022 #1701 F1 - 280

I. EXECUTIVE SUMMARY

A. Project Title: ***Mercury fluxes in the Cache Creek watershed: characterization of mercury speciation and transport from mine wastes, mine drainages, and natural sources.***

Applicants: James J. Rytuba, Charles N. Alpers, Gordon E. Brown, Jr., George A. Parks, Ron Churchill, Trude V. King, Christopher S. Kim, Howard E. Taylor, David A. Roth

B. Project Description and Primary Biological/Ecological Objectives: This project addresses the issue of water quality and specifically mercury as an ecosystem stressor on aquatic species in the Bay-Delta. We propose to characterize the spatial distribution and mercury speciation in mercury mine wastes, mercury mine drainages, and natural sources such as thermal springs in the Cache Creek watershed (Fig. 1) that impact the downstream loading of mercury into the Bay-Delta and uptake of mercury by fish. This two-year Phase 1 effort is important in developing scientifically based mitigation and remediation strategies at mercury mine sites and areas of naturally elevated mercury in order to implement Phase 2 remediation and mitigation to decrease the flux of mercury species that impact fisheries from these contaminated sites. Continued monitoring of ecosystem benefits from remediation and mitigation will represent Phase 3 of the project.

C. Approach/Tasks/Schedule: The approach for Phase 1 of this project will be implemented as eight tasks. Task 1 delineates the location and spatial distribution of mercury mine wastes and estimates residual amounts of mercury remaining in mine wastes and undeveloped mercury sources using historical data and aerial photography. A map and description of mine wastes is for the watershed. Task 2 uses airborne imaging spectroscopy (AVIRIS) and hand held imaging spectroscopy to map the distribution of processed mine wastes using mineral species such as hydrous ferric oxides coatings on mercury mine tailings (calcines). AVIRIS data will be processed to also delineate thermal areas and other natural sources of mercury. AVIRIS and Task 1 maps are combined to provide a comprehensive watershed map of mercury contaminated materials and sources. Task 3 characterizes the physical properties, mercury content, and mercury speciation (in conjunction with Task 4) of the various types of solid mine wastes, mercury mine drainage waters and sediments, thermal waters, and undeveloped mineralized areas. The relative contribution of these sources to the total mercury flux from the Cache Creek watershed is quantified. Task 4 involves a detailed micro-analytical study of the speciation of mercury in mine tailings. This task will employ detailed spectroscopic and laboratory studies of both natural and synthetic samples to examine physicochemical factors that control the mobility of mercury in aquatic systems, including sorption, precipitation, desorption, and dissolution. Sorption and desorption of mercury from hydrous ferric oxides are both important processes because sorbed mercury in mine wastes is associated with these oxides. Task 5 establishes gaging stations at critical sites in the watershed in order to establish Task 6 monitoring of fluxes of mercury species from the watershed through a scheduled sampling and analysis program. Task 7 documents the ground water at mercury contaminated sites and Task 8 provides a protocol for the assessment of mine sites and natural sources in other mercury impacted watersheds.

D. Justification for Project and Funding by CALFED:
Mercury mines, mine drainages, and natural geologic sources such as thermal springs and bedrock with elevated mercury content are major sources for mercury introduced into watersheds and the Bay-Delta. Because of this widespread distribution of mercury, every region of the Bay-Delta is affected by this contaminant and both the priority habitats and priority species identified by CALFED are impacted by mercury. Several California agencies have identified mercury as a contaminant of major concern to aquatic species and to humans. The formation of methylmercury in a variety of habitats is of primary ecological concern because of the uptake of this toxic contaminant by aquatic organisms and biomagnification upward in the food web, with fish commonly being highly contaminated. The primary pathway of exposure of mercury to humans is through the consumption of mercury-contaminated fish and the highest risks to humans occur in pregnant women where fetus development is potentially

compromised. Although methylation of mercury is dependent on many variables, the flux of ionic mercury and sulfate, constituents common in mercury mine drainages, are important in controlling rates of methylation.

The Cache Creek Watershed has several mine sites and natural geologic sources that contribute significant mercury fluxes to the watershed and the Bay-Delta. It is important to establish the mercury speciation of geologic materials in these sources and their relative importance to the total flux of mercury species from the watershed. The results of this project are important for evaluation of ongoing studies by the U.S. Fish and Wildlife Service and U.S. Geological Survey studies on the impact of mercury on fish, amphibians, and birds in the watershed. Phase 1 of this project provides information critical to subsequent Phase 2 remediation and mitigation of mercury sources that impact fisheries and habitats of the Bay-Delta, a goal consistent with CALFED objectives of water quality and ecosystem improvement.

