at Clarkdale to obscure at Stoddard's Ranch. Limited access to private property and other factors precluded close study any of the sites. At Stoddard, Big Bug (Henrietta), and Copper Chief, clasts of slag were found in arroyos, and presumed to be derived from those historic smelters. Large amounts (10-20 percent) of smelter slag were observed in recent alluvium in the Agua Fria drainage 0-10 km south-

southeast from the Humboldt (Valverde) smelter, and lesser amounts of slag were observed in alluvium in Copper Basin Wash, 0-5 km south of Copper Basin, and in Lynx Creek, 0-2 km east of the Howell's smelter near Walker. Slag is abundant in the bed of the mine railroad between the United Verde mine and Clarkdale; the slag probably came from the original smelter at the United Verde mine site near Jerome. Smelter slag has been used in construction of railroad tracks in many parts of Arizona (N.J. Neimuth, oral commun., 1994).

Soil Geochemistry as a guide to Contamination by Smelter Smoke

Smoke from smelters is a likely source of contamination and could continue to be a problem if soils in the vicinity of smelters retain heavy metals 50 to 100 years after deposition. There are no published studies of such contamination in Yavapai County, but elsewhere historic and modern smelters have been shown to create large plumes of contamination (Canney, 1959; Buchauer, 1973; Wood and Nash, 1976; Hutchinson, 1979). Soils and vegetation contain high concentrations of many metals for distances of 5-10 miles from smelters. Early chemical studies (Harkins and Swain, 1907) of arsenic poisoning related to smelters at Anaconda, MT, contained grim descriptions of smoke and its effects on livestock. The devastating effects of smelters at Sudbury, Ontario, were possibly the worst in the world (Hutchinson, 1979; Jeffries, 1984). The magnitude and distribution of the contaminants depend on factors including ore composition, technology, topography, and prevailing wind directions. Vegetation tends to be killed by smelter emissions, but that effect is not evident in the Prescott National Forest area (or probably most vegetation has recovered). Systematic, quantitative botanical surveys adjacent to smelter sites could provide useful information.

Geochemical results for 60 soil samples collected in this study provide a preliminary indication of the magnitude of contamination created by smelter smoke and its spatial relation to smelter sites. Because the number of samples collected is small, there is a large uncertainty in the statistical parameters. Also, only a small part of the area of possible influence was sampled, and that was done with the questionable assumption that predominant wind direction is to the northeast. These initial samples suggest that substantial amounts of arsenic, cadmium, copper, lead, and zinc were added to the upper layer of soils. The results for soils are summarized in Table 6, and shown on figures 7 to 10.

Concentrations of heavy metals span a large range, and some are very high. The high values approach those determined for mill tailings. One sample collected near Clarkdale contained 760 ppm Cu, 310 ppm Pb, 710 ppm Zn and 120 ppm As, and may reflect more contamination than from smelter smoke alone. Concentrations in the range of 100 to 600 ppm for Cu, Pb, or Zn are very high geochemically, about 5 to 10 times normal background concentrations seen in apparently uncontaminated deep soil samples.

Anomalous amounts of heavy metals are suggested by three aspects of the soil data. 1) Concentrations tend to be high or very high in the vicinity (1-3 miles) of smelter stacks, and decrease with distance from the suspected source. 2) Concentrations in surface soils (top 2 inches) are higher than in deep soils (about 5-8 inches); at most sites of paired surface and deep soil samples, the concentrations of heavy metals in surface samples are about twice that in the deep soil. 3). Maps of element concentrations show that values greater than the anomaly threshold occur up to about 10-12 miles from the smelter sites. The anomaly thresholds are defined as slightly lower than arithmetic mean values because the mean is highly influenced by the high percentage of contaminated samples; the threshold values are selected by considering the means for both surface and deep (uncontaminated) samples. The important question, however, is not the concentration selected as anomalous, which may be debatable, but the significance of the many heavy metal concentrations that are far above the threshold.

Slag chemistry

Slag contains very high concentrations of heavy metals, especially lead and zinc (table 5). Copper also is highly concentrated, despite it being the element of prime interest in the concentration processes. Arsenic, antimony, and sulfur concentrations are quite high, even though these elements were supposed to be volatilized in the roasting process. No gold was detected in significant amounts, but silver concentrations in the range of 45 to 260 ppm would imply that valuable amounts were lost to the slag. It is clear that the 19th Century smelters were not very efficient.

Slag is a dense, vitreous material that appears to be refractory. Conventional wisdom holds slag to be inert and thus useful as roadmetal and railroad track ballast. Most slag that we have seen, whether on original slag piles or as cobbles in stream sediment, appears to be fresh and minimally altered. Unlike rocks and ore samples that show rinds of oxidation and mineral alteration from weathering processes, only a small amount of slag showed such alteration megascopically; microscopic alteration is possible and would require special tests for confirmation. Undisturbed piles of slag appear to be relatively impervious to rainwater and probably are the least likely to react and release heavy metals. However, cobbles of slag in active alluvium are abraded during storm events and this will enhance the reactivity of surfaces and add contaminated fine particles to the sediment load. Our laboratory tests (described later) suggest that gravel-sized slag fragments release very little heavy metal to water or alkaline solutions, but that acidic waters (even dilute acids) are capable of extracting significant amounts of heavy metals.

CONTAMINATION RELATED TO MILL TAILINGS

The finely ground, sand-like, tailings that are produced in the beneficiation of ore pose a significant environmental risk because the minerals are highly reactive when exposed to air and water. Mechanical erosion of tailings, evident in most old impoundments in the Prescott National Forest area, compounds the problems associated with these fine-grained materials because it both disperses them downstream and enhances chemical reactions. Although the milling processes were designed to remove ore minerals, the tailings nonetheless retain elevated concentrations of heavy metals. Also, milling technology in the 19th Century was not efficient and left more metals in the tailings than do modern methods. Indeed, many 19th Century tailings in the Western U.S. contain such high metal concentrations that they often are reprocessed, at a profit, by modern techniques. Whether metal leaching occurs *in situ* or during mechanical transport during flash floods, metals from tailings will tend to enter surface or groundwater.

The locations of 31 millsites and tailings impoundments are shown on figure 11. The size of the tailings piles range from huge (many acres, easily shown on topographic maps) to small (tens of square feet). The largest tailings impoundment is 1 mile east of Clarkdale, where tailings from the Clarkdale mill (United Verde mine ore) were placed into an abandoned channel and oxbow lake along the Verde River. Other notably large and precarious tailings piles are at Humboldt and at the Binghampton mine. Over the years flash floods have cut into these ponded sands and carried them into the Agua Fria River. Several mill sites (cement foundations with a distinctive series of downward steps) contain few or no tailings. One large, fairly new metal-framed mill (c. 1920's?, name uncertain) is on a cliff above the Hassayampa River approximately 0.5 miles west of Hassayampa Lake. No tailings are visible, and one can only guess that long ago the tailings were swept down the river. Tailings at the old Senator millsite are in a perennial stream and create an obvious plume of iron stains and less obvious acid waters. Most of the mill tailings in the Prescott National Forest area are on private property (commonly patented claims). Two medium-sized tailings dumps on Prescott National Forest land near Cleator (Golden Turkey and Golden Belt mines and mills) are immediately adjacent to, and are eroding into, Turkey Creek.

The chemical and mineralogical composition of the tailings reflect the character of the ore processed and the technology of the mill. Simple visual inspection of many tailings suggests that there is a substantial range in mineralogy, often reflected in reddish hues from iron oxides or grays from sulfides, both from site to site and between layers in the ponded tailings. Some tailings contain carbonate minerals from altered wallrocks, which would play an important role in neutralizing acid generated by oxidation of sulfide minerals in the tailings. Chemical analyses of the tailings are an easy, effective way to characterize their potential contamination; mineralogical analyses would be more difficult to accomplish but would provide important information. Chemical analyses of 40 tailings samples from the Prescott National Forest area are summarized in table 7.

The composition of waters draining from tailings impoundments differs greatly from site to site according to the few detailed studies that have been published (Blowes and Ptacek, 1994; Frind and Molson, 1994; Jambor, 1994). The chief factors are climate, permeability, sulfide mineralogy and abundance, and bedrock character below the tailings. Typical flow rates are very slow (roughly 1 to 10 feet per year), such that an increment of water can take tens of years to move through a 10- to 30-foot thick tailings impoundment (dimensions typical of those in the Prescott National Forest area). Details of reactions are too complex to review here. At least four factors influence the amount and type of drainage. 1) Mineralogy: the amounts and kinds of sulfide minerals are important criteria for anticipating acid generation, and mineralogy largely determines reactivity in the surficial environment. Tailings that are mostly comprised of oxidized minerals (oxides and sulfates) are much less likely to release metals to drainage (Alpers and others, 1994) than sulfide-rich tailings that will eventually oxidize, generate acid, and release metals. 2) Chemical composition: analyses show a range in elemental composition, and tailings with higher content of arsenic, cadmium, and lead are especially problematic. 3). Climate: exposure to seasonal rain and snow will enhance chemical reactions and higher amounts of moisture will increase the possibility of metalliferous drainage. 4). Physical stability: mechanical erosion, especially into a stream, will enhance reactions and release of metals. Special equipment is required to sample and characterize drainage from tailings piles. We could only make qualitative tests on pore fluids and found that several tailings contain highly acidic fluids.

SOLUBILITY OF METALS IN TAILINGS AND SLAG

Solubility of metals in tailings and slag is perhaps more important than the concentration of metals in these materials. If the metals are insoluble and non-reactive, as some assume for slag, then there is no problem for the environment. We made preliminary laboratory tests on natural materials to estimate their reactivity to water, acidic, and alkaline solutions. The materials were samples of 1) typical slag (crushed to sand size as it is in drainages), 2) untreated tailings, and 3) efflorescent mineral crusts taken from the top layer of tailings and from dried puddles on mine dumps.

Leach tests were made in the laboratory using three solutions that resemble natural waters: 1) pure water (deionized water); 2). weakly acidic solution with pH 3.1 (1 drop concentrated sulfuric acid per liter); and 3). carbonate-buffered solution saturated with $CaCO_3$ with pH of 8.4. Natural samples were immersed in 250 ml of solution and shaken for 2 to 24 hours, the solution decanted, filtered (to pass 0.4 micron) and analyzed by ICP-MS. These three solutions were selected as being similar to natural waters; the sulfuric acid solution resembles acid drainage from mines, dumps, and tailings. Results are summarized in table 8. They show that the weak acid leaches dissolved large amounts of metals, whereas carbonate solution and water alone took very little into solution. Shaking the materials for longer time intervals increased the amounts of metals by about 20-40 percent when the time was doubled (4 hours vs. 2 hours), but longer times had less effect. Leaching of finer-grained materials (pulverized) yielded higher metal concentrations than did coarser equivalents.

Leaching tests with pure water dissolved substantial amounts of calcium and magnesium, but only very minor amounts of heavy metals from samples of tailings and slag.

Leaching tests with very weak sulfuric acid dissolved much more heavy metal than did pure water or carbonate solution, approximately 5 to 1,000 times more. The sulfuric acid leaches dissolved significant amounts of heavy metals from slag (notably iron, copper, cadmium, lead, and zinc). These initial leaching tests raise questions about the stability of slag in the surficial environment: it may not be nearly as inert as normally claimed.

Because slag contains higher concentrations of metals than do ores (many are in the 1 to 5 percent range), leaching of even a small percentage of the metals could mobilize substantial amounts of metal.

Leaching of efflorescent crusts with either acid or pure water dissolves the minerals and yields a solution with very high amounts of metal, especially copper, lead, and zinc. The water leach tests emulate what happens during episodic storms, which would dissolve the crusts and send a burst of metal-rich waters down the drainages during the first part of the storm runoff. Acidic solutions are especially effective at dissolving and transporting metals from the crusts.

Extrapolating these results to natural conditions is not simple as there is a high uncertainty in the ratio of material to water, which strongly influences the final concentration in the water. If the amount of solution is low, relative to the volume of tailings or slag, the resultant drainage could contain high and hazardous amounts of metals. If the amount of solution is high, as in the case of the Verde River washing slag at Clarkdale, the concentration of metals is presumed low. Other factors being equal, acidic solutions will mobilize much more metal than neutral or alkaline waters; this acidic condition can develop by oxidation of sulfide minerals in the tailings or slag. Even a drainage with low metal concentrations could pose problems : the cumulative effects can be significant and initially low metal concentrations can be raised to hazardous levels by evaporation or other processes.

CONTAMINATION RELATED TO MINES AND WASTE DUMPS

Metallic mineral deposits are naturally occurring materials from which elements or commodities of economic value can be extracted. With very few exceptions, unusually high concentrations of metals must be present to meet the economic definition. The ore minerals and associated gangue minerals can be an asset (to a prospector or mining company) or a liability. Prospects, which are undeveloped ore deposits or sub-economic deposits because of size, grade, or location, are not currently valuable but have the chemical composition of an ore-grade deposit. In recent years, the adverse effects of mineral deposits on water quality, human health, and on wildlife have been emphasized. Because mineral deposits tend to have consistent mineralogical, chemical, and geologic characteristics according to their mode of origin, these characteristics can be utilized to predict environmental signatures and potential for creating contamination when influenced by weathering processes or mining (Plumlee, and others, 1994; Smith and others, 1994; Plumlee and Nash, 1995; du Bray, 1995).

The chemical composition of the mineral deposits in the region is well known from geologic by studies by Lindgren (1926) and by numerous recent studies. We collected representative samples from mine dumps to confirm chemical compositions (Table 8). Select samples from mine workings and mine dumps are described and chemical analyses reported by Neubert (1995). Available information indicates that compositions of the deposits in the study area are similar to others of the same type around the world, suggesting that results of geochemical studies elsewhere can be applied here (subject to local climate and geomorphic conditions). Most of the Prescott deposits are rich to very rich in base metals and many are rich in sulfide sulfur (Table 8). Field observations suggest a range in oxidation state of sulfide minerals; further systematic studies of sulfide and sulfate concentrations of ores and waste rocks are needed. Also, systematic study of some trace elements such as selenium and tellurium would clarify the potential for hazards associated with them.

Waste rocks in mine dumps pose problems that are similar to mine drainage, although technical details differ (Ritchie, 1994). Acid rock drainage is especially problematic at large open pit mines that create large waste dumps containing substantial amounts of pyrite. Dumps typically have low permeability from stratified zones containing abundant clay and other fine-grained materials. The low permeabilities limit flow rates to a few feet per year. Oxidation of sulfide minerals is slow (limited by input of oxygen) but continues for tens or hundreds of years (Ritchie, 1994). Acid rock drainage from dumps in the Prescott National Forest area probably is roughly equal in magnitude and composition to that from mine workings. At many sites mine drainage flows into dumps, and the two drainages are not easily isolated for characterization without going into abandoned mine tunnels. The largest volumes of sulfidic waste, which are in the Verde district, are derived from massive sulfide deposits. A fair approximation of dump size can be made from production statistics (table 3), with adjustment for degree of pre-mining oxidation if an estimate of sulfide tonnage is required.

CONTAMINATION FROM NATURAL SOURCES

Unmined, natural exposures of mineral deposits and associated rock alteration can contribute substantial amounts of acid and heavy metals to the surficial environment (Runnells and others, 1992 Miller and others, 1995a; Miller and others, 1995b). In fact, this natural contamination is generally what prospectors use to find mineral deposits, such as through discovery of eroded clasts of ore-bearing rocks or by geochemical analysis of stream sediments shed from the exposed mineralized rocks. Analyses of exposed mineralized rocks and overlying soils from the Jerome, Walker, Copper Basin, and Crown King districts reveal high to very high concentrations of arsenic, copper, iron, lead, and zinc: the same suite of elements in the ores, at lower concentrations but present over many square miles.

Laymen tend to believe that only mines produce acid drainage and heavy-metal contamination, but unmined rocks can produce similar effects in several scenarios. One is exposed and weathered ore; in an area that is a thoroughly prospected as the Prescott National Forest area, this is probably unlikely at this date, but would have happened in the past and would have shed geochemically anomalous alluvium into streams and valleys. A second scenario is weathering of small veins and uneconomic extensions of orebodies, either in the past or today, and possibly after nearby ore was mined. A third scenario is weathering of dispersed alteration that typically surrounds orebodies. This rock is typically reddish in the weathering zone, where original sulfide minerals are oxidized, as is quite evident for approximately 1 mile beyond the massive sulfide mines at Jerome, and in the unmined rocks around the mines in the Copper Basin and Crown King districts. The concentrations of sulfide minerals and heavy metals in rocks subjected to weathering in scenarios 2 and 3 are generally not as high as in ore (table 9), but are significant for many metals such as arsenic, copper, iron, lead, and zinc. Because large volumes of mineralized rocks are involved in weathering processes, the cumulative contribution to the surficial environment can be significant. The contributions of unmined, natural sources to contamination should be determined quantitatively for calculating geochemical backgrounds, but the procedures are complicated and subject to large errors (such as estimation of volume of mineralized rock that has a certain composition).

CONTAMINATION EXPRESSED IN STREAM ALLUVIUM

The composition of alluvium in streams tends to closely reflect the composition of rocks, or contaminants, in the basin above. Thus, for decades prospectors and geochemists have utilized stream sediments as a prospecting tool (Rose, and others, 1979). By the same logic, the chemistry of stream sediments can be used to monitor the dispersion of metals from mines, dumps, mills, or smelters. A database of chemical analyses for more than 30 elements in 1,123 samples of stream sediment was generated for this study. It is very useful for characterizing the geochemical background of the Prescott National Forest area and for outlining areas having anomalous compositions attributable to undiscovered mineral deposits or to contamination from mining. A summary of the stream-sediment geochemistry is given in table 10. The distribution of the sample sites is shown on figure 12.

The maximum values are much higher than expected of normal rocks (table 10). Spatial and statistical analyses show that the high values for many base metals, gold, silver, arsenic, and antimony, occur in the vicinity of known mines and prospects, and occur together in elemental associations that closely resemble those in ore deposits. For this database, nearly all of the anomalous sediment compositions are from sites downstream from known mines and prospects (as shown on fig. 5 or on 1:24,000 scale topographic maps). The spacing of most sites is not sufficient to indicate whether the sources are mines, dumps, mills, smelters, or unmined altered rock. The distributions of anomalous sites (figs. 14-18) closely mimic the major mining districts. This contrasts with observations in most areas of the western U.S. where regional stream-sediment geochemistry delineates many areas that are favorable for undiscovered mineral deposits, in addition to the known districts (e.g., Nash, 1988). For the Prescott National Forest area, the stream-sediment data provide a good indication of the many areas where base metals are being dispersed from mines and associated infrastructure, and only a few sites reflecting undiscovered or undeveloped mineral deposits.

CONTAMINATION EXPRESSED IN WATER CHEMISTRY

Field tests and chemical analyses of ground- and surface-water samples show a wide range in water quality in the Prescott National Forest area. The major findings of our reconnaissance water sampling program are summarized in table 11. We collected 89 samples and made more than 150 field measurements on these and other waters for pH and conductivity using conventional portable meters. Two samples were collected: 1) untreated, unfiltered for analysis of major and trace constituents, and 2) filtered through 0.4 micron filter and acidified with 1 ml of HNO_3 for analysis of major cations.

Detailed hydrologic and geochemical interpretations of the water chemistry are beyond the scope of this report. Brief comments will be made to describe some of the unusual features in a geologic context and comparison to some National water quality summaries (Hem, 1970; EPA, 1986). Water quality standards for Arizona (ADEQ, 1995) are very specific as to use and type of stream, but the values are roughly the same as National standards.

The location of water-sample sites and the magnitude of metal concentrations are shown on figures 19 to 22. All of the very highest metal values are from local drainages that are very acidic (pH 2.2-4.2). The volume of flow in the highly acidic drainages that we observed is small (less than about 5 gallons per minute), and there is evidence that the water quality is improved a short distance downstream by dilution with other streams or by neutralization. The drainage sites of greatest concern actually have lower concentrations of metals (denoted by diamonds) but have more flow volume--thus the "loading" is higher (loading is the product of concentration times flow volume). Loading cannot be quantified here because no reliable flow measurements were made.