E. Budget Costs and Third Party Impacts:

Total project costs: $2,513,058; Total requested from CALFED: $1,701,471. No third party impacts.

F. Applicant Qualifications:

The applicants and members of this project have an established record of developing and successfully completing studies related to the tasks proposed in this project. The principal applicants all have an established record of Ph.D.-level research and all of the collaborators have experience in the approaches defined by this project. Dr. Rytuba is the USGS mercury commodity specialist and both he and Dr. Alpers have extensive experience in geochemical and hydrogeologic studies of mine drainages, their environmental impacts, and their remediation. Dr. Brown, Dr. Parks and their associates are recognized leaders in the use of advanced micro-analytical techniques in the evaluation of environmental metal contaminants. Dr. Churchill has extensive experience in the evaluation of mines and mineral deposits and Dr. King is a recognized expert in the evaluation of imaging spectroscopy and its application to environmental problems. Dr. Taylor and Dr. Roth both have extensive experience in mercury analysis and its application to environmental problems.

G. Monitoring and Data Evaluation:

This project plans to work closely with the Cache Creek Mercury Technical Group, a working subgroup of the Cache Creek Watershed Stakeholders group organized through the Colorado Center for Environmental Management. We will provide this technical group with information generated from each of the tasks and will solicit peer review and provide status reports at monthly intervals. Phase 1 of the project establishes gaging stations and a sampling and analytical program to monitor mercury and associated metals and anions in the watershed. This monitoring effort is important in establishing background fluxes of mercury species prior to Phase 2 remediation and mitigation efforts and provides the basis for post-remediation Phase 3 monitoring to assess the effectiveness of these efforts on water quality and ecosystem health.

This project will collaborate with other mercury-related projects funded by CALFED and with other ongoing activities in the watershed such as the U.S. Fish and Wildlife Service and USGS project to assess impact of mercury on fish, amphibians, and swallows and the U.C. Davis project assessing mercury bioaccumulation in invertebrates. Our sampling and analytical approach will be coordinated with the sampling sites for organisms in the watershed and will provide mercury speciation data on water, colloids, and sediments for evaluation and subsequent integration into these studies of organisms. We will provide monitoring data to the State and Regional Water Quality Control Boards and solicit review by these agencies.

H. Local Support:

The USGS will provide matching funds and in kind support for all tasks in Phase 1 of this project. We will collaborate with other USGS projects and cooperate with other projects addressing mercury in the Bay-Delta as a participant in the proposed project by Suchanek et al., "Integration of Mercury Studies/Results in the San Francisco Bay-Delta System."

I-006104

II. Title Page

a. Title of Project

**Mercury Fluxes in the Cache Creek Watershed:
Characterization of Mercury Speciation and Transport
from Mine Wastes, Mine Drainages, and Natural Sources**

b. Name of Applicants/Principal Investigators

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c. Type of Organization and Tax Status
U. S. Federal Government, tax exempt

d. Tax Identification Number
Federal tax exempt number for USGS 80503683

e. Technical and Financial Contact Persons
Same as Principal Investigators in part "b."

f. Participants/Collaborators in Implementation
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g. RFP Project Group Types
Group 3, Services: Water Quality, Mine Drainage, and Monitoring and Reporting

I-006105

III. Project Description.

a. Project Description and Approach. This project addresses the issue of water quality and specifically mercury as an ecosystem stressor on aquatic species in the Bay-Delta. We propose to characterize the spatial distribution and speciation of mercury in mercury mine wastes, mercury mine drainages, and natural sources such as thermal springs and mercury alteration zones in the Cache Creek watershed (Fig. 1). These sources impact the downstream loading of mercury from this watershed into the San Francisco Bay-Delta system. This proposal requests funding for Phase 1 of this project, which is important in developing scientifically based information on factors controlling the distribution and concentration of mercury species present in various mercury mine wastes and natural sources and their relative importance in contributing to the mercury fluxes from these sites to the Cache Creek watershed and the Bay-Delta system. An important component of this project is a study of the physicochemical factors that affect the partitioning of mercury from aqueous to solid phases and *vice versa*, including the processes of adsorption, precipitation, desorption, and dissolution. This will require careful laboratory work on synthetic model systems, coupled with detailed micro-analytical studies of contaminated mine wastes, stream sediments, and colloids isolated from surface waters. We propose to establish strategically located gaging stations that continuously monitor flows in the Cache Creek watershed and to initiate a monthly sampling program. These studies are a prerequisite for subsequent Phase 2 of this project, involving the remediation and mitigation of these geochemically complex sites with the purpose of decreasing the flux of potentially bioavailable mercury species within the watershed and to the Bay-Delta. Analysis of samples for mercury species and related chemical constituents, such as sulfate, that contribute to methylation of mercury, will provide background monitoring information on the mercury fluxes prior to and after implementation of remediation and mitigation efforts to be done in Phase 2.