Acidic conditions, indicated by pH values in the range of about 2 to 5, are not common in the Prescott National Forest area (fig. 19). We searched for drainages with acidic water, and sampled them whenever we could. We sampled only 13 acidic drainages, and this number overestimates the incidence of acidic drainage because we biased sampling to include the acidic type and several sites were resampled. More importantly, the flow volume the acidic drainages is very low and highly localized, representing a very small fraction of the flow in the watershed. Observations of drainage flow and measurements of pH in the field show that most acidic drainages from old mine workings in sulfidic rocks and from waste dumps flow less than 100 yards before disappearing into alluvium. In nearly all cases alluvium and altered rocks adjacent to mines contain sufficient calcite to neutralize the initially acidic waters. Good illustrations of this natural remediation include the massive sulfide mines of United Verde, Binghampton, Blue Bell and DeSoto. Water draining the old United Verde mine comes out of the drainage tunnel as a neutral water, but does contain high sulfate and earned the name "Bitter Creek." Flow through Paleozoic limestones appears to effectively neutralize the United Verde waters, but we did not make any definitive studies underground. Water draining the DeSoto mine is immediately neutralized by calcite-bearing metavolcanic rocks. The water is collected at the portal and piped to nearby troughs for use by livestock.

A few local acidic drainages in the Prescott National Forest area carry high to very high quantities of base metals, as is common in oxidizing base-metal sulfide mineral deposits (Plumlee and others, 1993; Plumlee and Nash, 1995). Samples collected adjacent to deposits (hundreds of feet distant) contain low levels of most base metals and have near neutral pH's. We interpret this improvement in water quality to reflect a combination of neutralization by wallrocks and dilution by uncontaminated waters. One area where this trend is shown in our limited sampling is in the headwaters of the Hassayampa River, where drainage from several workings of the Senator mine complex are acidic, but after mixing with the heavy flow of the main stem of the Hassayampa, the pH rises to 7.7 and water quality appears to be good.

Water quality in the headwaters of Lynx Creek, in the vicinity of the community of Walker, is possibly the most problematic in the Prescott National Forest area. Mining of polymetallic vein deposits at the Sheldon mine and many nearby mines left dumps rich in sulfide minerals and base metals, and underground mine workings channel groundwater through sulfidic materials left in the walls. This is an area of fairly high annual precipitation as both snow and rain. The uppermost two miles of Lynx Creek and a western fork show abundant hydrated iron oxide mineral coatings in the streambeds, visible evidence of mineral precipitation as acidic drainage is gradually neutralized by natural processes. We made five pH measurements in this area and found the range to be 3.5 to 6.5. The most acidic waters carried high concentrations of iron, cadmium, copper, zinc, and lead. At a site about 1 mile north of Walker (at the boundary of the Prescott National Forest, and downstream from several tributaries) the Lynx is a large stream with pH 6.5 and base metal concentrations are slightly above background levels. Neutralization by carbonate-bearing minerals and dilution by numerous springs and streams greatly improves the water quality.

Similar conditions exist in the headwaters of the Hassayampa River, on the northwest flank of Mt. Union. Numerous mines formerly worked sulfide veins, and some such as the Senator and Cash went to depths of 800 feet or more (Lindgren, 1926). As many as four mills treated the ores and placed tailings into the streams. Today, ocher iron oxy-hydroxide coatings on stream gravel are visible indications of acid waters, which is confirmed by pH measurements of 3.2 to 3.7 and chemical determinations of high base-metal concentrations. Acidic, base-metal-rich conditions persist downstream from the junction with the branch draining Hassayampa Lake, but two miles to the west the main stem of the Hassayampa has a pH of 7.8, low conductivity, and low metal contents. A mine portal (probably draining the Senator-Cash mine complex) produces high water flow with weakly alkaline pH (7.1 and 7.9 during May and September of 1994) and low concentrations of most metals, but high concentrations of zinc.

Seemingly pure to the eye, because no iron oxy-hydroxides are seen, some drainages with weakly alkaline pH (7 to 8) carry notable amounts of zinc and cadmium. Six samples from the flank of Mt. Union, one below the McCabe mine on Ticonderoga Gulch, and two below massive sulfide deposits are in this class that has been noted elsewhere in carbonate-buffered systems (Plumlee and others, 1993; Plumlee and others, 1995). The pH's range from 7.1 to 8.4 and zinc concentrations range from 1,500 to 13,000 ppb. Other than the presence of base-metal sulfide deposits in the general area, there is little reason to suspect the zinc-rich compositions. These waters show evidence of formerly being acidic and neutralization by natural reactions with calcite. The high metal concentrations, especially zinc, in near-neutral waters occur in situations where there is little iron oxide to remove the metals by sorption (Plumlee and others, 1993). These innocent-appearing weakly alkaline waters need to be tested for other metals that are soluble in anion form (molybdate, arsenate, selenate), as well as metals that form soluble carbonate complexes (chiefly uranium).

Uranium concentrations are high in about 12 percent of the water samples. The uranium-rich waters can be either acidic or alkaline. The acidic drainages with high uranium and other metal concentrations generally can be identified by the associated iron oxide coatings deposited on alluvium, but the weakly alkaline waters with high uranium can only be identified with chemical analyses. High uranium concentrations are found in several geologic situations, thus no simple generalizations are evident. Acidic drainages at some massive sulfide deposits can mobilize uranium, even though uranium is not rich in the host rocks or sulfide ores. Waters with high uranium concentrations are associated with Precambrian granitic rocks, as in the Crown King district, which is not surprising because these rocks are known to be enriched in uranium.

Radon is known to be enriched in water in parts of the study area. Uranium-rich rocks in certain geologic formations are known to create anomalous concentrations of radon gas that can be a hazard if concentrated indoors or in ground water (Duncan and Spencer, 1993A, 1993B; Proctor and others, 1993). The distribution of uranium-rich rocks is well known from aerial surveys and geochemical studies of the NURE program, and provides a warning to the public about potential hazards from radon, which is produced by the normal isotopic decay of uranium (Spencer, 1993). The distribution of radon in detail, at the scale of homesites and wells, is subject to numerous local aspects of geology and hydrology have not been mapped and quantified in this USGS study. Although further studies of radon in the Prescott National Forest area are warranted, and monitoring of radon should be done, the publications cited provide a good introduction to this particular geochemical hazard.

Nitrate is present in notable concentrations (1 to 25 ppm) in about 10 percent of the water samples. Nitrate is generally related to human, agriculture, or livestock activities (Hem, 1970). Many of the high nitrate water samples are from the Agua Fria River.

Sulfate concentrations are higher than 250 ppm in about 25 percent of the samples. Many of these water samples are acidic and were collected near sulfidic deposits, but others are waters of neutral to weakly alkaline pH that probably were formerly acidic. During oxidation of pyrite or other sulfide minerals, sulfate ions are released to the water. If the acid water is neutralized, sulfate ions remain. The high sulfate waters are indicated by high conductivity readings in the field. This is a simple preliminary test of water quality for uses such as livestock.

NATURAL MITIGATION OF DRAINAGE CONTAMINATION

Many hydrologic processes in a variety of geologic situations can significantly mitigate hazardous mine and rock drainage (Smith and others, 1994; Plumlee and others, 1994). A common and very effective process is neutralization of acid pH by calcite (or other carbonate minerals) and consequent decrease in the metal concentrations in the ongoing water. A change in pH from below 4 to near 7, as produced by carbonate buffering, causes most metals to precipitate or adsorb on iron oxides (Smith and others, 1993; Alpers and others, 1994). Zinc and arsenic are among the few metals that do not drop out of solution in this process.

Three lithologies in the Prescott National Forest area appear to be effective for mediating acidic drainage: 1) Paleozoic limestone and dolomite, such as on Mingus Mountain above Jerome; 2). calcium carbonate in the form of "caliche" that cements Quaternary alluvium in the intermountain valleys; and 3). calcite-bearing alteration assemblages, especially the green propylitic alteration (chlorite plus calcite) of metavolcanic rocks that enclose massive sulfide deposits. There are some variants on item 1, including calcite in Tertiary lacustrine beds of the Verde Valley and calcite cement in Paleozoic sandstones. A variant of item 3 is widespread but subtle calcite-bearing alteration or veinlets in granitic rocks; this lithology is inferred from water chemistry but has not been seen in outcrop. The distribution of alluvium that has high buffering capacity can be inferred from the map of high calcium concentrations (fig. 13; concentrations greater than about 6 wt. percent probably reflect calcite).

From our reconnaissance sampling of waters in the Prescott National Forest area we can see the mediating process in pH measurements and in chemical analyses of waters. We are impressed by several examples that demonstrate the efficacy of these processes. East of Jerome, waters draining the United Verde mine (Howell Tunnel) are neutral to weakly alkaline by the mediating effects of carbonate strata east of the Verde Fault, and probably also from carbonate rock clasts and caliche in alluvium. Bitter Creek, which flows east from Jerome, may have gotten its name from high content of dissolved solids (bad taste); at the surface it is not acidic, but probably was in the mine prior to flow through carbonate rocks and alteration. Acid drainage from the Copper Chief mine (pH 2, very low flow) disappears into alluvium, and all nearby waters in streams and wells have pH 7 to 8, suggesting buffering by carbonate in alluvium. At the DeSoto massive sulfide mine, water collected in the lower portal is used for watering livestock; the pH of 8 indicates buffering by carbonate, such as in propylitic altered wallrocks enclosing the orebody.

ASSESSMENT OF GEOCHEMICAL CHARACTER

Predictions Based on Known Examples Elsewhere

One approach to predicting geo-environmental signatures of mineral deposits in the Prescott National Forest area is to compare them with well-studied examples elsewhere through the use of models that summarize pertinent aspects of geology, chemistry, climate, and deposit attributes. The literature on mineral deposit geochemistry is abundant, and geo-environmental aspects have been summarized recently (du Bray, 1995). The following descriptions are taken from papers in that book.

1. **Massive sulfide deposits**, also known as volcanogenic massive sulfide deposits (Taylor and others, 1995), tend to be relatively small (1-10 million tons), but characterized by very high concentrations of sulfide minerals (10 to 90 percent). Pyrite is present in massive amounts in lenses, along with chalcopyrite, sphalerite, galena, and other sulfide minerals. Volcanic wallrocks tend to be altered to chlorite and carbonate minerals (calcite, ankerite). Drainages from mines and waste can locally be acidic to extremely acidic, and those acidic waters can carry high to extremely high concentrations of iron, aluminum, copper, zinc, and lower concentrations of cadmium, lead, arsenic, and other metals.

2. **Porphyry copper deposits** are very large (hundreds of million tons) deposits in felsic to intermediate composition stocks and adjacent wallrocks (Cox and others, 1995). The deposits typically are zoned with copper and molybdenum rich in the core, lead and zinc more abundant in an outer zone. A large halo of pyrite-bearing rock is barren of valuable metals. Alteration also is zoned, and the silicate minerals in zones that tend to be mined have little or no acid buffering capacity; outermost pyrite zones that may contain carbonate minerals are generally not mined. Many porphyry copper deposits are deeply weathered and oxidized, a condition that tends to reduce their potential to generate acidic drainage. However, the total amount of sulfide minerals in these systems is large, and the mines (chiefly open pits) and waste dumps can develop acid drainage that carries high concentrations of base metals. Carbonate sedimentary rocks, if present adjacent to the ore deposits, can effectively buffer pH and reduce the mobility of metals (although high amounts of copper, zinc, and cadmium can be carried in the neutralized solution.

3. **Polymetallic vein deposits** tend to be small (< 1 million tons) but locally rich in copper, lead, and zinc sulfide minerals, and most contain economically important amounts of silver and gold (Plumlee and others, 1995). Many of these deposits contain broader zones of replacement ore in carbonate rocks adjacent to veins. Deposits in or near carbonate rocks have fewer environmental problems because the carbonate buffers the pH of waters and most base metals are not transported. However, deposits lacking carbonate wallrocks can generate highly acid drainage along vein structures and underground mine workings, and these waters can carry high to extremely high concentrations of base metals. Arsenic can be a greater problem in these deposits than in most ore types. Distal parts of veins, often unmined, tend to contain propylitic alteration that includes carbonate

minerals, which can buffer pH if in the flowpath of acidic drainage. Many of these deposits in the western U. S. were mined in the 19th Century, and associated mills and smelters produced widespread contamination of lead, zinc, arsenic, copper, and other metals.

4. Gold-quartz veins, as at Cherry, are generally similar to deposits called 'low-sulfide gold quartz veins' elsewhere (Goldfarb and others, 1995). These deposits generally are small to very small (most <100,000 tons, a few are larger) and localized in veins along faults. The veins and wallrocks contain much lower amounts of base metals than most ore types, although up to a few percent of pyrite, arsenopyrite, chalcopyrite, galena, and sphalerite can occur. Some wallrock varieties tend to alter to assemblages containing carbonate minerals (calcite, ankerite). Most mined and unmined examples produce drainage with no chemical problems because sulfide content are low and wallrocks provide adequate buffering capacity. A few deposits produce waters with weakly alkaline pH and high arsenic concentrations. A few rare mines and waste dumps produce acidic drainage carrying high amounts of iron, zinc, copper, and lead. Mercury contamination from mineral processing is a common problem in districts that mined these ores.

5. Placer gold deposits, not reviewed in the geo-environmental models book (du Bray, 1995), are expected to pose few problems because they contain few to no sulfide minerals in oxidized detritus. High mercury levels may be present, the result of amalgamation processing.

As reviewed briefly here, these deposit types differ greatly in size, sulfide mineral content, amount of base metals, and wallrock buffering capacity. Interpretations of geo-environmental problems must consider these factors, as well as depth of oxidation, topography, and climate (Plumlee and Nash, 1995). Although there are many predictable geochemical signatures for these deposits, there is wide variation in the magnitude of drainage problems--a reflection of diverse local conditions. Those local conditions, and local observations in the Prescott National Forest area are considered next.

Tuning Models Applied to Prescott National Area

Environmental signatures of mineral deposits from other parts of the world provide useful guidelines for Prescott National Forest area, but must be modified to account for known or likely conditions in the study area that differ from examples elsewhere. Some of the key variables that must be considered are climate, host rocks, and ancient weathering. The climate in the Prescott National Forest area is generally drier than in most of the examples elsewhere. In more detail, precipitation varies substantially within the study area as there is much more precipitation as rain and snow at the higher elevations, evidenced by conifers and perennial streams. In hotter, drier Sonoran and Chapparal zones, there is small to nil drainage from mine workings, the maximum being a few gallons/minute. The low precipitation should have the effect of minimizing chemical reactions and transport of metals in solution, although brief periods of flushing by seasonal rains after a dry period could carry high concentrations of metals tied up in desiccated mineral crusts (Nimick and Moore, 1991; Alpers and others, 1994; Plumlee and Nash, 1995).

Judging from published descriptions (Lindgren, 1926) and new data collected in this study (table 9), as well as results from the U.S. Bureau of Mines (Neubert, 1995), the chemical composition and mineralogy of mineral deposits in the Prescott National Forest area appear to be similar to others of the same type elsewhere. Available information for the Prescott National area deposits, and inferences from many deposits elsewhere, indicate that most of the deposits are rich in base metals, especially iron, copper, and zinc. Arsenic content of massive sulfide, polymetallic vein, and gold-quartz vein deposits is relatively high, as compared to other deposit types. Sulfide content of the major deposit types, excepting gold-quartz veins, is noteworthy: original contents below the zone of weathering is generally in the range of 1 to 10 percent, but some veins or lenses of ore can contain more than 50 percent sulfide minerals.

Mineral deposits of the Prescott National Forest area are more deeply oxidized than in most parts of the world, as described well by Lindgren (1926). The deep oxidation was produced in the last 10 or so million years by faulting and uplift of mountain blocks, placing the upper parts of ore bodies above the water table. Mining, especially prior to 1900, focused on the bonanza ores that were rich in easily recoverable silver and copper in the oxidized zone, and mining did not have the problems and costs of pumping water until mining progressed to deep levels 400 or more feet below the surface. Abandoned mine workings in the oxidized zone produce little or no surface drainage today, and most waste dumps from oxidized deposits contain much lower concentrations of sulfide minerals than the ores contained originally (millions of years ago). Chemical analyses show that base metals are rich in the oxidized ores and waste, but the form of the elements is more stable in slightly soluble oxide and sulfate minerals than in the original sulfide minerals (Alpers and others, 1994). Most of the metals of concern, such as iron, copper, lead, and arsenic are relatively unreactive and immobile in the form of oxide and sulfate minerals and mineral coatings. Because the solubility of the many oxide and sulfate minerals varies greatly, the specific mineralogy of the deposits should be determined.

Carbonate-bearing rocks and alluvium are abundant near most of the mining districts. Limestones are present near the massive sulfide deposits of the Jerome district, downfaulted next to ore and present as clasts in Quaternary alluvium in stream beds. Carbonate-bearing caliche also is abundant in the alluvium of all of the valleys. Most Precambrian metavolcanic rocks contain some calcite or ankerite as part of the metamorphic or alteration assemblage near mineral deposits. Even the Precambrian granitic plutons that appear to be devoid of carbonate minerals have enough of these minerals in veinlets scattered through the rocks to create weakly alkaline (carbonate buffered) ground and surface waters, as shown by field measurements of pH and by chemical analyses of waters. Sulfide minerals are known to be rich in some rocks that lack buffering capacity, thus can create acid drainage locally, but our geologic observations indicate that these acidic waters encounter carbonate-bearing rocks within a few hundred feet and are neutralized.

These general observations, supported by site analyses described elsewhere in this report, suggest that the potential for acidic mine drainage and associated high concentrations of base metals is much lower than for most districts having the same deposit types elsewhere in North America. Many generalizations based on deposits in other parts of the world probably do not pertain to the Prescott National Forest area. This is especially true for the massive sulfide deposits, because local conditions differ in important ways, as outlined above. For example, the extremely acidic waters with very high metal loadings found in the Shasta district, Calif. (Filipek and others, 1987; Alpers and Nordstrom, 1991), related to massive sulfide deposits and mine waste, should not be considered typical for this deposit type and applied to the Prescott National Forest area.

The predicted relative environmental impact of the five ore deposit types in the Prescott National Forest area is summarized in table 12. These guidelines and specific site observations will next be used to assess the geo-environmental character of mining districts.

Character of Districts

Generalized summary characteristics of the many mining districts in the Prescott National Forest area can be made from the new chemical determinations made in this study, from geologic traits, and by analogy to better known districts (du Bray, 1995). Some pertinent attributes are listed for the districts in table 12. Some explanations are required for several of the attributes in the table. Natural mitigation of acidic drainage can be expected from certain alteration assemblages and wallrocks that contain calcite or other carbonate minerals. (Wallrock is used in a nontechnical sense for rocks of any age in the vicinity of deposits, such as the Paleozoic limestones that are younger than Verde district massive sulfide deposits but today have an influence of groundwater conditions in the district). An important feature of most of the polymetallic vein deposits is alteration that contains calcite--best inferred from water compositions, discussed earlier, because this calcite commonly is not obvious in the rocks. These ores also commonly contain vein-filling carbonate as a gangue mineral, and are best seen on dumps. These carbonate minerals are favorable for mitigation of acid generated from sulfide minerals. Estimates of natural contamination from weathering of unmined, non-ore grade rocks in districts are based on our field observations in the districts and on the known distribution of mineralization halos in certain types of deposits (du Bray, 1995). Porphyry copper-molybdenum deposits are famous for their large halos of altered rocks that commonly extend more than a mile beyond ore. Massive sulfide deposits have a reputation for having narrow aureoles, but there is visible reddish alteration well beyond the mined deposits of the Verde, Mayer, and Agua Fria districts. The estimates of contamination from production are based on the production tonnage figures (table 4), and our observations of amounts and kinds of materials on mine dumps. Mill and smelter contamination was discussed earlier.

Estimates of drainage type for the districts (Table 13) are highly simplified to provide focus in this initial survey. The models predict acidic drainage carrying high concentrations of base metals, and this has been confirmed by some of our field measurements of pH's below 4 and by water analyses. The major questions are: how much? how often? and how far? In nearly all of the deposits that we examined the acidic drainage appears to be a local phenomenon, within a few hundred yards of a deposit or dump. Attenuation by dilution and by reactions with wallrocks and caliche appears to occur in close proximity to most deposits. Thus these drainages are termed "locally acidic." The composition of these waters evolves during mixing and neutralization, and the ongoing drainage appears to be weakly alkaline (about pH 8) with a tendency to carry zinc after most base metals are taken from the originally acidic drainage. In the porphyry copper-molybdenum deposits, molybdenum may also be carried onward in solution as molybdate that is soluble in alkaline waters. Arsenic might also be transported as arsenate in these alkaline waters. There possibly should be more concern for the weakly alkaline, metal-bearing waters than for the acidic drainages because the alkaline waters may carry some metals for substantial distances, possibly several miles, before dilution and sorption reactions can mitigate the problem.

Finally, an estimate is made of possible impacts beyond the deposits and districts (Table 13). These estimates are qualitative for distances of about 1 to 5 miles. For instance, these estimates consider the likelihood of drainage problems impacting lands outside of the mining district or outside of typical parcels of private land (patented mining or milling claims). Districts considered to have possible or probable impact beyond the districts are those with little natural mitigation (wallrock buffering), high acid generation, and large size of deposits and mining disturbance. The districts are ranked in Table 13, and their character shown on figure 23.

IMPACTS ON WATERSHEDS

According to new data in this reconnaissance study and information in the literature that is available to us, most of the districts in the Prescott National Forest area appear to be contributing little or no geochemical contamination to watersheds, . However, in a few areas there are one or more geochemical indications of natural or anthropogenic contamination that could be hazardous to pity, wildlife, livestock, or people. Six watersheds may be at risk and should be studied much more systematically than was possible in this study, especially the four that have degraded water quality. The six watersheds are (alphabetically): 1. Agua Fria River; 2. Copper Basin Wash; 3. Hassayampa River; 4. Lynx Creek; 5. Turkey Creek; and 6. Verde River (fig. 24). The geochemical characteristics of these watersheds are ranked in Table 14.

Agua Fria River: The headwaters of this major watershed, for approximately 10 miles southeast of Humboldt, are at risk from several sources: 1. smelter slag from the Valverde smelter at Humboldt that has been carried by flash floods as fine and course detritus for at least 10 miles; 2. Smelter emissions that contaminate soils within about 5 miles of the Valverde smelter; 3. Mill tailings from several operations in the headwater area that are actively eroding and releasing contaminants in both solid (silt) and aqueous forms. 4. There are a moderate number of mine workings and waste piles in this area that may occasionally release contaminants, such as during flash floods. However, there are several positive geochemical signs that the contamination may not be serious. First, the water quality does not appear to be degraded when measured at sites more than a mile from mines, mills, or smelters. Second, pH's of water samples indicate effective buffering to neutral-weakly alkaline values that we consider good. The geochemical balances in this area appear to indicate that natural attenuation of geochemical contamination occurs by carbonate buffering in bedrock and alluvial units, and by dilution. There is concern, however, for possible periodic release of heavy metals from the abundant smelter slag as it is abraded during flash floods. Also, some soils in the area near the Valverde smelter may contain enough heavy metals from smelter emissions to pose a hazard to livestock or crops.

Copper Basin Wash: This internal watershed has moderate contamination from an old smelter, from mine workings and waste dumps, and from natural outcrops of mineralized rocks. Surface water, of low volume near the headwaters, is contaminated by heavy metals, but pH is buffered in a short distance before the flow disappears into the subsurface, which suggests that natural processes are mitigating the contamination. Slag is present in the alluvium, but is relatively small in volume. Several square miles of altered rocks crop out in the headwater area of this basin and could be the chief contributor to the contamination. Further study could provide quantitative assessment of the various contributions, but may not be necessary if the natural mitigation processes are as effective as they appear to be.

Hassayampa River: The headwaters of this major river show direct and indirect signs of contamination. The most significant sign is the elevated content of heavy metals and somewhat acidic pH in samples of the river. Very high water flow in the spring of 1995 did not dilute and diminish the contamination. Indirect evidence for contamination is the presence of many old mine workings and waste dumps in the headwater area. Reddish coatings form on alluvium in streams below more than one old mill and tailings site. Also of concern is the absence of tailings at one mill, evidently washed downstream years ago. Natural mitigation appears to be less likely in the rocks of this watershed than in others described in this section: carbonate-bearing rocks, alluvium, and alteration appear to be very limited in abundance. The high water flow in the Hassayampa downstream of the mining districts may allow dilution and attenuation of contamination.

Lynx Creek: this creek flows north from the Walker district, where it receives a large input of acid and heavy metal contamination. There are numerous sources of this heavy metal contamination in the many small and large mine working, waste dumps, several mills, and also natural drainage from unmined mineralized rocks. Ocher coatings of iron oxide minerals on cobbles in streams are a sign of the high metal loadings and precipitation as acidic waters are neutralized. The numerous summer homes in the Walker area appear to complicate an already complex condition: roads and building sites that are cut into old mine dumps accelerate reactions that release acid and metals, and the septic waste-waters that are added to mineralized rocks also enhance reactions. Water analyses from the Lynx as it flows into the Prescott National Forest, approximately 2 miles downstream from

Walker, show notably high amounts of heavy metals. From available geochemical data, and visible signs of contamination of the side streams in the headwater region, the anthropogenic contamination of Lynx Creek appears to be the most intense and serious of those recognized here. The complex ownership pattern of private and public lands in this watershed poses problems for the further investigations that are needed.

Turkey Creek: This small, intermittent stream drains the eastern flank of the Bradshaw Mountains where it traverses several mining districts that were formerly active on massive sulfide and polymetallic vein deposits. Two mills processed ores from the vein deposits, but ores from the massive sulfide mines were carried by train out of the watershed to be processed at the Valverde mill and smelter (Humboldt). The chief environmental concerns here are the three abandoned mills and their tailings piles, two of which are large and being eroded by the creek. Drainage from mine workings and dumps, and from unmined mineralized rocks may be a problem, but there is evidence that carbonate-bearing altered wallrocks do a remarkably good job of buffering initially acidic waters. A good example is at the DeSoto mine, where the lower haulage level accumulates water that has a pH of 8.3 and is used to water livestock. The climate in this watershed is drier than others discussed in this section, and may pose problems related to seasonal variation in precipitation. In this climate episodes of rainfall after dry periods tend to create a sudden "flush" of acidic, metal-rich waters as mineral crusts on mine dumps and stream alluvium formed by evaporation are dissolved in the first few minutes of rain (Nimick and Moore, 1991). These "flush" runoffs are difficult to characterize unless one waits for a storm, but our lab tests show that the white mineral crusts on the Turkey Creek mill tailings are readily soluble in water, as well as in dilute acids.

Verde River (headwaters): This major river in the Verde Valley is a prime source of water and is popular for recreational activities. The condition of the Verde watershed near Clarkdale is uncertain because the balance of contamination and attenuants is difficult to determine: the quantity of contaminants is large, but the flow of uncontaminated water is high, and the buffering capacity of rocks and alluvium is high. Major ore deposits penetrated by mine workings and large piles of sulfidic waste rock flank the Verde Valley. Mine drainage is locally highly acidic (pH 2.2) and charged with heavy metals. However, our reconnaissance water samples a mile or so east of the mines show alkaline pH, high dissolved salts (sulfate), but remarkably low heavy metal contents. Carbonate minerals in rocks and alluvium appear to be mitigating water quality within a short distance of the mines. Possibly of greater impact are the products of milling and smelting. Mill tailings were placed in an abandoned channel of the Verde River, slag from the Clarkdale smelter is partly in the river, and slag from the Clemenceau smelter is now surrounded by homes and businesses in Cottonwood. Soils are enriched in heavy metals within about 4 miles of the smelters and appear to be a record of emissions from smelters. Much additional work in needed in this area. The good news is that geologic mitigation appears to be quite effective and minimizes the effects of contamination that otherwise might be severe.

CONCLUSIONS AND RECOMMENDATIONS

Numerous natural and mining-related sources contribute heavy metals to the surficial environment in the Prescott National Forest area. Ore deposits of the area that have been mined over the past 125 years are rich in copper, zinc, lead, silver, and gold, and are accompanied by high amounts of iron, arsenic, cadmium, and other metals. The altered rocks and ore detritus in alluvium that attracted prospectors in the 19th Century are natural contaminants which contribute heavy metals to the environment; the amount of this contribution is difficult to quantify but is believed to be substantial. A small number of sites are characterized by acidic drainage carrying high concentrations of metals. Most surface waters are neutral to weakly alkaline and of good quality. In most mining districts of the Prescott National Forest area water quality is naturally mitigated by reactions with carbonate minerals in wallrocks and alluvium or by dilution. Some districts, watersheds, and geologic environments contain sufficient heavy metals to be of concern and should be investigated further.

Mining districts of the Prescott National Forest area that contain deposits of heavy metals in the form of sulfide minerals have a tendency to generate acidic drainage where mine workings and dumps are wet and oxidized. Acidic conditions appear to be maintained for only short distances (hundred of feet) before natural mitigation processes neutralize pH and precipitate most base metals. The greatest amount of acidic, metal-rich drainage occurs at high elevations that receive the most precipitation as rain and snow. Our water analyses show the most degraded quality in waters of the Hassayampa, Walker, and Mt. Union districts on the flank of Mount Union. Estimated impacts of the districts are ranked in Table 13.

Six watersheds may be at risk from one or more types of contamination. Water quality is good at most sites, suggesting that local contaminants are effectively mitigated by natural processes. Several miles of the headwaters of Lynx Creek and the Hassayampa River have degraded quality; there is low buffering capacity in rocks in these areas, but dilution eventually works to improve water quality. Parts of the headwaters of the Agua Fria River, Copper Basin Wash, and Verde River are contaminated by products of mining and by altered rocks; in these areas the cumulative effects of low levels of heavy-metal contamination could pose a problem. Particulate contamination from smelter smoke also is present in the Verde and Agua Fria watersheds and could enter surface waters and vegetation.

Our initial results show that soils in the vicinity of historic smelters are sufficiently enriched in base metals to be a potential threat to health. These results need to be substantiated and expanded by more detailed sampling. Sampling should be done in a more random manner relative to smelter sites, in case predominant winds do not carry the pollution only to the northeast. Also, future sampling should test for possible inversion of clouds at certain elevations, as is known to happen in intermountain valleys elsewhere and can be seen in clouds and fog in valleys of the study area. Much of the probable smoke-related pollution is on private lands, but a large area of the Coconino Forest north of the Verde River at Clarkdale appears to be contaminated. Questions of toxicity and bioavailability should be addressed by health scientists and biologists.

Tailings impoundments are numerous and scattered across the Prescott National Forest area. These finely ground materials contain high concentrations of heavy metals and enough sulfide minerals to generate acid when wet. Efflorescent crusts form on the surface of most tailings during dry periods; these highly soluble salts are capable of releasing base metals to a brief flush of runoff during a storm. Only a few tailings impoundments are physically stable, and most are being eroded and tailings carried into nearby streams or arroyos. Remediation of the larger impoundments, especially those with abundant sulfide minerals, should be a high priority. Use of tailings as a convenient source of road or building material should be discouraged because such practices carry contamination into populated areas and increase the chances for undesirable chemical exposure.

Concentrations of base metals in slag are sufficiently high that mobilization of even a small percentage in dust or water might pose health risks. Storage of large slag piles in populated areas and use as inexpensive construction materials should be evaluated relative to health risks.

Many mines and nearby waste dumps contain moderate to high concentrations of base metals known to be toxic when mobile in water or dust. Additional work is needed to determine the character of derelict mine sites and possible remedial action, if necessary. The practice of building homes on patented mining claims accelerates chemical reactions in mineralized rocks and aggravates pre-existing contamination problems. The majority of the larger derelict mines are on private property; only a few abandoned mines on public lands appear to be producing acidic drainage or other chemical contamination.

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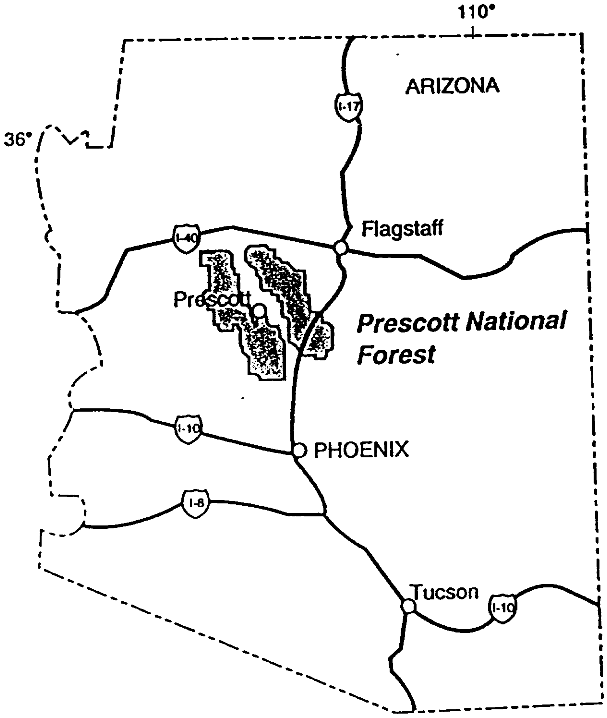

Figure 1: Location of the Prescott National Forest, Yavapai County, AZ

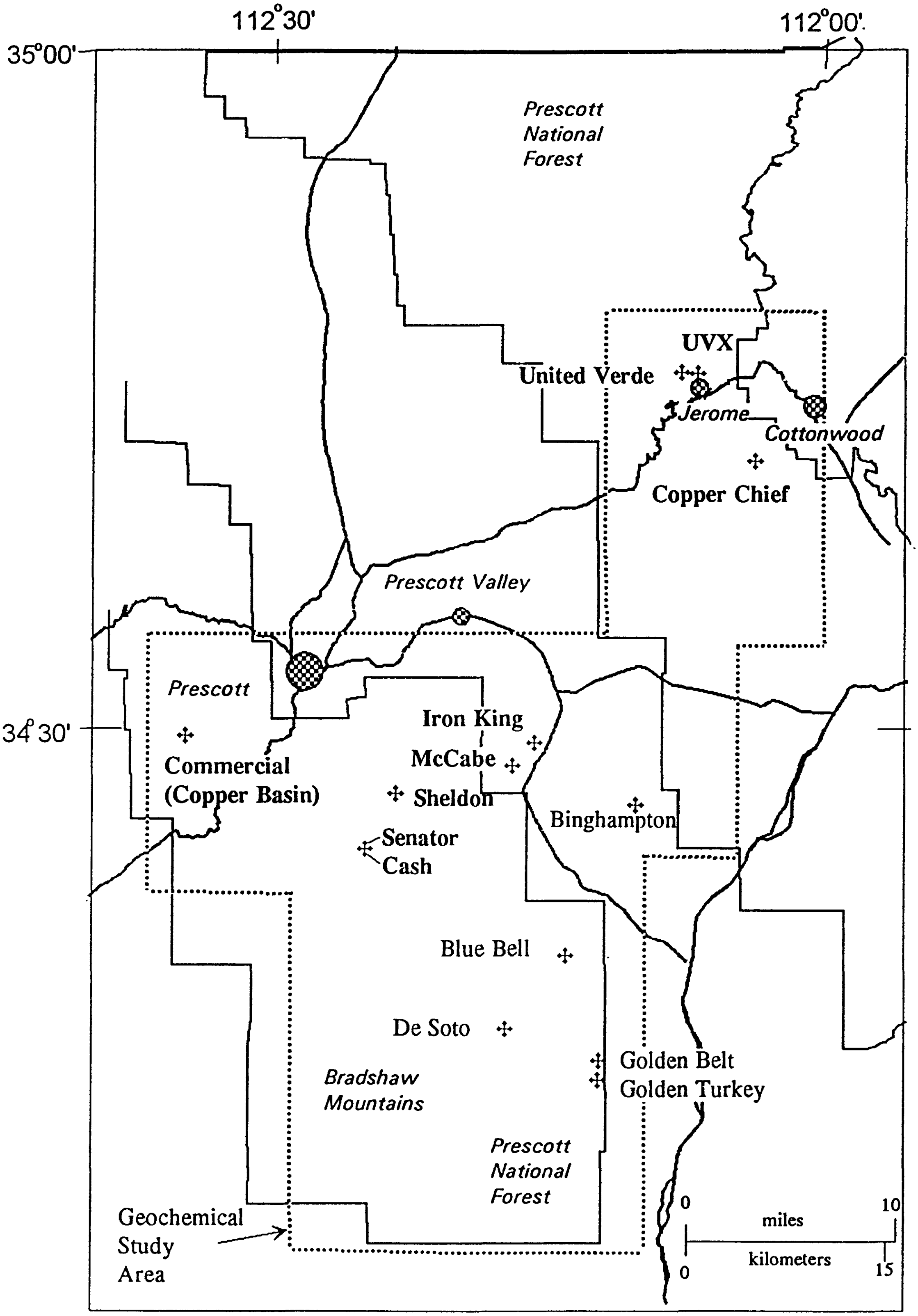

Figure 2: Location of the area of major mining that was the focus of this study. The major mines mentioned in this report are shown.

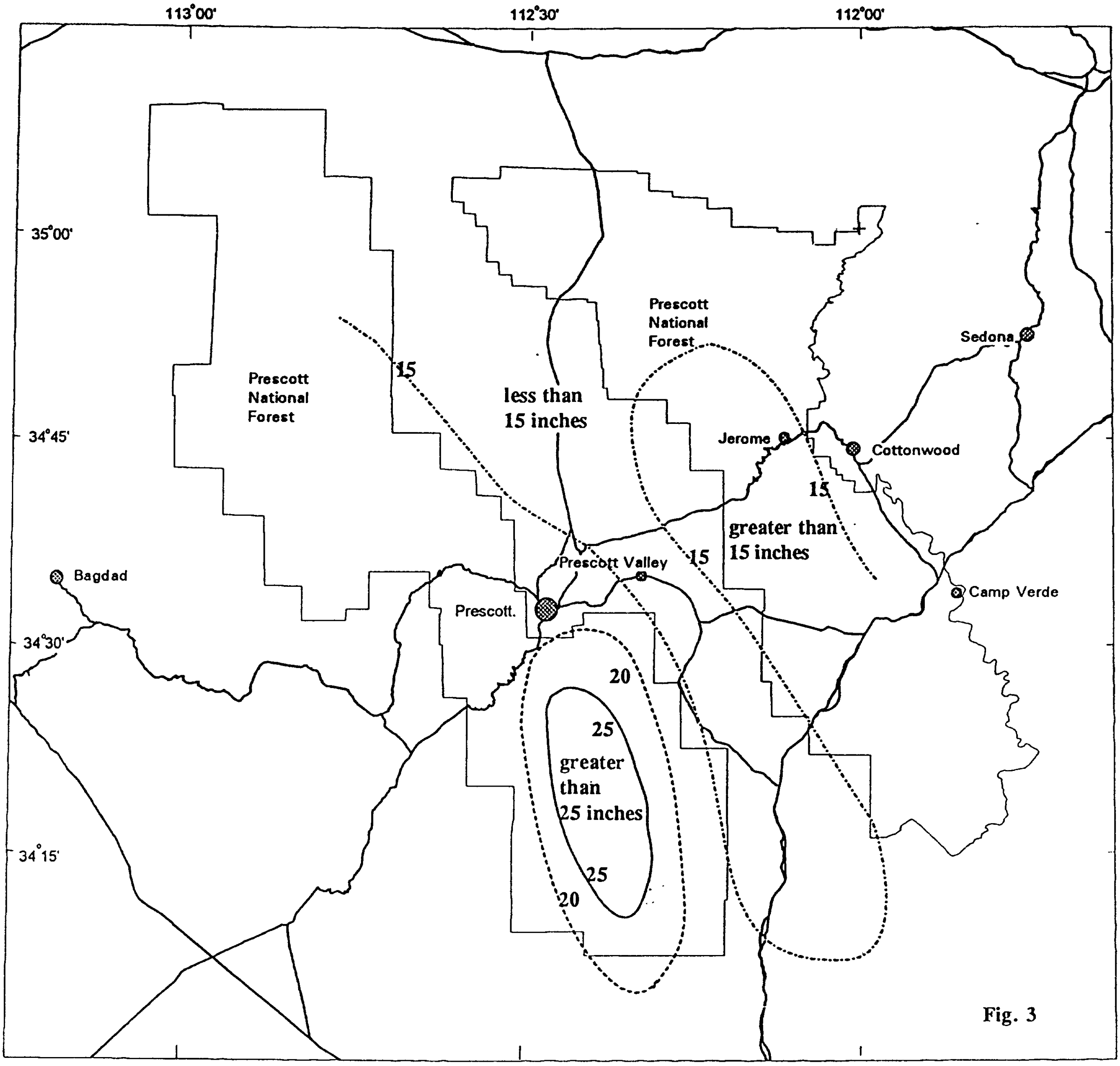

Figure 3: Mean annual precipitation in the Prescott National Forest area (from Sellers, 1960).