b. Location. The Cache Creek watershed is located in Lake, Yolo and Colusa Counties (Fig. 1).

c. Expected Benefits. Mercury has been identified as a primary contaminant of concern throughout the San Francisco Bay and Delta. The bioaccumulation and biomagnification of mercury concentrations, particularly with regard to methylmercury, in food webs potentially affects all Priority Species and Priority Habitats in the CALFED Implementation Strategy. Toxic effects of mercury on higher trophic level consumers of aquatic organisms are well established. Fish species of particular concern are green sturgeon and striped bass, for which health advisories have been promulgated with regard to human consumption. The proposed restoration of Seasonal Wetland and Aquatic Habitats in the Yolo Bypass and in the Bay-Delta may be accompanied by increased rates of mercury methylation, with potentially adverse effects on various Priority Species.

Phase 1 of this project includes information critical to the success of contaminant control actions with regard to mercury in the Cache Creek watershed and downstream habitats, including the Yolo Bypass and the San Francisco Bay-Delta. Phase 1 work will identify mercury pollution sources from mine drainage, describe in detail the fate and transport of the mercury in terms of its chemical and physical properties, and provide critical baseline monitoring data that will allow the quantification of the benefits of remediation and mitigation activities to be carried out in Phase 2.

Secondary benefits from the proposed network of continuously gaged streams in the Cache Creek watershed include flood forecasting and water management. Cost sharing of construction, operation, and maintenance of the new stream gages with the Yolo County Flood Control District indicates the multiple benefits of real-time gaging infrastructure. Another secondary benefit of the stream-gage network will be realized in terms of assisting State and Federal agencies in meeting the regulatory requirement that Total Maximum Daily Loads (TMDLs) of contaminants be established for surface waters of impaired quality. Cache Creek has been listed by the Regional Water Quality Control Board as an impaired water quality stream based on its mercury concentrations. Establishment of TMDLs is required and will be facilitated by the proposed USGS stream gages.

d. Background and Biological/Technical Justification. Mercury mines, mine drainages, and natural geologic sources such as thermal springs and bedrock with elevated mercury content are major sources for the mercury introduced into watersheds and the Bay-Delta. Because of the widespread distribution of mercury, every region of the Bay-Delta is affected by this contaminant and all of the Priority Species and Priority Habitats identified by CALFED are impacted by mercury accumulation. The formation of methylmercury in a variety of habitats is an ecological concern because of the uptake of this toxic contaminant by aquatic organisms and biomagnification upward in the food web with fish being highly contaminated. The primary pathway of exposure of mercury to humans is through the consumption of mercury-contaminated fish and the highest risks to humans occurs in pregnant women where fetus development is potentially compromised. Although methylation of mercury depends on many variables, the flux of ionic mercury and sulfate are two variables important to rates of methylation.

The Cache Creek Watershed has several mine sites and natural geologic sources that contribute significant mercury fluxes to the watershed and the Bay-Delta. It is important to establish the mercury speciation of geologic materials in these sources and their relative importance to the total flux of mercury from the watershed. This is because the chemical speciation or form of heavy metals like mercury play a major role in controlling their mobility, bioavailability and their environmental fate. The approach and results of this project are important for evaluation of ongoing studies by the U.S. Fish and Wildlife Service and the USGS Biological Resources Division on the impact of mercury on fish, amphibians, and swallows in the Cache Creek watershed. This project is also necessary to identify the specific location and distribution of those sources with bioavailable mercury of major environmental concern to fisheries and habitat so that subsequent remediation and mitigation strategies accomplish a reduction in the loadings of mercury that are released from the watershed and into the Bay-Delta.

The mercury fluxes from the watershed contribute significantly to the total flux of mercury impacting the Bay-Delta system, primarily during initial annual flood events as documented by the Regional Water Quality Control Board (Chris Foe, pers. commun.). Mercury levels in aquatic invertebrates at selected sites throughout the watershed indicate significant uptake of mercury by these organisms and that very high mercury levels in biota occur in several tributaries to Cache Creek (Slotton et al. 1997). Sites with highly elevated mercury in biota are located downstream from mercury mines, hot springs, and areas where naturally elevated mercury is associated with hydrothermal alteration, indicating that these are important sources of mercury species available for uptake by aquatic organisms. It is important to distinguish between downstream loading of aqueous and adsorbed mercury species, which can be methylated and contribute to the accumulation of methylmercury in fish in the Bay Delta, and insoluble mercury species in solids such as cinnabar (HgS), which are not methylated until the solids are oxidized and/or dissolved.

Mercury mine drainages provide an optimal environment for methylation of mercury; and furthermore, in these drainages amorphous iron hydroxides effectively sorb methylmercury (Rytuba, 1997). Mercury mine drainages provide a previously unrecognized source of methylmercury to the total flux of mercury impacting fisheries in the Bay-Delta. Three distinct sources of mercury are present in these drainages: (1) ionic, elemental, and methylmercury present in solution; (2) ionic mercury and methylmercury sorbed onto iron hydroxides present as colloids in surface waters; (3) and iron hydroxides with high methylmercury (110 ppt) and total mercury (110 ppb) that accumulate as sediment in the bedload, sorb mercury and methylmercury during the dry season, and contribute to downstream loading, especially during the first storms of the wet season (Rytuba, 1997). Solid mercury mines wastes such as condenser ash, calcines, efflorescent salts, and waste rock contain a large range in mercury concentrations, species, and secondary mercury minerals that are also important sources to the mercury fluxes from these sites (Rytuba, and Kleinkopf, 1995).

e. Proposed Scope of Work. The proposed work constitutes Phase 1 of a multi-phase project with the overall goal of achieving cost-effective remediation and mitigation of potentially bioavailable mercury sources to the Bay-Delta from the Cache Creek watershed. The primary objectives of Phase 1 effort are: (1) to identify and characterize sources of mercury contamination as targets for remediation, (2) to collect pre-construction baseline monitoring data in terms of quantitative fluxes of mercury in dissolved, colloidal, and coarse sediment phases, and (3) to describe the fate and transport behavior of mercury with regard to its chemical speciation and methylation and its association with oxides, sulfides, and organic substances.

Phase 1 work consists of eight tasks: (1) Location and distribution of mine waste and mine drainages, (2) Imaging spectroscopy of mine wastes, thermal springs and mineralized areas, (3) Mercury speciation of mine wastes, mine drainages, hot springs, and natural mineralized areas, (4) Speciation of mercury in solid phases and sorbed on particle surfaces, (5) Establishment of new gaging stations in the Cache Creek watershed, (6) Water-quality monitoring at gaged sites in the Cache Creek watershed, (7) Hydrogeologic characterization of abandoned/inactive mercury mine sites, and (8) Protocol for the environmental evaluation of mercury mine sites and thermal springs.

Task 1: Location and distribution of mine waste and mine drainages. We propose to document and delineate in detail the location (Fig. 1), past production, and amount of mine workings and mine wastes generated during mercury mining using historical data from the mercury mine files in the CA Division of Mines and Geology and the USGS Mercury Commodity File. From these historical records, we will identify the ore processing techniques used and estimate the efficiency of mercury recovery in order to establish the residual amount of mercury remaining in the mine wastes, mine tailings (calcines), and unprocessed low grade ore. We will delineate the aerial distribution of solid mine wastes at mercury mine sites within the watershed using historical photos, archived USGS aerial photography, and mine reports. We will field check information to delineate location of mine sites and the distribution of various mine wastes. Evaluation of historical mine data, map and photo analysis, and mercury recovery calculations are initiated in first six months of the project. Field checking and detailed mapping of mine wastes occurs in the next six months producing a regional map of mine waste in the watershed and detailed maps of mine wastes for use in mineral characterization by AVIRIS and imaging spectroscopy, Task 2, mine waste sampling, Task 3, and mercury phases analysis, Task 4.