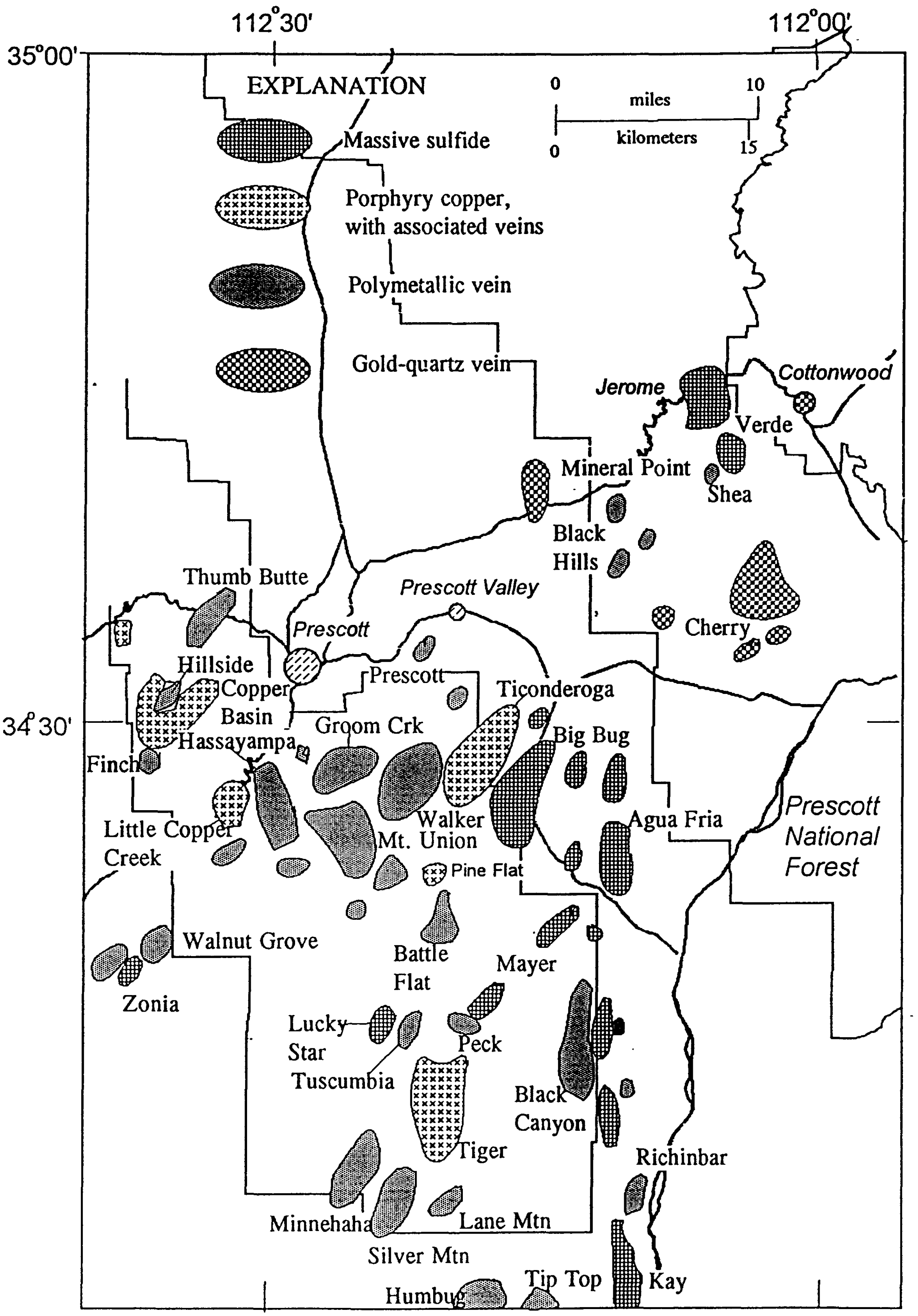

Figure 4: Metallic mining districts in Prescott National Forest area (modified from Keith and others, 1983)

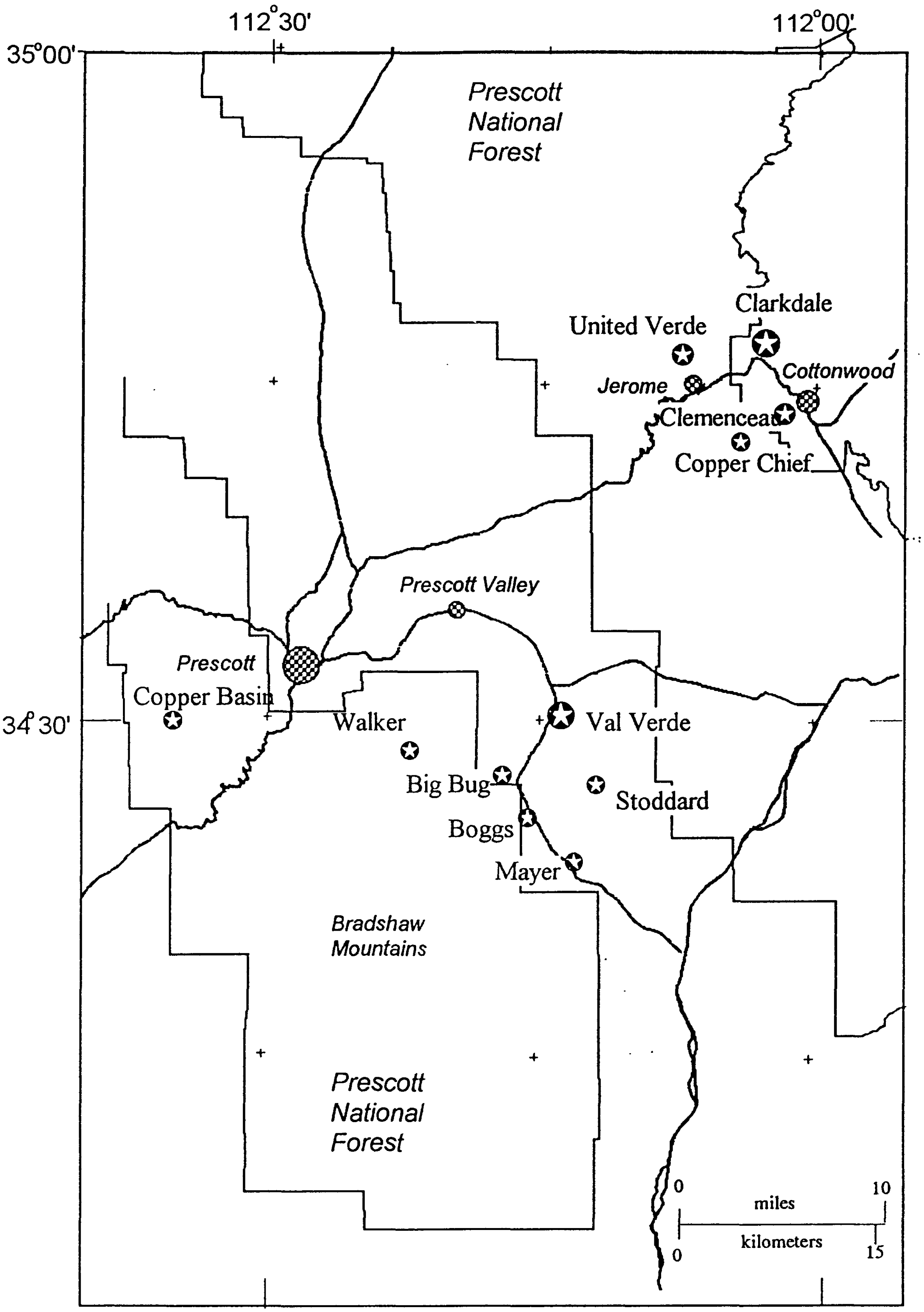

Figure 5: Distribution of mines and prospects, classified by deposit type. Localities are from the Mineral Resources Data System (MRDS) of the US Geological Survey; classification is by Nash.

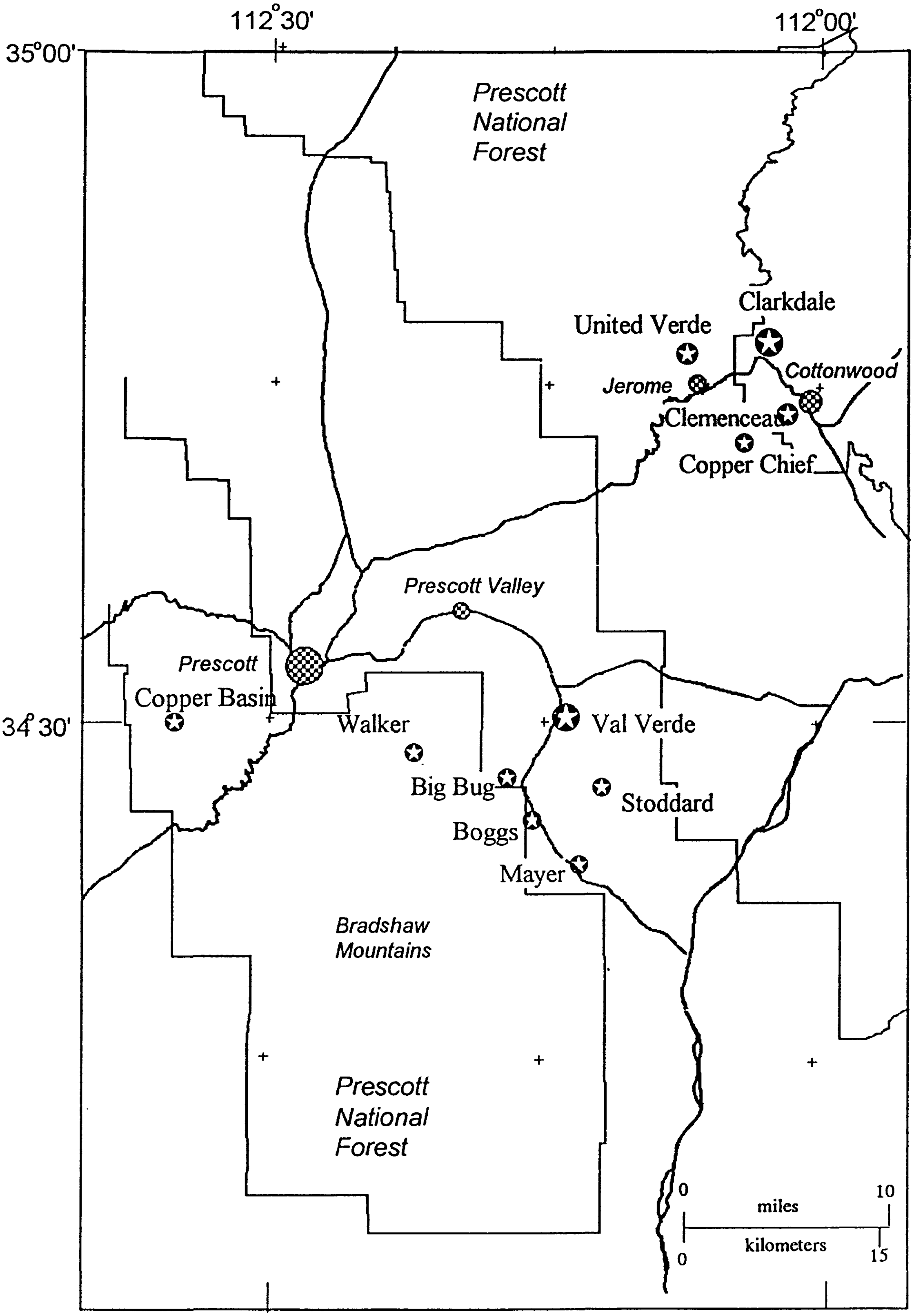

Figure 6: Location of smelters in Prescott National Forest area.

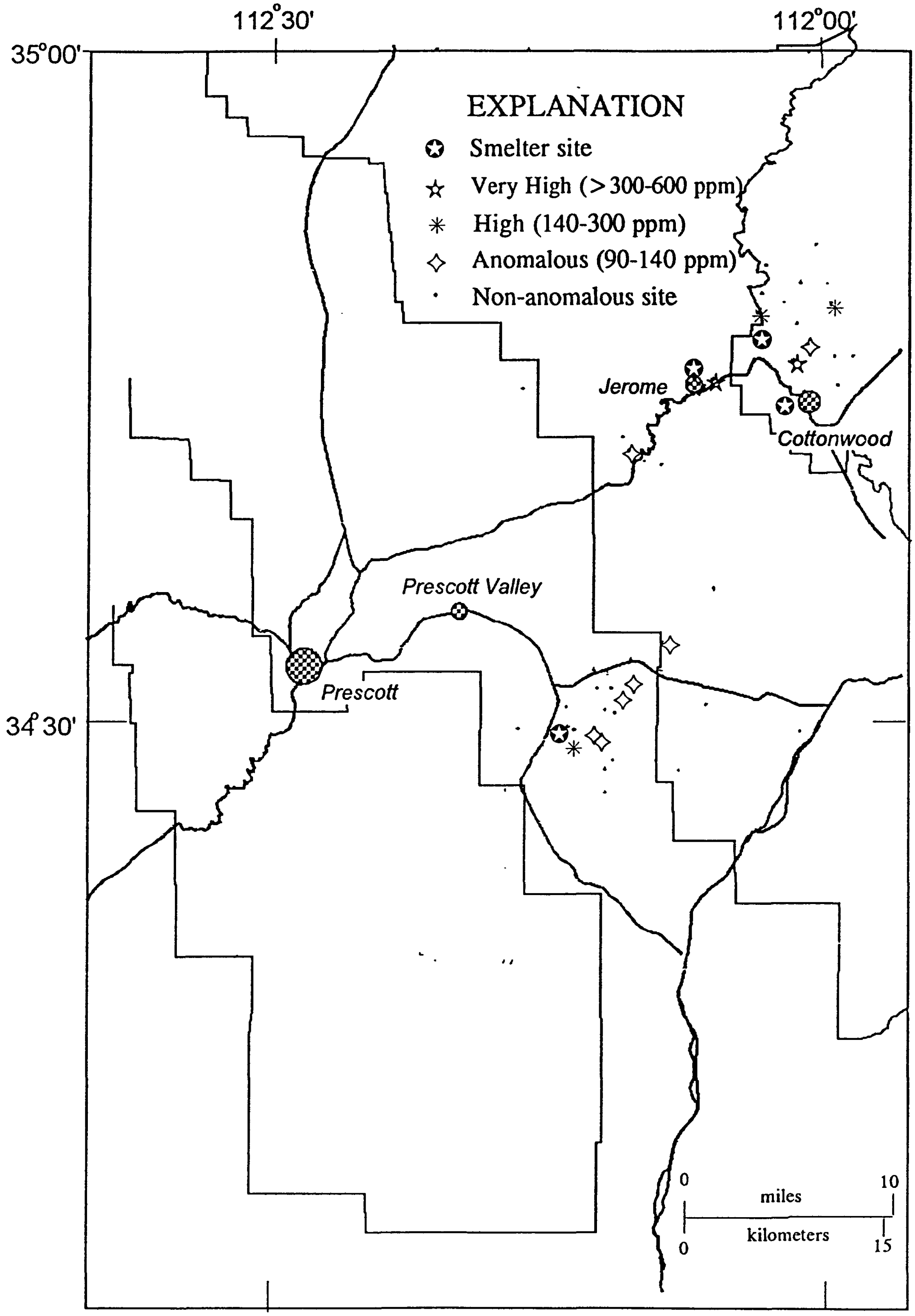

Figure 7: Soil geochemistry in relation to smelters: distribution of high zinc values.

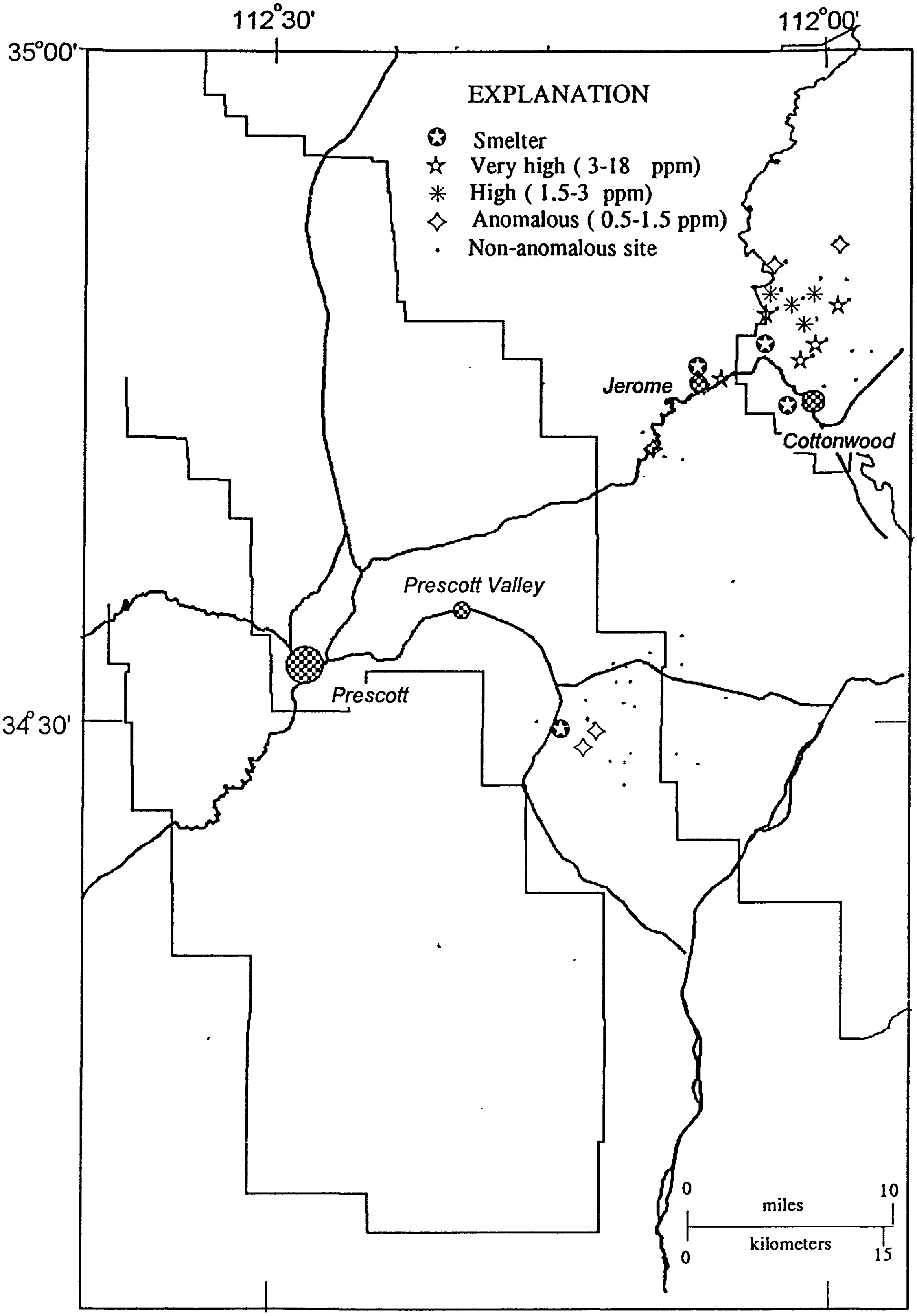

Figure 8: Soil geochemistry in relation to smelters: distribution of high cadmium values.