Task 2: Imaging spectroscopy of mine wastes, hot springs and mineralized areas. Airborne imaging spectroscopy (AVIRIS), hand-held field spectrometry, and laboratory measurements will be used to map the distribution of mineral species associated with mercury deposits, alteration zones, and hot springs in the watershed. Imaging spectroscopy is a diagnostic tool for mapping OH-bearing minerals, iron-bearing minerals (Fe^{2+} and Fe^{3+}) and other minerals commonly present in mercury mine wastes and alteration zones. A map of secondary minerals and amorphous material is important because these phases are common in mineralized areas and are important sources of both mercury and anions such as sulfate that contribute to methylation of mercury. AVIRIS data acquired July 8 1997 are provided as in-kind support for use in this project. Mineral maps of the watershed areas impacted by mining and natural sources of mercury will be constructed using field studies to "ground-truth" the AVIRIS data. Mine wastes such as calcines have often been removed from mine sites for road construction throughout the watershed. AVIRIS constructed maps of high ferric oxide concentration will provide a surrogate map for the distribution of calcines. In conjunction with Task 1, AVIRIS data will be used to create a map of the watershed showing the distribution of mine wastes, hot spring areas, alteration zones and undeveloped mineralized areas. This final product is completed in 4/99 and complements the map of mine wastes generated as part of Task 1, both of which help direct the mine waste sampling and mercury phase analysis proposed in Tasks 3 and 4.

Task 3: Mercury speciation of mine wastes, mine drainages, hot springs, and natural mineralized areas. We propose to characterize the physical properties and mercury content of the various types of solid mine wastes, mercury mine drainage waters and sediments, hot springs and associated precipitates, and hydrothermal alteration zones (undeveloped mineralized areas) that contribute to the mercury fluxes in the watershed (Fig. 1). Mercury speciation of waters are part of this task and Task 4 determines mercury speciation and phase analysis of solid mine wastes because specialized microanalytical techniques are required. Mercury mine sites contain several types of processed and unprocessed solid mine wastes (Rytuba, 1996). Soot or ÒashÓ is derived from the condenser system and commonly has the highest concentration of mercury at mine sites. Mine tailings (calcines) are coated by ferric oxide and hydroxide phases which contain sorbed elemental mercury and distinct mercury sulfate and mercury oxychloride minerals. Efflorescent salts containing various forms of mercury form on mine wastes and are readily dissolved during the wet season. Unprocessed ore contains low concentrations of mercury primarily as cinnabar. Waste rock consists of unaltered and hydrothermally altered country rock with low concentrations of mercury for which the speciation of mercury is typically uncertain. These mine wastes will be mapped and sampled in detail using maps generated by Tasks 1 and 2 and analyzed for total mercury and methylmercury. Samples are analyzed by Task 4 for mercury species and mineral phases. The combined data will be used to assess the relative importance of these sources for downstream loading of bioavailable mercury. A watershed map and supporting data will delineate the sources for various mercury species as a preliminary product in 6/99.

Mercury mine drainages contain a wide range in total mercury concentration, (0.01-340 ppb) (Rytuba, 1997). Mercury mine drainages provide an optimal environment for the methylation of mercury because of high ionic mercury, sulfate, and sulfate-reducing bacteria with methylmercury concentrations in the 10 to 80 ppt range (Rytuba 1997). Amorphous iron hydroxides in mine drainages effectively sorb both mercury and methylmercury, accumulate in the bedload of streams impacted by mine drainage during the dry season, and are readily transported in suspension during initial phase of the wet season (Rytuba, 1997). We will analyze mercury mine drainages in the watershed to characterize the concentration and flux of mercury species. Solid phases will be characterized in Task 4. Hot springs will be similarly characterized. Hot springs are associated with several of the mercury deposits (Fig. 1) (Rytuba, 1993) and in the Sulphur

Creek tributary are a source of ionic mercury (450 ppb) and mercury sulfide encapsulated within iron sulfide particles which contribute to the downstream loading of mercury (Rytuba, 1997; Janik et al., 1994). Characterization of mercury sources, species, and fluxes in the watershed will be integrated with data and maps from all tasks to produce a final Phase 1 report on 1/2000.

Task 4: Speciation of mercury in solid phases and sorbed on particle surfaces. Mercury can occur in a variety of solid phases in the earth's near-surface environment (Rytuba and Tunnell, 1978), at trace or high concentration levels, and can also be sorbed on particle and colloid surfaces. A detailed knowledge of the speciation of mercury [i.e., its oxidation state, physical form (presence in a crystalline or amorphous solids, sorbed on a particle or colloid surface, or presence as an aqueous complex), molecular structure and composition, and if sorbed, type of sorbed species (inner vs. outer sphere adsorption complex or precipitate)] is critical for predicting its mobility in natural waters and, in turn, its bioavailability. For example, mercury in a highly soluble solid phase can be released into solution when the solid phase dissolves. When sorbed on a particle or colloid surface, mercury may be released even more easily than from solid phases when groundwater or surface waters become more acidic (such as waters associated with acid mine drainage) or have high chloride concentrations (Gunneriusson, 1993). Under acidic conditions, sorbed mercury may desorb rapidly, depending on the type of sorption complex. In addition, when associated with colloids, sorbed mercury species such as methylmercury can be transported great distances from the mercury source. Without quantitative, molecular-scale information on the speciation of mercury in mine tailings and drainage waters, it is not possible to make accurate predictions about its potential release into the biosphere under varying solution conditions.

The types of solid phases containing mercury in the environment depend heavily upon the composition of local water, pH, and dissolved oxygen concentration or oxidation potential. In a typical water containing 1mM each of chloride and sulfate at pH 7, cinnabar (HgS) is the stable solid under reducing conditions, and elemental or metallic mercury is the stable form under oxidizing conditions. The intrinsic solubility of cinnabar is very low, whereas the solubility of metallic Hg exceeds some water quality standards. For this reason, it is commonly supposed that Hg will precipitate as HgS and be rendered harmless in buried sediments where sulfate is reduced to sulfide by bacterially mediated reactions. This is true in a very narrow range of oxidation potentials, but in buried sediments or tailings containing high levels of organics, oxidation potentials can be reduced to a point where sulfide ion complexation of Hg increases its solubility and hence mobility by orders of magnitude (see, e.g., Engler and Patrick, 1975). In addition, changes in solid speciation can change the effective equilibrium solubility/mobility of Hg over 6 to 7 orders of magnitude from highly reducing sediments to highly aerated surface streams.

There have been a number of studies of mercury speciation in contaminated soils and other geological materials using selective chemical extraction techniques (e.g., Barnett et al. 1995). However, such methods are capable of altering Hg speciation so that the original species is not detected, which makes it difficult or impossible to assess the potential hazard of Hg from a contaminated site. The same problem exists for other common heavy metal contaminants such as arsenic, selenium, and lead. During the past few years, we have developed an analytical approach that allows us to study the speciation of these heavy metal contaminants with minimal sample preparation and no need for selective chemical extraction. We employ a battery of standard micro-analytical methods such as the electron microprobe, scanning electron microscope, and transmission electron microscope, together with bulk methods such as x-ray diffraction and ICP-MS analysis, to determine what phases are present in a multi-phase mixture, including those containing major quantities of the heavy element, and the concentration of these elements. What makes our approach relatively unique, however, is our use of more sophisticated methods such as synchrotron radiation-based x-ray absorption fine structure (XAFS) spectroscopy. XAFS spectroscopy is non-destructive, requires minimal sample preparation, and can be performed under ambient conditions. It is capable of providing detailed information on the molecular-scale structure and composition of heavy metal species when they are present in concentrations higher than 20-40 ppm (Brown et al., 1988). XAFS spectroscopy is particularly useful in identifying sorbed species, which are virtually impossible to study directly under ambient conditions by any other analytical method (Brown, 1990).