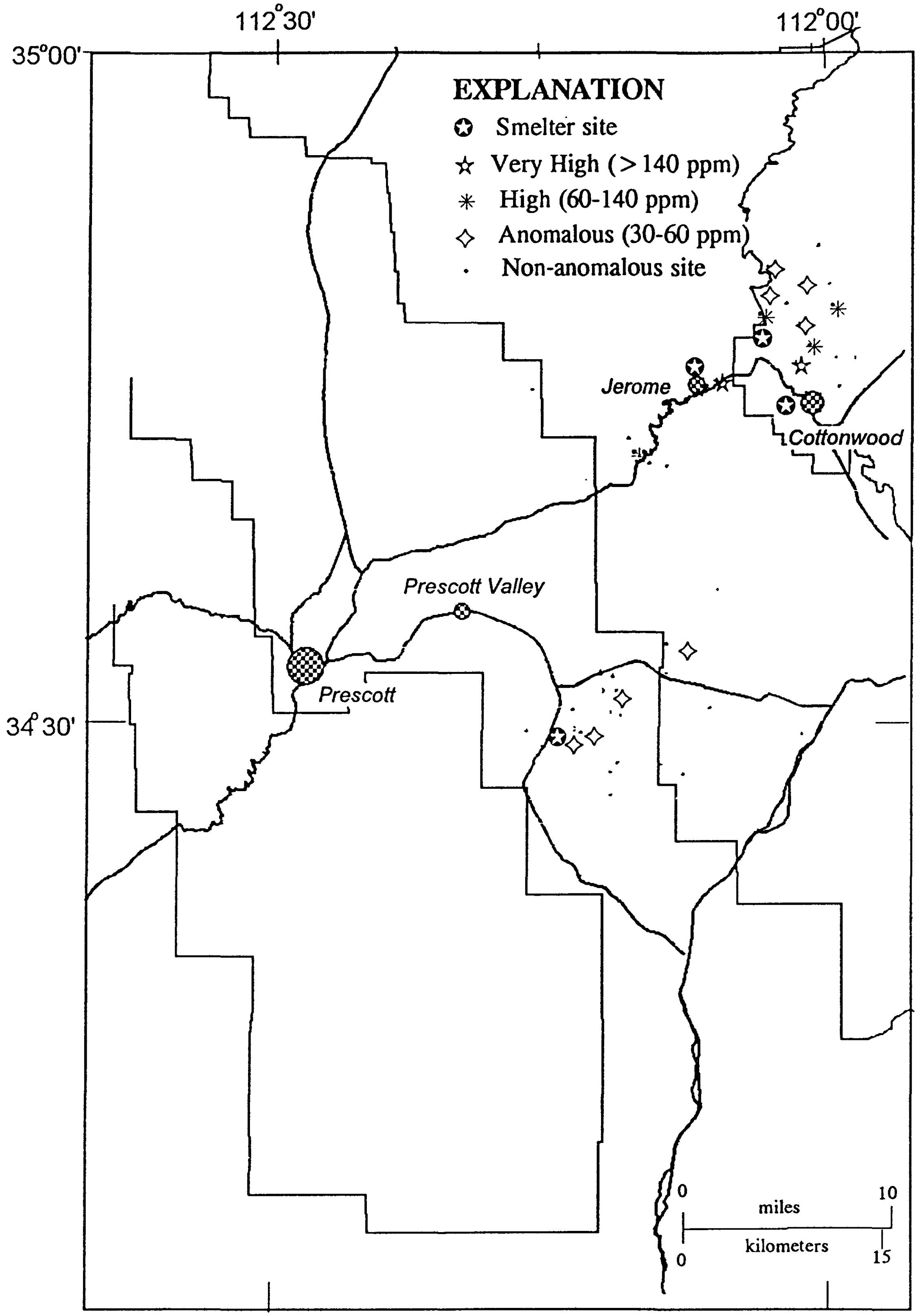

Figure 9: Soil geochemistry in relation to smelters: distribution of high lead values.

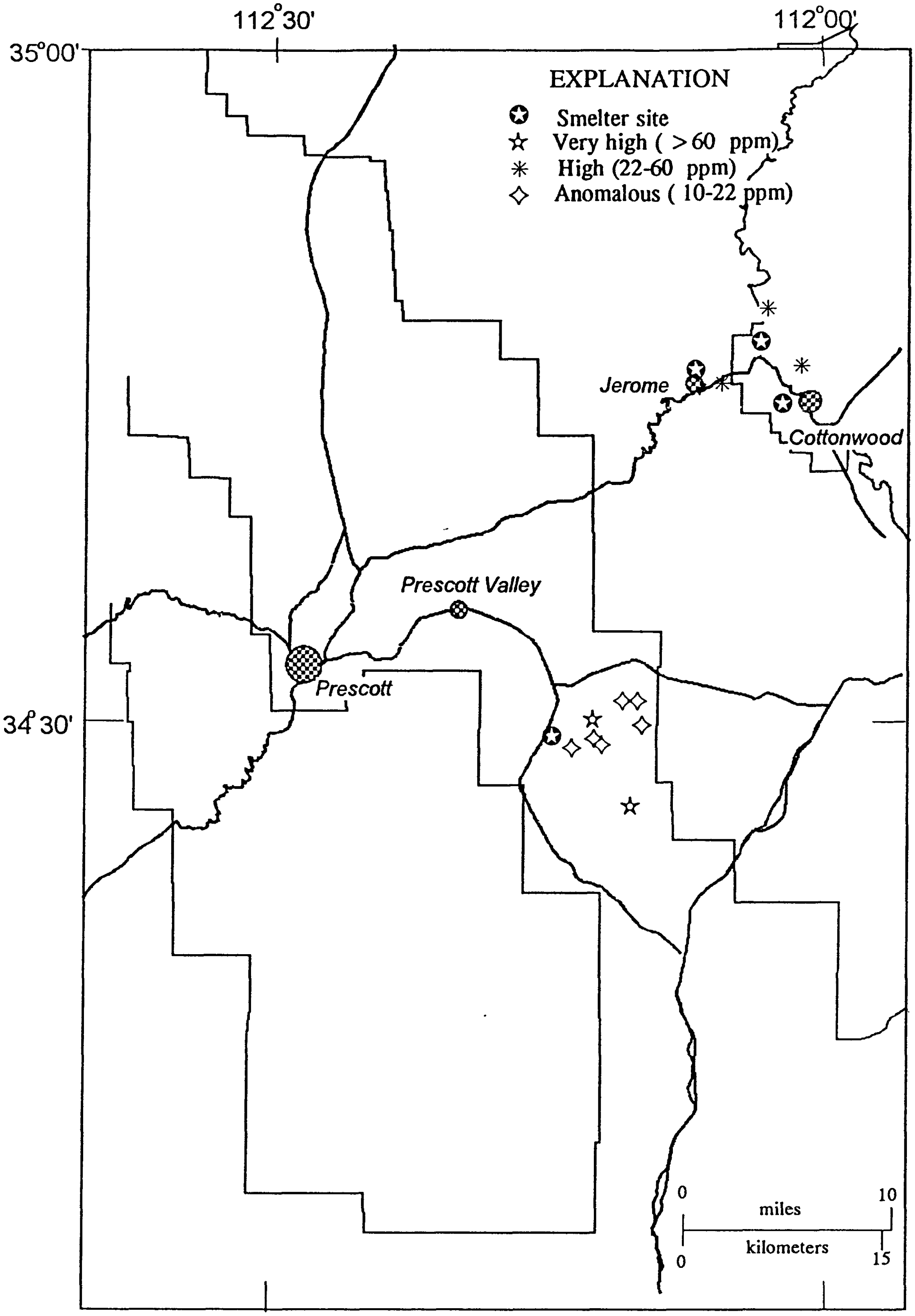

Figure 10: Soil geochemistry in relation to smelters: distribution of high arsenic values.

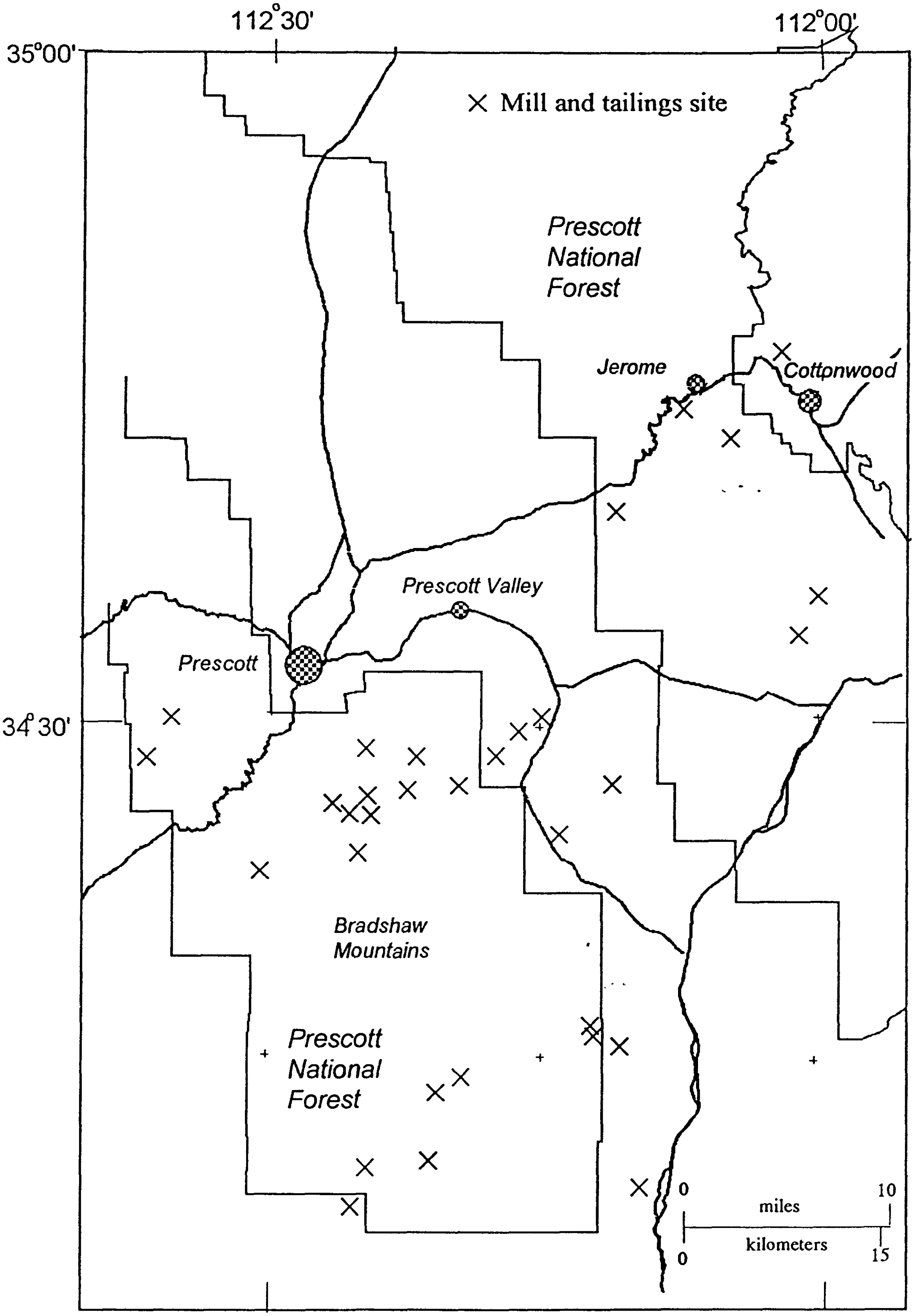

Figure 11: Location of mills and tailings in Prescott National Forest area.

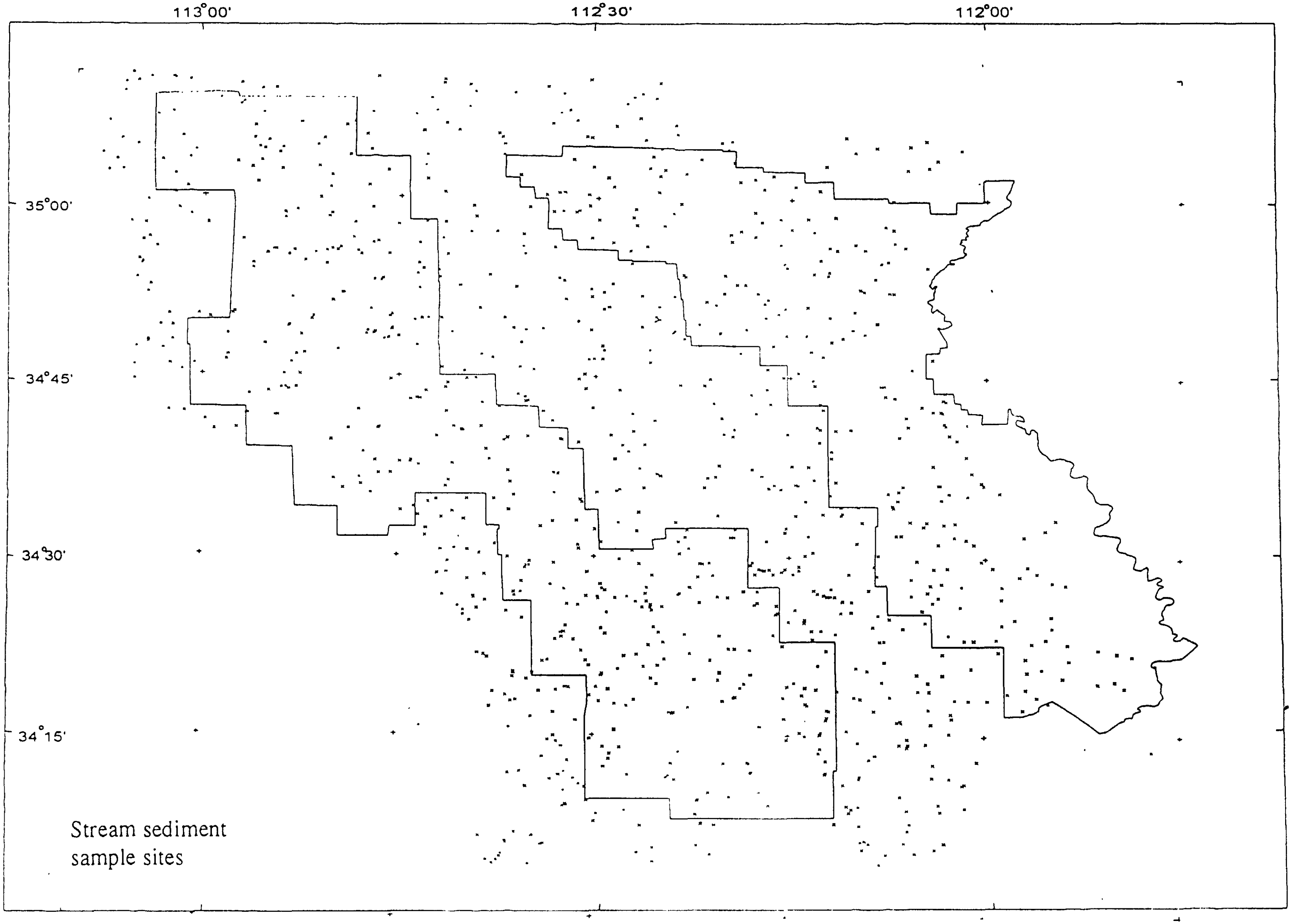

Figure 12: Localities of stream-sediment samples in and near the Prescott National Forest.

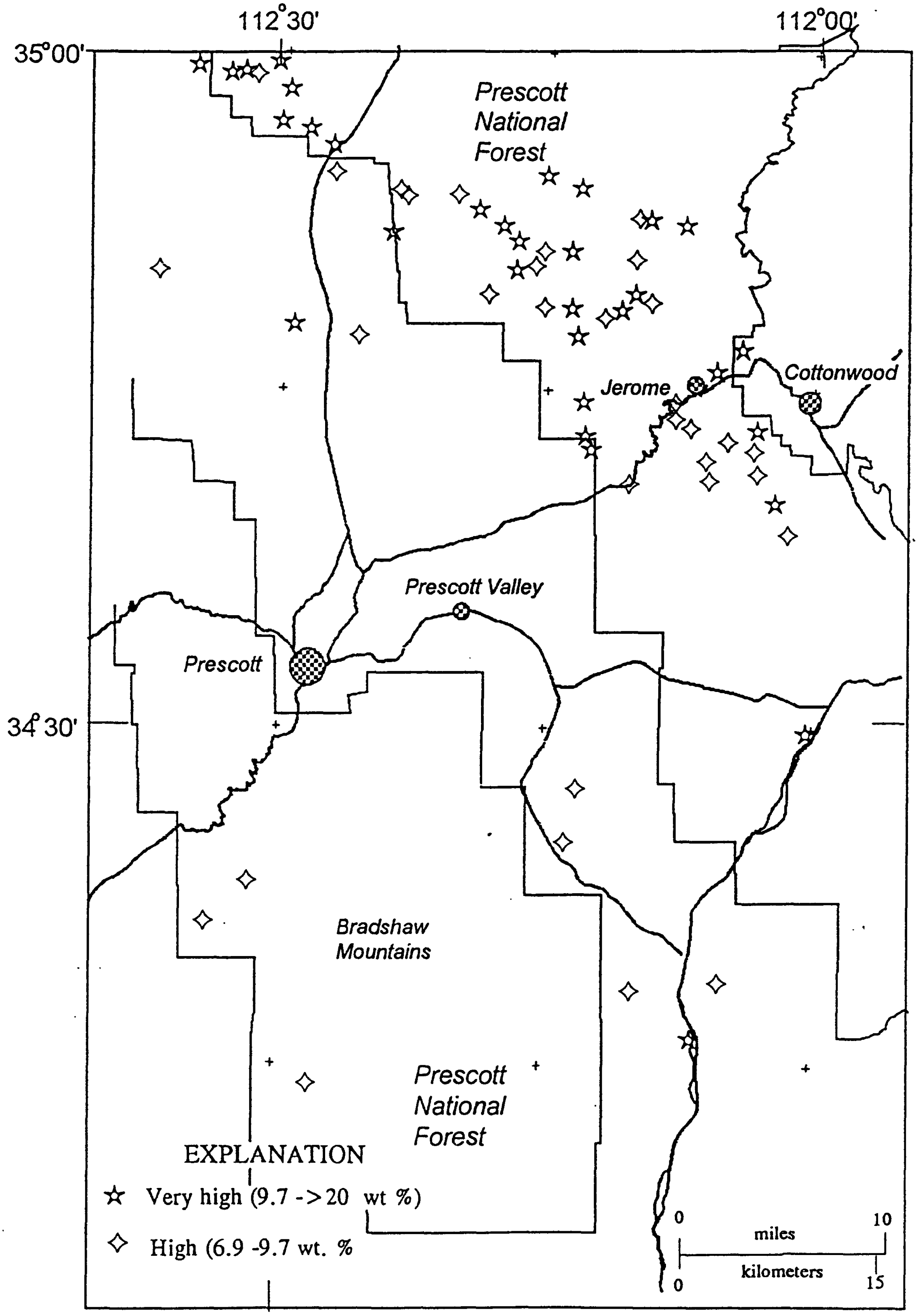

Figure 13: Stream-sediment sites having high concentrations of calcium.

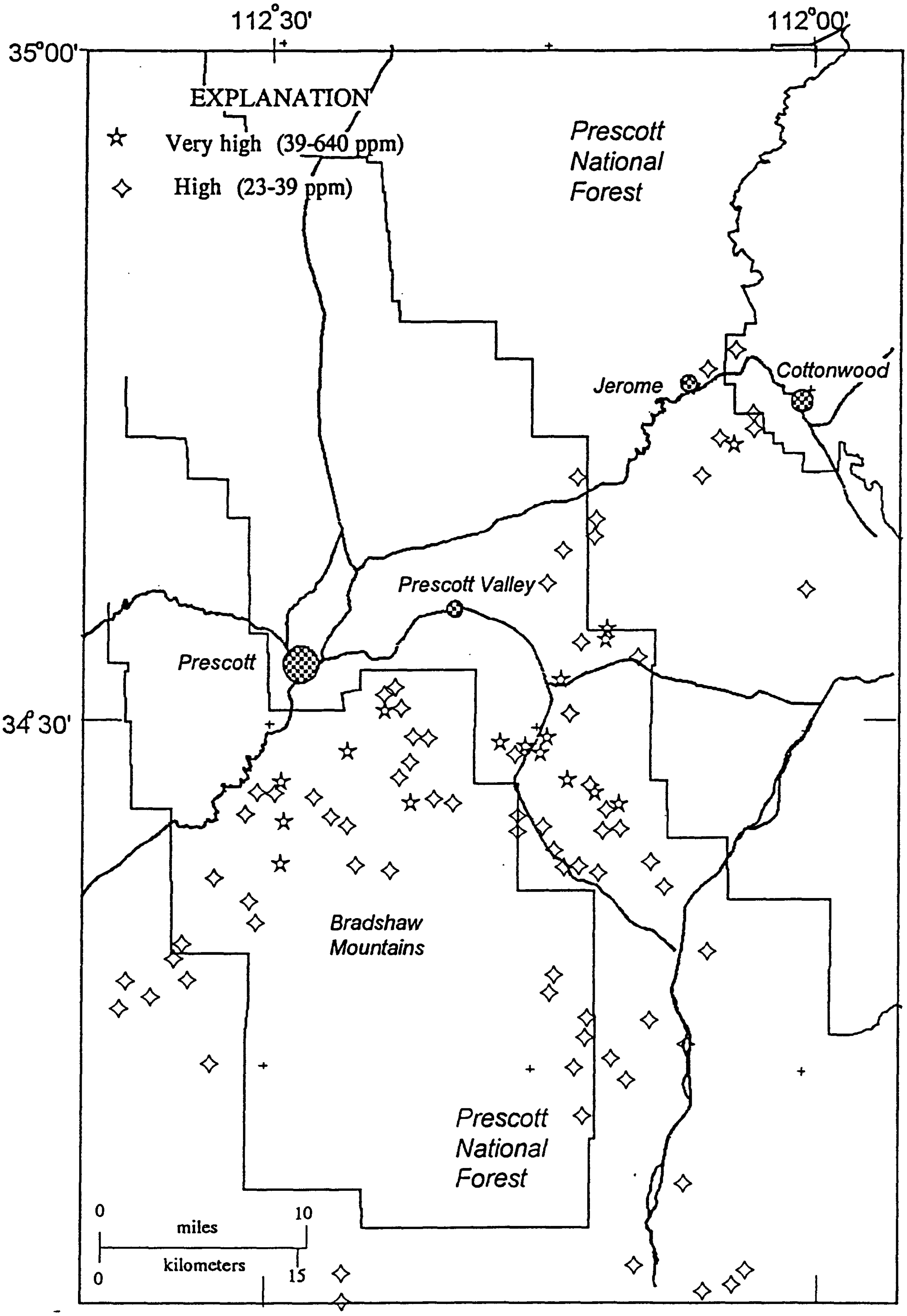

Figure 14: Stream-sediment sites having high concentrations of arsenic.