Using XAFS spectroscopy at the Stanford Synchrotron Radiation Laboratory, we have carried out extensive studies of the speciation of Cr, Se, As, and Pb at concentration levels as low as 20 ppm in both contaminated natural samples (Pickering et al., 1995; Tokunaga et al., 1996, 1997; Peterson et al., 1997a, 1997b; Foster et al., 1997a, 1997b, 1997c; Ostergren et al., 1996, 1997; Julliot et al., 1997) and in synthetic model systems (Hayes et al., 1987; Chisohlm-Brause et al., 1990; Roe et al., 1991; Bargar et al., 1997a, 1997b, 1997c; Peterson et al., 1997c). We propose to use a similar approach to determine Hg speciation in mine tailings and natural samples from the Cache Creek Watershed mercury mines. We have already initiated studies of Hg(II) sorption on iron hydroxides using XAFS methods and have shown that chloride forms ternary surface complexes with Hg(II) on these surfaces (Bargar et al., 1997c). Such hydroxides are often the most important solid phase to which Hg species sorb in environmental settings such as mine tailings. XAFS spectroscopy studies of synthetic model systems in which the heavy metal is sorbed to sample surfaces or is present in pure solid phases, combined with XAFS studies of natural contaminated samples, provide a powerful approach to the study of the speciation of a specific heavy metal in contaminated samples. We plan to use this same approach in our study of Hg speciation in the proposed study. Our proposed study will benefit from a new high flux hard x-ray beam line we are currently building at the Stanford Synchrotron Laboratory that is specifically optimized for XAFS studies of heavy metals, such as Hg, in natural and synthetic samples. It will also benefit from a new state-of-the-art multi-element Ge-array detector for x-ray fluorescence XAFS studies of extremely dilute samples. Mercury speciation studies of solid mine wastes will occur in conjunction with characterization studies of mine wastes in Task 3 during the first year and continue into the second year along with synthetic studies in order to integrate speciation analysis with final report of Task 3.

Task 5: Establish new gaging stations in the Cache Creek watershed. Accurate and reliable data on water flow is essential to determining fluxes of contaminants such as mercury. At present, the only continuously gaged stream site in the Cache Creek watershed is Cache Cr. at Rumsey. Additional discharge data are available for the spillway from Clear Lake, which feeds Cache Cr., and for the outfall from Indian Valley Reservoir, which feeds the North Fork of Cache Cr. The USGS proposes to establish stream gages at six other sites in the watershed so that reliable data on mercury and associated metal and anion loadings can be computed based on periodic sampling by the USGS and others.

The most critical sites for additional stream gaging are: (1) Sulphur Cr. above the confluence with Bear Cr., (2) upper Bear Cr. above the confluence with Sulphur Cr., (3) lower Bear Cr. at Cache Creek, (4) Grizzly Cr. below the Turkey Run and Abbott Mines and above Bear Cr., (5) Davis Cr., and (6) North Fork, Cache Cr. above Cache Cr. (Fig. 2). These gages are sited at optimal locations to monitor flows and mercury loadings from tributaries in the watershed impacted by mercury mining, and sources. Gages will be instrumented to record continuous turbidity data, which correlates with suspended sediment concentration, and provides timing of peak sediment transport in relation to peak flows, and guides sampling to measure the maximum mercury concentrations during storm runoff.

It is recommended that a continuous record of flow and turbidity be collected at these sites over at least two years prior to proposed remediation of mine sites, so that pre-remediation baseline conditions can be established and the sites providing the largest mercury loadings can be targeted for remediation and/or mitigation. We propose one year of gaging and monitoring at these sites as part of Phase 1 of this project, and Phases 2 and 3 will continue the gaging and monitoring program in conjunction with remediation planning and implementation, and post-construction monitoring. Gage construction occurs in 4-6/98, and continuous flow data will be reported beginning 7/98. Real-time USGS data will be available on the internet (http://water.wr.usgs.gov). USGS will annually publish daily mean discharge values for each site.

Task 6: Water-quality monitoring at gaged sites in the Cache Creek watershed. Water-quality monitoring at gaged sites will permit quantitative determination of contaminant loadings for mercury and sulfate within the watershed. Sulfate loadings are important because sulfate contributes to methylation of mercury (Rytuba, 1997). Chemical analysis of whole (unfiltered) water samples, plus filtrates from conventional 0.45 micron filters and ultrafilters with an effective pore size of 0.005 microns, will allow the quantification of mercury transport in dissolved, colloidal, and suspended sediment phases. The determination of both total mercury and methylmercury in a subset of these whole water samples and filtrates will be of interest, particularly in high flow regimes, to evaluate the importance of the methylmercury flux from the watershed *versus* the methylation that takes place largely downstream in the Yolo Bypass and the Bay-Delta, partly in response to loadings of mercury and sulfate from the watershed.

Water-quality data and mercury loadings will be compiled, evaluated, and published by the USGS in preliminary data reports and peer-reviewed interpretive reports. For the first year's monitoring period (7/98 - 6/99), data reports are planned for 2/99 and 7/99 and an interpretive report would be available in draft form in 8/99 and in final form in 12/99.