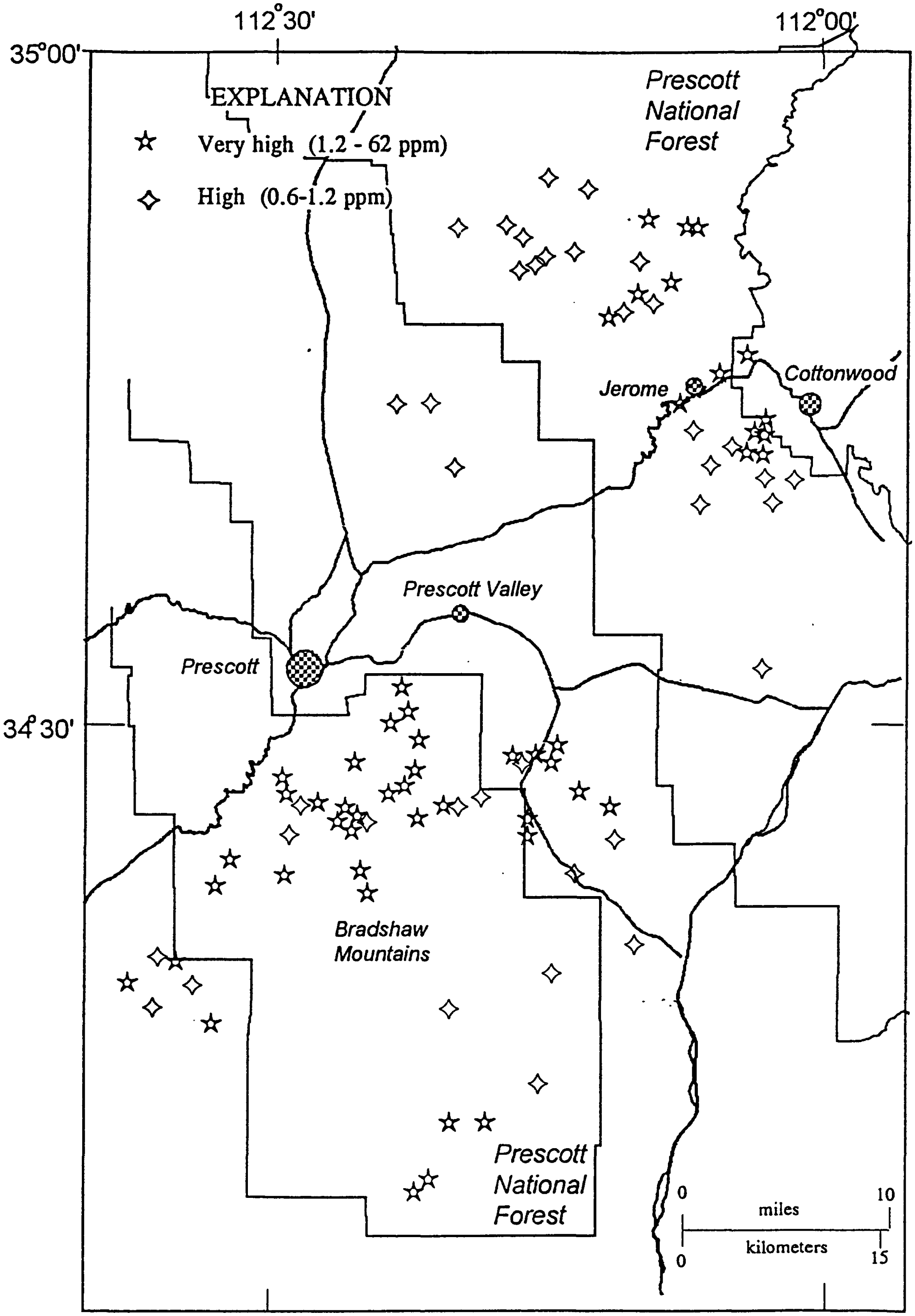

Figure 15: Stream-sediment sites having high concentrations of cadmium.

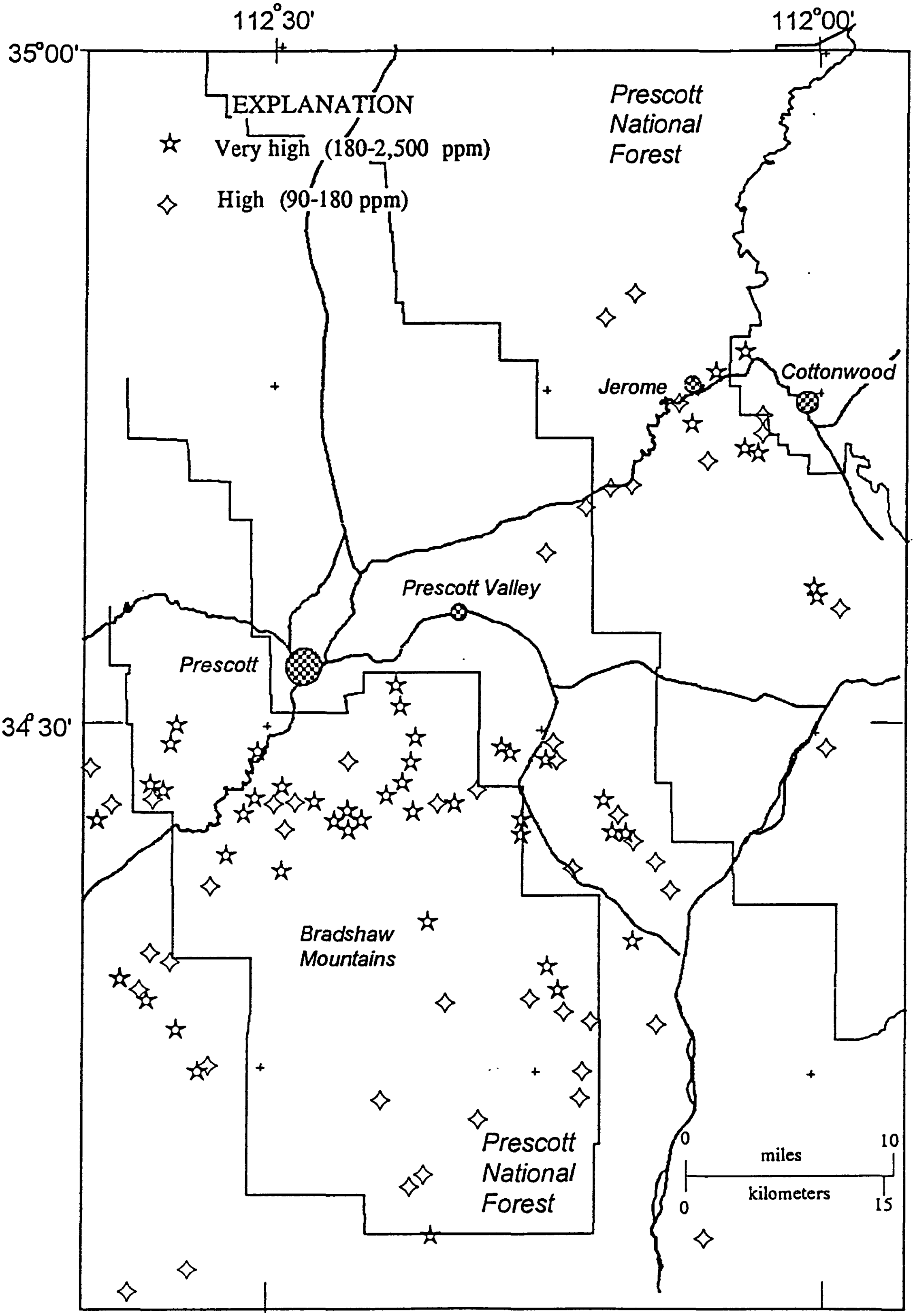

Figure 16: Stream-sediment sites having high concentrations of copper.

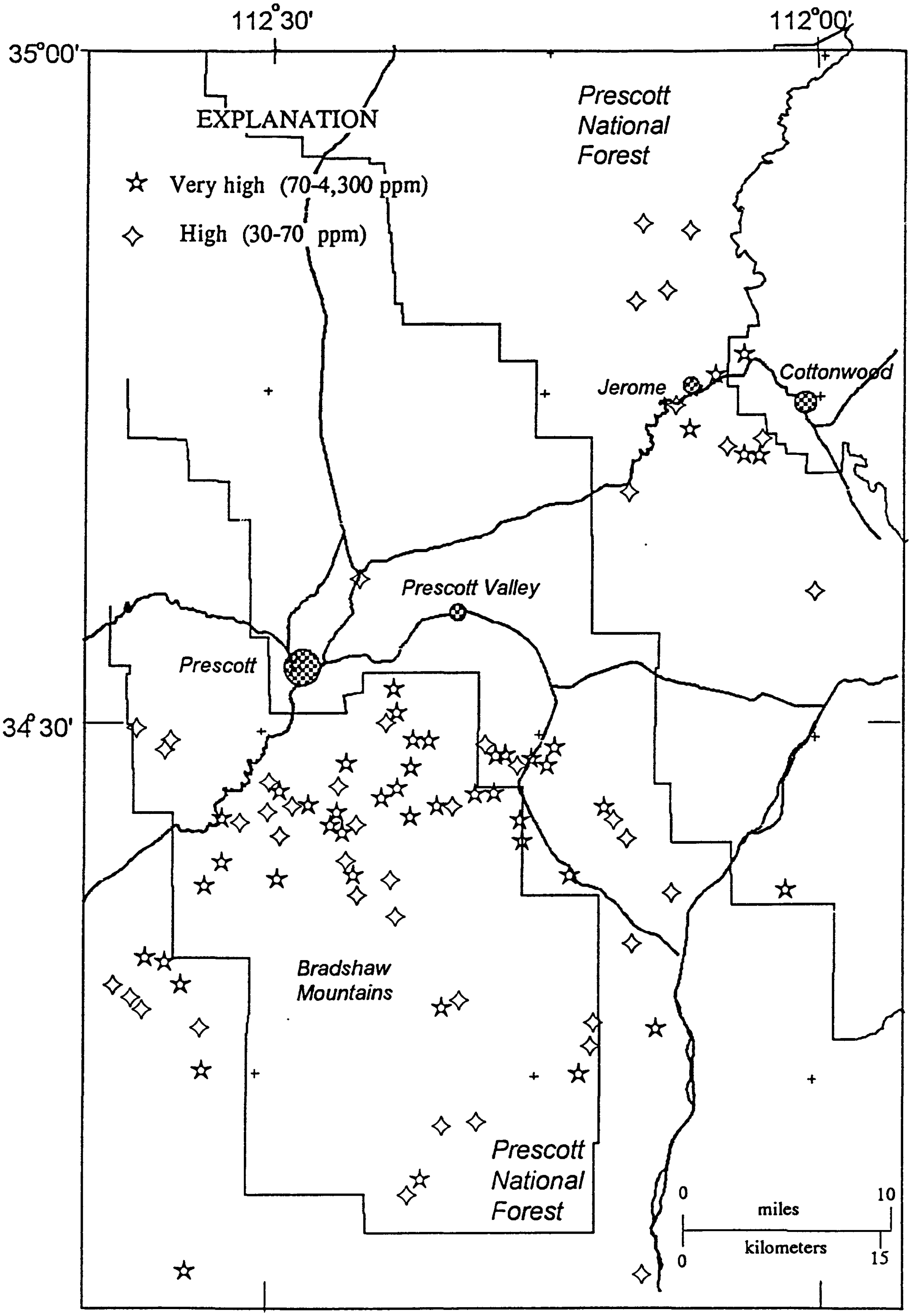

Figure 17: Stream-sediment sites having high concentrations of lead.

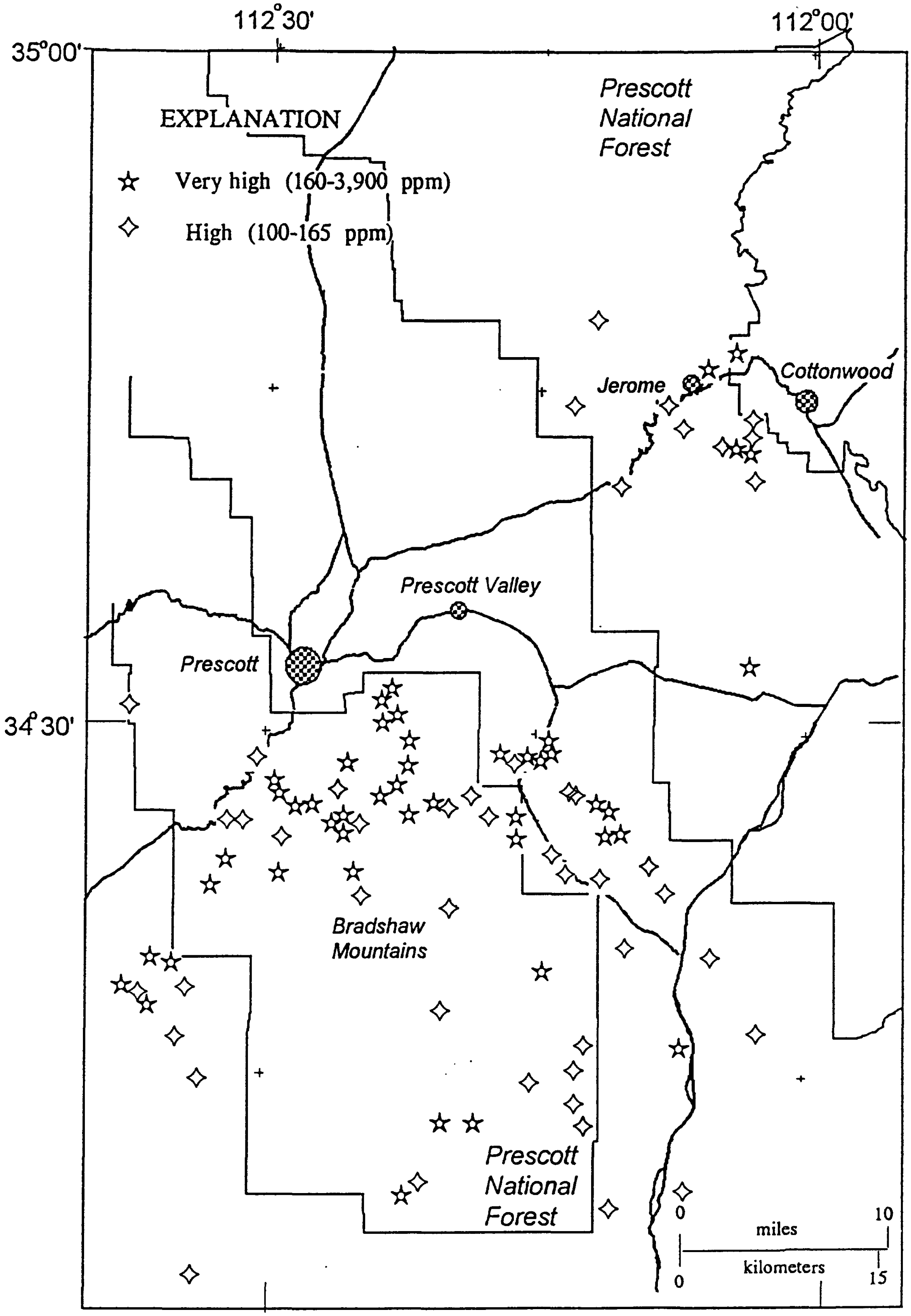

Figure 18: Stream-sediment sites having high concentrations of zinc.

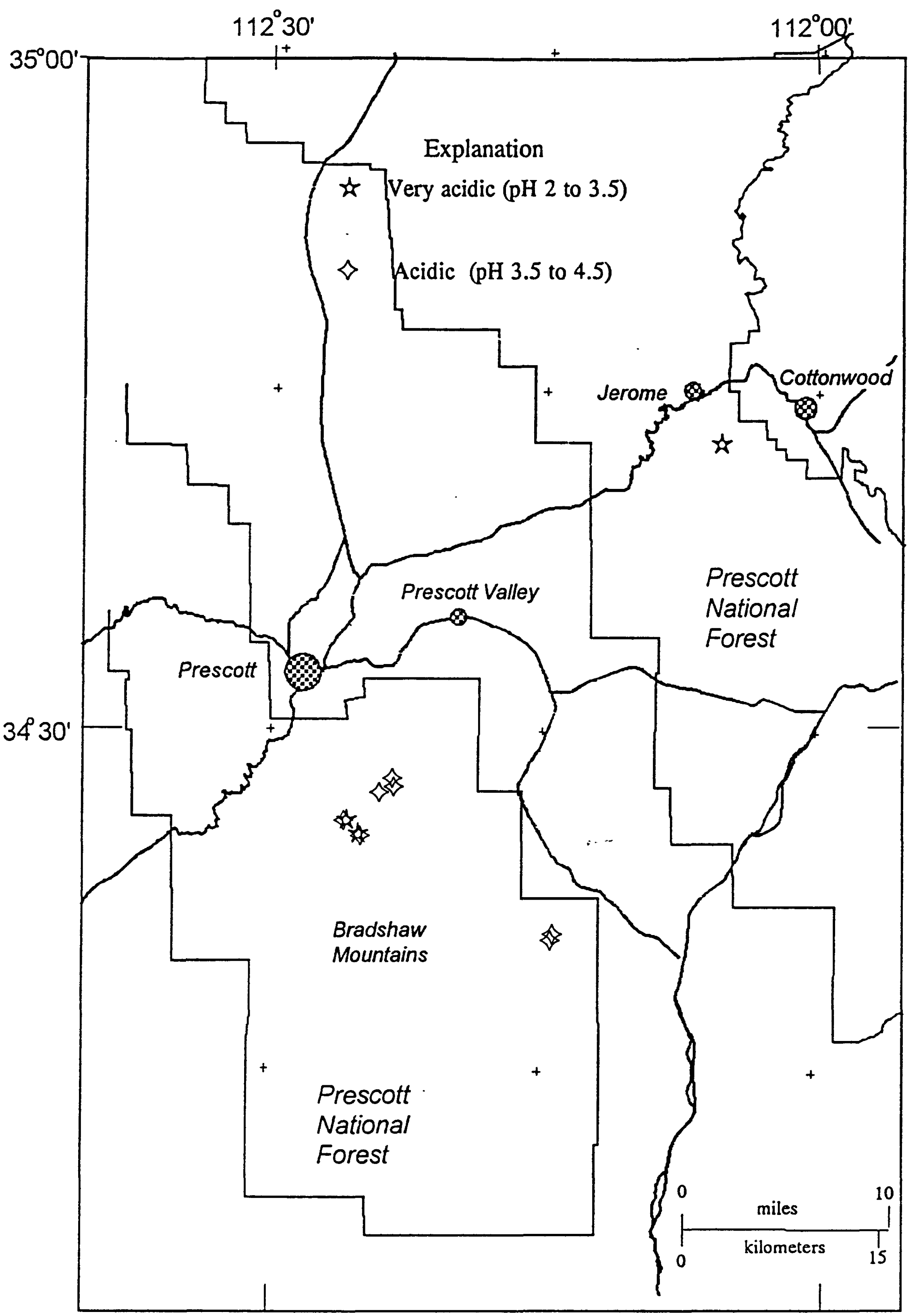

Figure 19: Water sites characterized by acidic pH.

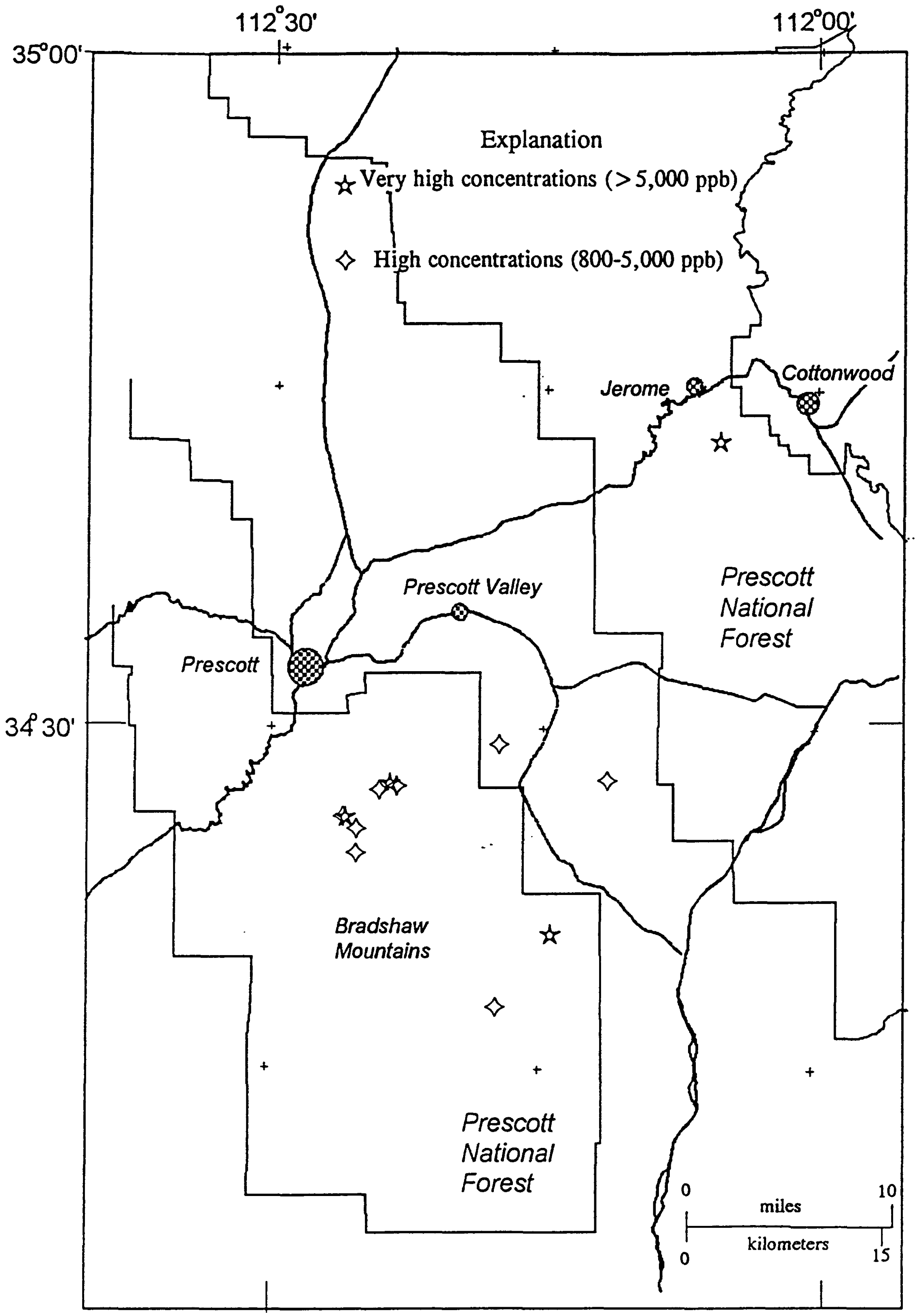

Figure 20: Water sample sites characterized by high concentrations of zinc.

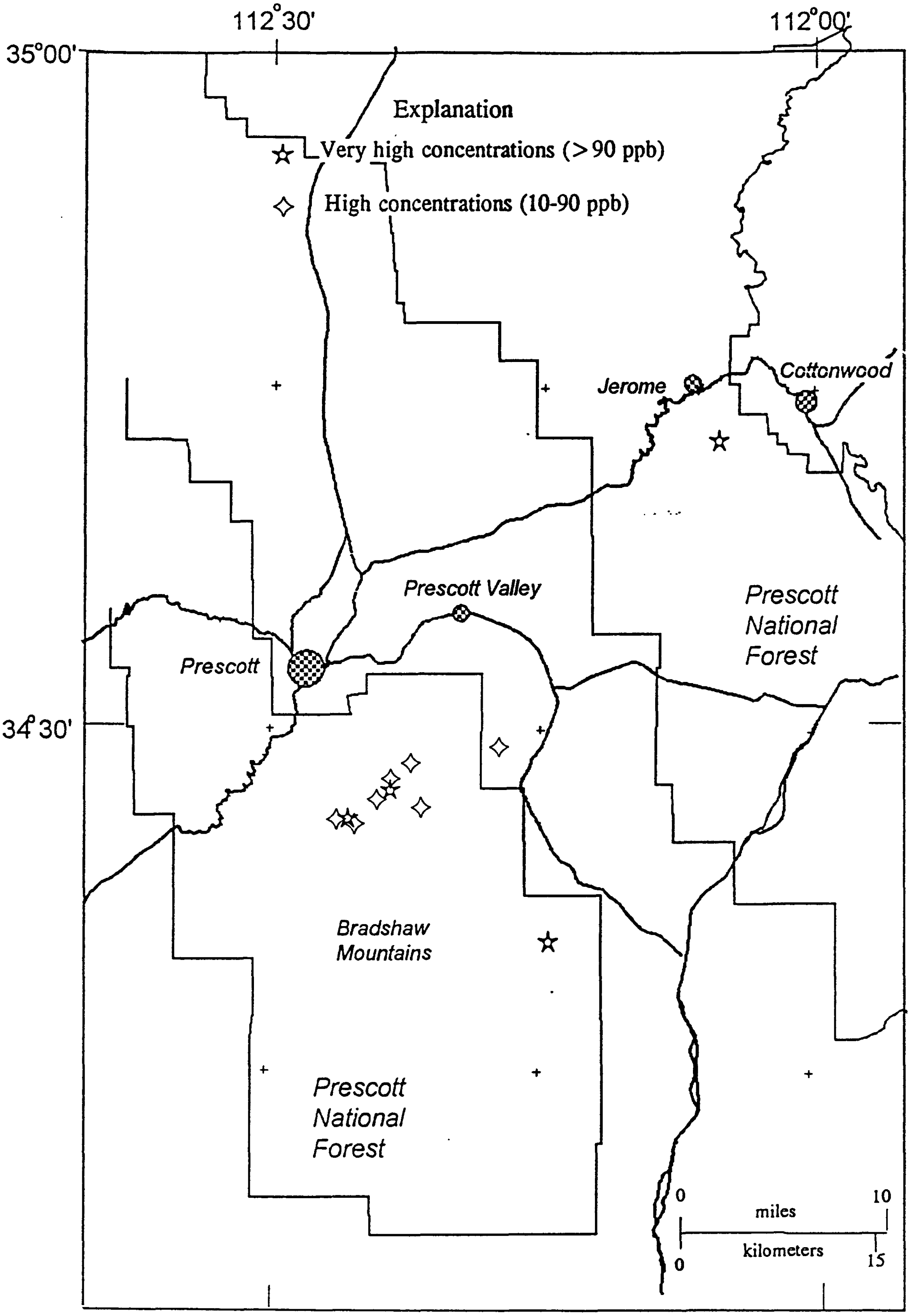

Figure 21: Water sample sites characterized by high concentrations of cadmium.

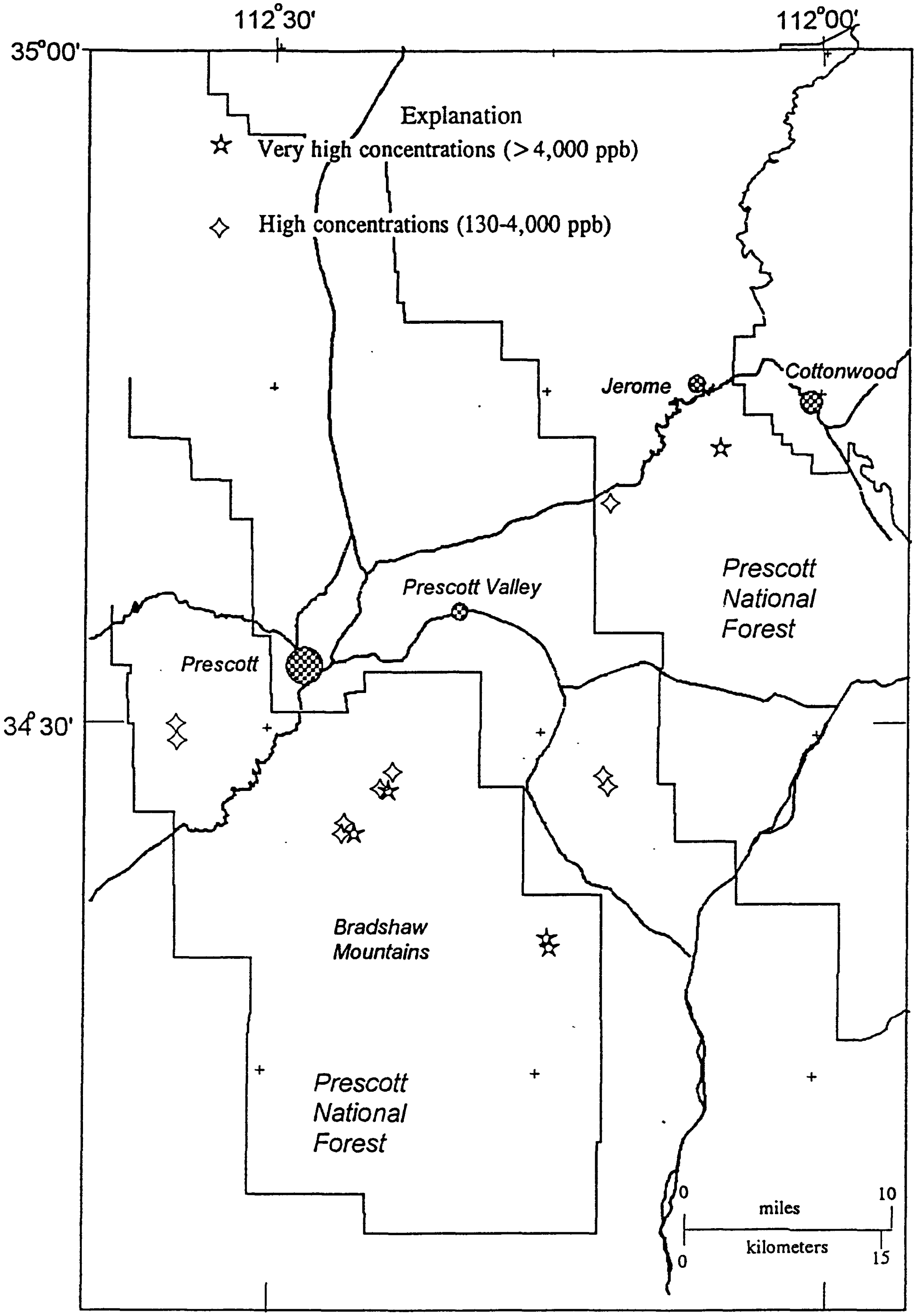

Figure 22: Water sample sites characterized by high concentrations of copper.

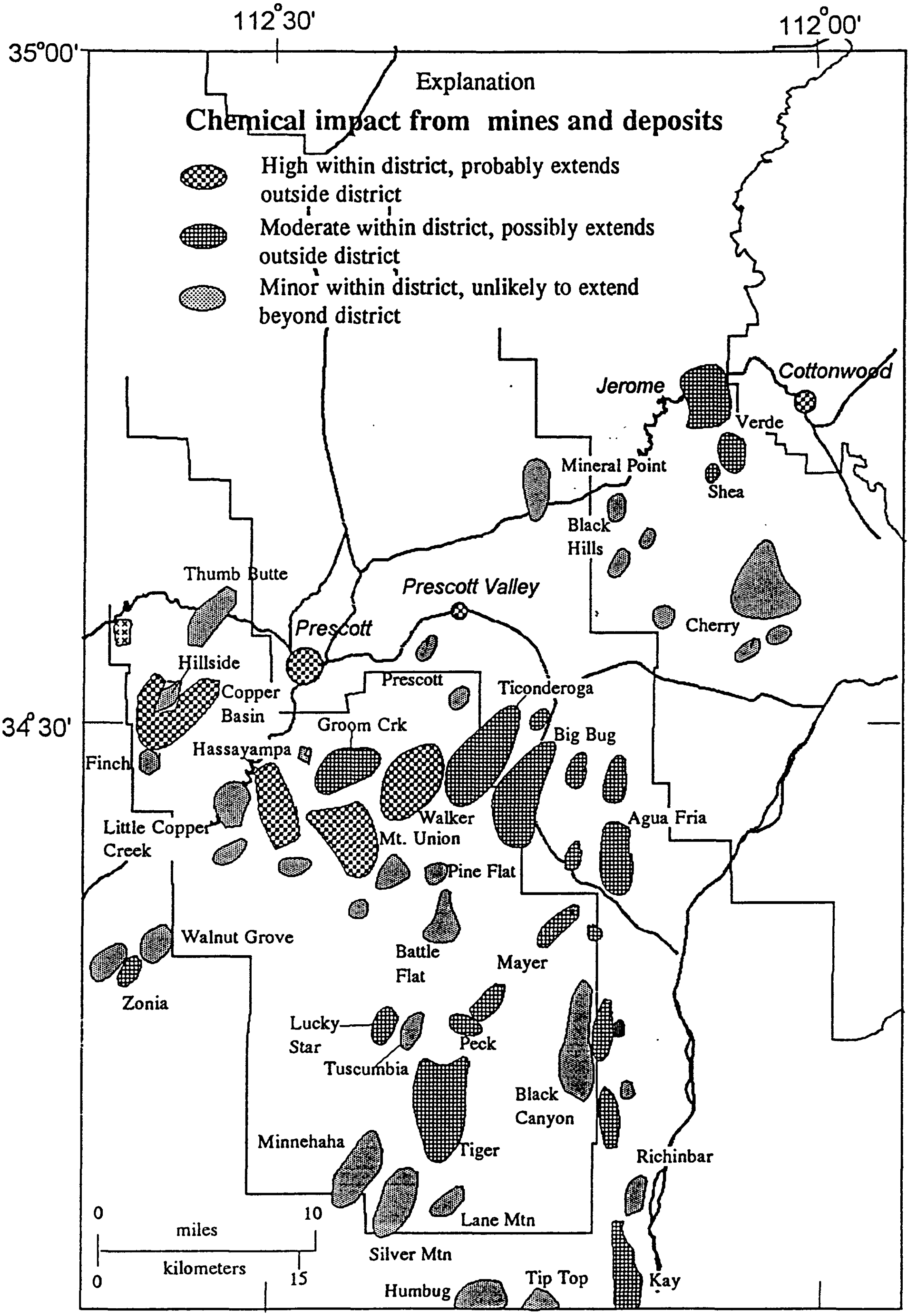

Figure 23: Map summarizing geochemical character of mining districts in the Prescott National Forest area. Mining districts are those shown on Figure 3.

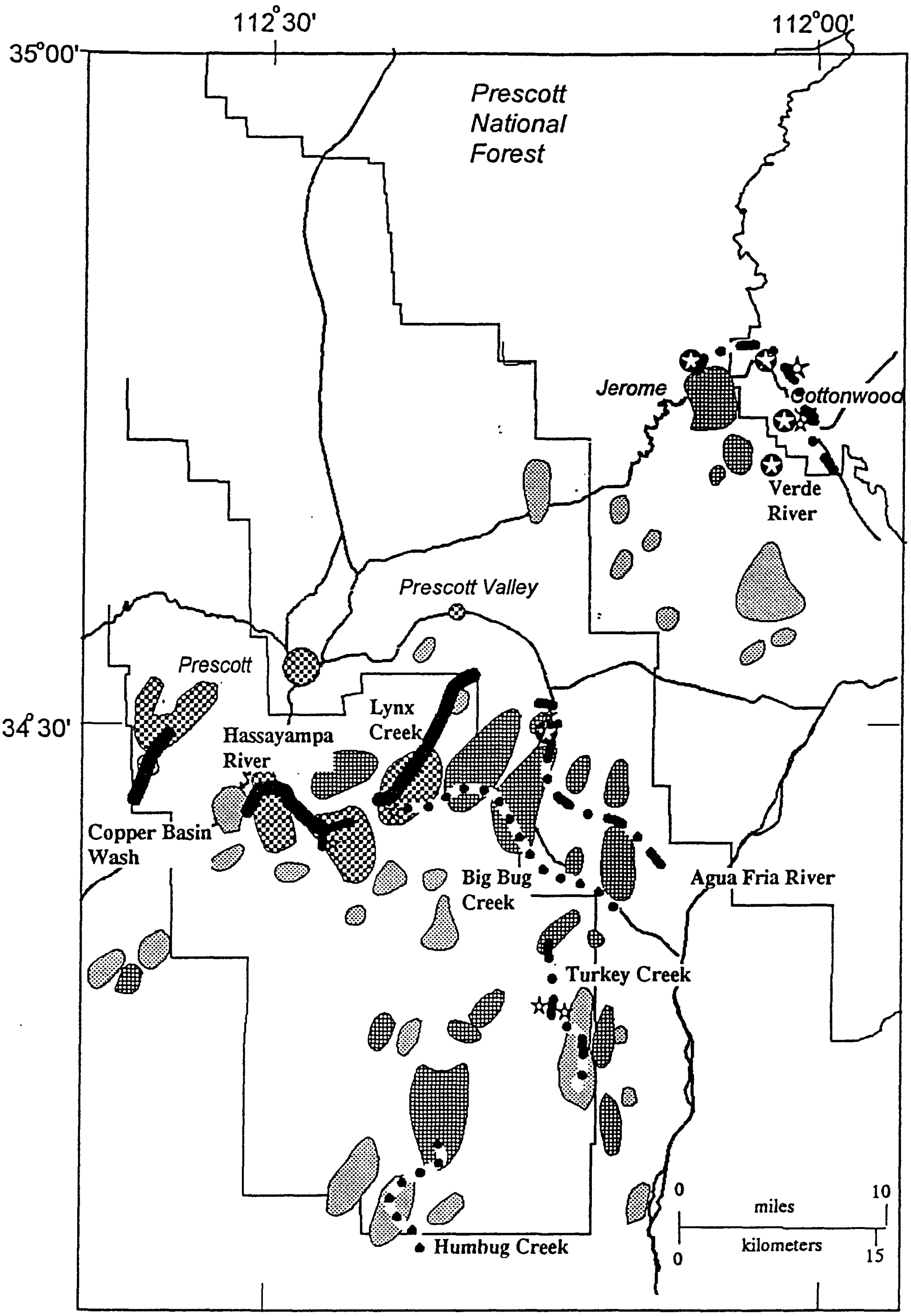

Figure 24: Map summarizing geochemical character of watersheds in the Prescott National Forest area. Mining district characterization is from figure 23. Explanation in page 63.

Explanation of Figure 24

Chemical impact from mines and deposits, district scale

▩ High within district, probably extends outside district

▦ Moderate within district, possibly extends outside district

░ Low within district, unlikely to extend beyond district

Mining-associated contamination

✪ Smelter (only most significant sites shown)
☆ Mill tailings (only most significant sites shown)

Interpretation of impact of mineral-related contamination on water quality

▬ High

▬ • ▬ Medium

▬ • • Low

Table 1. Summary of mean annual precipitation at seven stations in the Prescott National Forest area, central Arizona

Station	Mean Annual Precipitation (inches)	Elevation (feet)
Crown King	27.7	6,000
Drake	13.6	4,650
Jerome	18.2	5,245
Montezuma Castle	11.4	3,180
Prescott	19.3	5,410
Walnut Creek	16.9	5,100
Yaeger Canyon	17.9	6,000

Data are from Sellers (1960)

Table 2: Analytical Methods and lower limits of determination for selected elements in solids and water

Element		Solids (Rocks, soils)		Water
		ICP-AES (40)	ICP-AES(10)	ICP-MS
Aluminum	Al	0.005%	--	40 ppb
Antimony	Sb	--	1.0	0.2 ppb
Arsenic	As	10	1.0	0.8 ppb
Barium	Ba	10	--	0.2 ppb
Bismuth	Bi	10	1.0	2 ppb
Cadmium	Cd	2	0.05	1 ppb
Cobalt	Co	2	--	0.3 ppb
Copper	Cu	2	0.05	1 ppb
Gold	Au	8	0.10	0.1 ppb
Iron	Fe	0.02%	--	10 ppb
Lead	Pb	4	1.0	0.7 ppb
Magnesium	Mg	0.005%	--	50 ppb
Molybdenum	Mo	10	0.10	0.1 ppb
Nickel	Ni	3	--	0.2 ppb
Silver	Ag	2	0.08	0.1 ppb
Thorium	Th	6	--	1.0 ppb
Tungsten	W	--	--	0.2 ppb
Uranium	U	100	--	0.2 ppb
Vanadium	V	2	--	0.3 ppb
Zinc	Zn	2	0.05	1 ppb

Explanation: Values are in parts per million (ppm), except for aluminum, iron, and magnesiumwhich are in wt. percent; values for water analyses are in parts per billion (ppb). ICP-AES: inductively coupled plasma-atomic emission spectrometry ; ICP-MS: inductively coupled plasma-mass spectrometry; ICP-AES (40), four acid, total digestion, and determination of 40 elements (Briggs, 1990) ; ICP-AES(10): sample digestion in hydrochloric acid with hydrogen peroxide followed by solvent extraction of 10 metals as tertiary amine-halide complexes (Motooka, 1990). --, not determined.

Additional Notes: 1). Gold also determined by graphite furnace atomic absorption spectrometry with a lower limit of determination of 2 parts per billion (O'Leary and Meier, 1990); 2). Sulfur determined on selected rock samples by combustion, with a lower limit of determination of 0.05 wt. percent (Curry, 1990). 3). The ICP-MS method of water analyses employed by Meier is a research method that has not been published; this method is considered to be the state of the art for water, with excellent sensitivity for more than 50 elements; precision and accuracy vary from element to element and are influenced by sample composition.

Table 3: Summary of Mining Districts, deposit type, geology, and production, Prescott National Forest area, AZ

[Deposit classification is modified from Keith and others, 1983; geology from Lindgren (1926) and unpublished observations by the authors; production figures are from Keith and others, 1983]

District	Deposit type	Host rocks	Production						
			Total (tons)	Copper (lbs)	Lead (lbs)	Zinc (lbs)	Gold (oz)	Silver (oz)	Other
Agua Fria	VMS	Schist	160,000	11,600,000	3,000	16,000	900	48,000	
Battle Flat	PMV	Granite	200	2,000	1,000	400	--	7,000	
Big Bug	VMS	Schist	6,200,000	14,300,000	233,000,000	614,000,000	462,000	16,771,000	
Black Canyon	PMV	Granite, schist	265,000	263,000	3,580,000	225,000	32,000	949,000	
Black Hills	PMV	Granite, schist	23,000	1,900,000	25,000	--	--	64,000	
Camp Verde	Other	Granite	--	--	--	--	--		tungsten
Cherry Creek	GQV	Granite, gneiss	7,000	28,000	150	--	4,000	6,200	
Copper Basin	PCM	Granite, metamorphics	357,000	19,631,000	508,000	1,400,000	500	45,700	
Finch	PMV	Granite, metamorphics	500	17,000	--	--	100	1,000	
Groom Creek	PMV	Granite, schist	15,000	51,000	25,000	6,700	5,200	86,000	
Hassayampa	PMV	Granite, schist	18,000	151,000	409,000	530,000	9,200	78,000	
Humbug	PMV	Granite	4,200	105,000	48,000	--	1,700	8,300	
Kay	VMS	Schist	2,600	296,000	13,000	--	150	2,700	
Kirkland	GQV	Granite, metamorphics	900	--	30	--	450	200	

Little Copper Creek	PMV/PCM	Granite, schist	400	21,000	9,000	600	100	1,500	
Lane Mtn.	PMV	Granite, schist	5,000	--	--	--	250	360,000	
Mayer	VMS	Metavolcanic	1,424,000	92,000,000	--	--	71,600	1,786,000	
Minnehaha	PMV	Granite, schist	1,000	1,200	8,600	--	400	1,400	
Money Maker	Other	Granite, schist	--	--	--	--	--	--	tungsten
Mount Union	PMV	Granite, schist	108,000	1,663,000	1,827,000	485,000	51,700	593,000	
Peck	PMV	Schist, granite	26,000	27,000	365,000	--	130	1,374,000	
Pine Flat	PCM	Granite	<	--	--	--	<	<	
Prescott	PMV	Granite, schist	300	10,000	--	--	100	4,000	
Richinbar	PMV	Schist	32,000	7,400	7,000	--	4,800	1,500	
Seligman Iron	Other	Sedimentary rocks	--						iron
Shea	PMV	Diorite, schist	1,000	35,000	--	--	130	31,000	
Silver Mountain	PMV	Granite	50	9,400	--	--	20	600	
Squaw Peak	PCM	Granite	1,300	19,400	52,600	100	<	8,000	
Thumb Butte	PMV	Granite, schist	2,000	2,700	--	--	800	300	
Ticonderoga	PMV	Granite, schist	336,000	2,593,000	3,217,000	29,000	189,000	1,575,000	
Tiger	PMV/PCM	Granite, schist	270,000	1,518,000	806,000	3,312,000	122,000	1,115,000	
Tip Top	PMV	Granite, schist	28,000	2,800	28,000	--	9,800	1,910,000	
Turkey Creek	PMV	Schist, granite	5,000	38,500	1,214,000	4,300	1,600	198,000	

Tuscumbia	PMV	Granite	850	1,700	500	--	500	45,800
Verde	VMS	Schist	36,180,000	3,625,051,000	693	97,352,000	1,579,000	57,313,000
Walker	PMV	Granite, schist	213,000	3,940,000	4,473,000	524,000	65,000	871,000
Walnut Grove	PMV	Granite	6,000	40,000	560,000	--	200	30,000
Yarber Wash	PMV	Granite, gneiss	600	300	--	--	180	100
Zonia	VMS	Schist	5,692,000	30,317,000	800	--	250	4,000

Explanation: Deposit types: PMV, polymetallic vein; VMS. volcanogenic massive sulfide; PCM, porphyry copper-molybdenum; GQV, gold-quartz vein; other, miscellaneous deposits, chiefly tungsten and iron; several districts with PMV/PCM have had production from polymetallic veins, but geology of Cretaceous-Tertiary stocks suggests porphyry-copper-molybdenum deposit style (Keith and others, 1983). Geologic units: non-technical terms for major rock types, and age is not specified; <, production very small; --, no production.

Table 4: Classification and character of major metallic mineral deposits, Prescott National Forest area, AZ.

[Deposit attributes are highly simplified; for more details see Cox and Singer, 1986; Guilbert and Park, 1986; du Bray, 1995; heavy metals include As, Cd, Cu, Pb, Zn; mod.:moderate]

		Geo-environmental character	
Type	Geology	Rock geochemistry	Drainage geochemistry
Placer	Gravel, alluvium	Nil; no sulfides possible Hg from milling	Hg?
Polymetallic veins	Veins in Precambrian-Tertiary rocks	High heavy metals; mod. sulfides;	Locally acidic; heavy metals
Gold-quartz veins	Quartz veins in Precambrian rocks	Low heavy metals; low sulfides	Possibly Hg or cyanide from processing
Porphyry copper-molybdenum	Veins, disseminations Precambrian to-Tertiary stocks and fxwallrocks	Mod. heavy metals; mod-high total sulfide; low buffering capacity	Acidic from ores and waste, mobilizes heavy metals
Massive sulfide	Lenses and veins in Precambrian metavolcanic rocks	Mod. to high heavy metals; high sulfide; good acid buffering in wallrocks.	Acidic from sulfides, may become neutral in wallrocks

Table 5 : Summary of chemical analyses of slag samples, Prescott National Forest area, AZ

[Nine samples of slag, analyzed by ICP; results in parts per million, except for sulfur, in wt %]

Element	Arithmetic mean	Maximum
Ag ppm	45	260
As ppm	610	1,800
Au ppm	<1.5	<1.5
Cd ppm	13	30
Cu ppm	7,960	40,000
Pb ppm	25,600	153,000
Sb ppm	20	500
Zn ppm	17,600	28,000
Sulfide S, wt.%	1.0	1.9

Table 6: Summary of chemical results for soil samples, Prescott National Forest area, AZ

[Results shown are for 46 surface samples and 14 deep samples, in parts per million; maximum values do not include results for one sample with extremely high concentrations; anomaly threshold is below mean because the majority of samples collected are considered contaminated; nc, not computed because most results below limit of determination.]

Element	As	Bi	Cd	Cu	Hg	Pb	Sb	Zn
Surface soil samples (n=46)								
Arithmetic mean	13	<.5	1.3	78	.01	34	0.8	100
Maximum	120	1.9	7.6	370	.11	140	3.2	320
Deep soil samples (n=14)								
Arithmetic mean	9.0	<.5	0.4	55	.01	17	0.8	83
Anomaly threshold								
	10	nc	1.0	70	nc	30	nc	90

Table 7: Summary of chemical results for mill tailings, Prescott National Forest area, AZ

[Results for 40 samples, analyses by ICP and sulfur by combustion;
reported in parts per million,except Fe and S in wt. %; nc, not computed]

Element	minimum	maximum	arithmetic mean
Ag	<0.1	92	17
As	2	16,000	1,390
Au	<0.1	6.2	nc
Cd	0.1	97	13
Cu	20	10,000	1,080
Mo	0.6	93	10
Pb	12	16,000	4,440
Sb	1	2,600	98
Zn	60	19,000	2,090
Fe(wt. %)	0.1	7.4	1.5
S (sulfide,wt. %)	<0.05	4.9	1.2

NB: A great range in mineralogy and chemistry is represented in these analyses. Much more work is needed to determine which samples are representative of large volumes of mill tailings, and how reactive they are (dependent on mineralogy).

Table 8: Summary of results, laboratory leach tests of mill tailings, tailings crusts, and slag

[Samples leached by water, dilute acid, or carbonate solution, with frequent shaking for 4 to 24 hours, room temperature; resultant solution filtered and analyzed by ICP-MS; results are mean values reported as parts per billion (ppb), except for calcium in parts per million (ppm).]

Leach	Ca ppm	Cd ppb	Cu ppb	Fe ppb	Pb ppb	Zn ppb
			Mill Tailings			
water	68	1	5	90	<0.6	6
acid	58	270	2,500	6,200	2	20,300
			Tailings Crusts			
water	74	3	600	700	1	150
acid	240	9	950	225	<0.2	215
			Slag			
water	1	1	80	400	400	20
alkaline	8	1	4	90	1	6
acid	20	8	1,600	10,800	2,600	3,800

Explanation: water, deionized water; alkaline, saturated with calcium carbonate; acid, very dilute sulfuric acid (1 drop acid per liter); see text for details.

Table 9: Summary of chemical results for four ore types and mineralized unmined rocks and soils, Prescott National Forest area, AZ

[Arithmetic mean values are for 8 samples of gold-quartz veins, 12 samples of massive sulfide, and 30 samples of polymetallic veins, data for porphyry copper deposits from Cox and others, 1995; Table 1 and Copper Basin 4 samples this study analyses by ICP, except sulfur by cumbustion,; nd, not determined

Ore type	Sulfide S wt. %	As ppm	Cu ppm	Cd ppm	Fe wt. %	Pb ppm	Zn ppm
Massive sulfide							
mean	3.3	9,540	8,240	77	9.5	3,720	18,500
maximum	nd	64,000	23,000	370	16	15,000	92,000
Polymetallic vein							
mean	1.9	1,210	6,640	41	8.7	4,290	6,240
maximum	8.9	18,000	90,000	340	22	44,000	46,000
Gold-quartz vein							
mean	0.1	210	1,140	5	4.4	575	950
maximum	0.3	650	4,100	9	8.7	1,600	3,300
Porphyry copper[1]							
mean	nd	6	2,000	nd	4.1	49	130
maximum	nd	500	20,000	150	10	5,000	17,000
Copper Basin	nd	13	4,580	<.1	2.8	32	45
Outcropping rocks and soils, mineralized, unmined							
mean	0.7	980	3,400	1.3	10.2	1,800	275
maximum	4.1	4,000	16,000	6.0	18	21,000	1,100

Table 10: Summary of chemical results for stream-sediment samples, Prescott National Forest area, AZ

[Based on analyses of 1,123 NURE stream-sediment samples by ICP, except Au determined by graphite furnace atomic absorption; nc, not computed]

Element	Geometric mean	Max	Highly anomalous[1]	
			no.sites	value
Fe (wt %)	5.2	36	114	> 10.0
Ag (ppm)	0.03	26	112	> 0.15
As (ppm)	3.7	640	112	> 23
Au (ppm)	0.002	46	30	>0.04
Bi (ppm)	nc	37	66	> 1.0
Cd (ppm)	.16	62	113	>0.58
Cu (ppm)	27	2200	109	>75
Mo (ppm)	0.57	93	69	>2.0
Pb (ppm)	12	4,300	114	>31
Sb (ppm)	nc	78	111	>1.4
Zn (ppm)	53	3,900	109	> 100

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[1] Explanation: Highly anomalous is approximately the upper 10 percent of values, except for some elements such as Au that have a different frequency distribution, and for these the value is taken as the break in the distribution.

Table 11: Summary of new water analyses for PrescottNational Forest area, AZ

[Based on ICP-MS analyses and field measurements for 89 samples (anion analyses for 53 samples]

Parameter	Highly anomalous values in ppb[1]	number exceeding WQ standard [2]		Comments
pH	2.2-4.2	13	<4.3	Highly acidic only in low flow drainages; some pH 3-4 in small streams
Conductivity	2,160-18,590 µS/cm	14	>2,000	Tend to be high in neutral, SO_4 - rich waters, formerly acidic?
As	260-2900	8	> 50 ppb	High in acidic and weakly alkaline pH's
Cd	220-7300	22	>10 ppb	High in acidic waters; numerous
Cr	120	1	> 50 ppb	One high in extreme acid water
Cu	1300->100,000	27	>100 ppb	High in acidic waters; numerous
Fe	6700->2,000,000	29	>300 ppb	High in acidic waters; numerous
Pb	18-220	2	>50 ppb	High in acidic waters; rare
Zn	13000->1,000,00	9	>5000 ppb	High in acidic waters, pH <4.2
U	41-150	11	>10 ppb	High in acidic and alkaline waters
NO_3	1-25	0	45 ppm	High near developed areas
SO_4	1,250-33,300	24	>250 ppm	High in acidic and neutral pH's; common near sulfidic ore deposits

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Explanations: [1] Highly anomalous, data from this study, at the very high end of the range of determinations. [2]. Standards typically cited for water quality by Hem (1970), EPA (1986), and ADEQ (1995); note that there is no single standard value for an element because values vary for different uses of water and for several types of ground and surface waters.Note that values are in parts per billion (B!).

Table: 12: Relative environmental impact of ore deposit types, Prescott National Forest area, AZ

[Rankings are preliminary and highly simplified; values (low, moderate, high) are relative to other deposit types in the study area. Geographic scale: local: mine site, less than 1 square miles; district, about 3-10 square miles: watershed, about 10-100 square miles]

	Geo-environmental impact and geographic scale		
Type	Mine site	District	Watershed
1. **Placer**	low	low	low (1)
2. **Polymetallic veins**			
oxidized zone	low	low	low
sulfide zone	mod/high	mod.	low/moderate
3. **Gold veins**			
oxidized zone	low	low	low
sulfide zone	low/mod.	low	low
4. **Porphyry copper-molybdenum**			
oxidized zone	moderate	moderate	moderate
sulfide zone	high	high	high
5. **Massive sulfide**			
oxidized zone	mod/high	moderate	moderate
sulfide zone	high	high	mod./high

Table 13: Geochemical character of mining districts, Prescott National Forest area, AZ

[Deposit classification is modified from Keith and others, 1983; geologic notes are chiefly from Lindgren (1926) and unpublished observations by the authors; production figures are from Keith and others, 1983]

District	Host rock	Natural buffering capacity		Natural contamination	Production contamination	Mill contaminaton	Drainage type	Impact beyond District
		alteration	wallrocks					
		Massive sulfide districts						
Agua Fria	Schist	High	Med	Low	Med	Med	LA;AZ	Possibly
Big Bug	Schist	High	Med	Med	Med	Med	LA; AZ	Possibly
Kay	Schist	(High)	(Med)	(Low)	(Low)	(Low)	(LA; AZ)	(possibly)
Mayer	Schist	High	Med	Med	Med	Low	LA; AZ	Possibly
Verde	Schist	High	High	High	V High	VHigh	LA; AZ	Possibly
		Porphyry copper-molybdenum districts						
Copper Basin	Granite, schist	Low	Low	High	Med	Med	LA; AZM	Probably
Pine Flat	Granite	Low	Low	Med	Low	nil	(LA; AZM)	Unlikely
Squaw Peak	Granite	Low	Low	Low	Low	Low	(LA; AZM)	Unlikely
Little Copper	Granite, schist	Med	Low	Med	Low	nil	LA; AZM	Unlikely
Ticonderoga	Granite, schist	Med	Low	Med	Med	Med	LA; AZM	Possibly
Tiger	Granite, schist	Med	Low	Med	Low	Low	LA; AZM	Possibly
		Polymetallic vein districts						
Battle Flat	Granite	Med	Low	Low	Low	Low	(LA; AZ)	Unlikely
Black Canyon	Granite, schist	Med	Low	Low	Low	Low	(LA; AZ)	Unlikely
Black Hills	Granite, schist	Med	High	Low	Low	Low	LA; AZ	Unlikely
Finch	Granite, schist	Med	Low	Low	Low	Low	La; AZ	Unlikely
Groom Creek	Granite, schist	Med	Low	Med	Low	Low	La; AZ	Possibly
Hassayampa	Granite, schist	Med	Low	Med	Med	Med	LA; AZ	Probably
Humbug	Granite	Med	Low	Low	Low	Low	LA; AZ	Unlikely
Lane Mtn.	Granite, schist	Med	Low	Low	Low	Low	LA; AZ	Unlikely
Minnehaha	Granite, schist	Med	Low	Low	Low	Low	LA; AZ	Unlikely
Mount Union	Granite, schist	Med	Low	Med	Med	Med	LA; AZ	Probably
Peck	Schist, granite	Med	Low	Low	Low	Low	LA; AZ	Possibly

Prescott	Granite, schist	Med	Low	Low	Low	Low	(LA; AZ)	Unlikely
Richinbar	Schist	Med	Low	Low	Low	Low	(LA; AZ)	(Unlikely)
Shea	Diorite, schist	Med	High	Low	Low	Low	LA; AZ	Possibly
Silver Mountain	Granite	Med	Low	Low	Low	Low	(nil?)	Unlikely
Thumb Butte	Granite, schist	Med	Low	Low	Low	Low	(LA; AZ)	Unlikely
Tip Top	Granite, schist	Med	Low	Low	Low	Low	(LA; AZ)	Unlikely
Turkey Creek	Schist, granite	Med	Low	Low	Low	Low	(LA; AZ)	(Unlikely)
Tuscumbia	Granite	Med	Low	Low	Low	Low	(nil)	Unlikely
Walker	Granite, schist	Med	Low	Med	High	Med	A; AZ	Probably
Gold quartz vein districts								
Cherry Creek	Granite, gneiss	Med	Low	Low	Low	Low	nil	Unlikely
Other types of deposits								
Camp Wood	Granite, schist	(Med)	(Low)	(Low)	(Low)	(Low)	(nil?)	(Unlikely)
Money Maker	Granite, schist	(Med)	(Low)	(Low)	(Low)	(Low)	(nil?)	(Unlikely
Seligman Iron	Sedimentary	Low	High	Low	Low	Low	nil	Unlikely

Explanation: Drainage types: A, acidic for a mile or more from deposits; LA, locally acidic near deposits; AZ, alkaline waters (after neutralization) possibly carrying zinc; AZM, alkaline waters (after neutralization) possibly carrying zinc and molybdenum; entries is parens [(Low)}, are inferred from geology or from other districts studied.

Table 14: Ranking of relative geochemical character of six watersheds in the Prescott National Forest area, Yavapai County, AZ:

[Potential hazards are ranked from low (0 or 1) to high (5) in a relational scale that pertains only to this study area; the ranking values consider other parts of the study area not included in this table because they appear to have much lower geochemical risks. Potential for mitigation of geochemical hazards has a similar relational scale, but rankings are low (L), medium (M), and high (H) to avoid confusion with the numeric hazard scale. NB: these rankings are preliminary, are in a classsification system that is new and untested, and is based on reconnaissance data and observation. These rankings are intended to be guidelines and need much further study and multi-disciplinary discussion].

	GEOCHEMICAL INDICATORS					NATURAL MITIGATION		SUMMARY
Watershed	Water Quality	Stream sediment	Mines and mineralized rock contam.	Mill contam.	Smelter contam.	Buffering capacity	Dilution	RANKING
Agua Fria headwater	2	3	3	5	5	M	M	**2**
Copper Basin Wash	2	3	5	2	2	M	L	**3**
Hassayampa headwater	4	3	3	3	0	L	H	**4**
Lynx Creek	5	3	3	4	1	L	M	**5**
Big Bug Creek	2	4	3	2	1	L	M	**2**
Turkey Creek	3?	3	3	3	0	M	L	**3**
Verde River upper	1?	4	5	5	5	H	H	**2**