Task 7: Hydrogeologic characterization of abandoned/inactive mercury mine sites. Hydrogeologic characterization of surface and shallow ground water will be carried out at two or more mercury mines in the watershed, with the goal of providing information necessary for the selection of effective remediation alternatives. At the Turkey Run mine mercury mine wastes are in the flow path of hot springs effluent. The hydrology must be understood so relocation of this mine waste and diversion of the effluent will succeed in reducing mercury. At the Elgin Mine hot springs in the open pit mine contribute a significant flux of mercury to Sulphur Creek. Shallow wells will be installed, so that water levels and flow can be monitored and these will provide for water-quality sampling, to be carried out on at least two occasions including one wet-season and one dry-season. Weirs will be constructed to measure flow at times of water-quality sampling.

Water-quality and water-level data will be compiled, evaluated, and published in USGS preliminary data reports and peer-reviewed interpretive reports. For the Phase 1 project period (1/98-12/99), data reports are planned for 10/98 and 10/99 and an interpretive report for 8/99 (final form 12/99). It describes the consequences to the surface- and ground-water systems of remedial alternatives and provide a scientific basis for establishing cost-effective remediation activities at mercury mine sites in Phase 2 of the project.

Task 8: Protocol for the environmental evaluation of mercury mine sites A protocol will be developed for the assessment of mercury speciation and fluxes from mine drainages and mercury mine wastes for use in the evaluation of other mines in watersheds that impact the San Francisco Bay-Delta. A synthesis of approaches and methodologies established in the tasks of Phase 1 will be summarized in a USGS Open File Report (1/2000).

f. Monitoring and Data Evaluation

This project addresses a major concern of the Cache Creek Watershed stakeholders group that has been organized under the auspices of the Colorado Center for Environmental Management with the support of the State and Regional Water Boards. A working subgroup of this organization is the Cache Creek Mercury Technical Group, composed of stakeholders, regulatory staff, and researchers. We plan to work closely with this technical group by providing information as generated from each of the tasks in this project and will solicit peer review and monitoring of the tasks in this proposal at appropriate intervals. It is anticipated that Phase One of this project will contribute information critical to development of Phase Two remediation and mitigation efforts that will include projects initiated by the Cache Creek Watershed stakeholders group and thus we will involve this group in all aspects of the project. Establishment of the USGS gaging stations and mercury speciation analysis program provides an infrastructure and methodology for long-term monitoring of mercury and associated metals and anions in the watershed. This monitoring effort is important in establishing background fluxes of mercury species prior to remediation and mitigation efforts and provides the basis for post-remediation monitoring to assess the effectiveness and demonstrate the benefits of these efforts.

This Phase 1 project will coordinate and collaborate with other mercury-related projects funded by CALFED. We plan to communicate and cooperate with other CALFED-sponsored mercury projects, including the proposed project "Integration of Mercury Studies on the Bay-Delta System" (Suchanek et al.). Our sampling sites and analytical approach will be coordinated with those for organisms in the watershed and will provide mercury speciation for evaluation and integration into these studies. We will coordinate closely with proposed projects with a biological emphasis: (1) "The Role of Upstream Mercury Loading and Speciation..."(Suchanek et al.), and (2) "Adverse Effects of Mercury on Birds and Amphibians in the Cache Creek Basin" (Schwarzbach et al.)

The proposed project will share USGS personnel with another proposed CALFED project, "Localization and Characterization of Mercury Sources..."(Alpers et al.). These projects will be integrated, and use similar methodologies for sample collection, processing, and analysis. We plan to provide monitoring data to the State Water Resources Control Board, the Regional Water Quality Control Board as well as other interested parties and to solicit review by the State and Regional Waters Boards of our monitoring, quality assurance/quality control, and data evaluation process.

g. Implementability. The project team members have a long record of research activities in the field of evaluation of mercury mines, mercury speciation of mine wastes and mine drainages, and techniques to evaluate phases of mercury in mine wastes and waters and natural sources. Facilities to accomplish the tasks in this project are presently available and being used by the project members as part of other programs to evaluate the environmental aspects of mercury. The USGS has a long record in the successful establishment and monitoring of stream gages and can establish these gages in compliance with local laws and regulations and in cooperation with local governments and landowners.

The hydrologic and climatic conditions will be considered in designing the sampling plan, choosing optimal sites for stream gage stilling wells, and timing sampling events to capture high-flow events. Handling of hazardous materials at mine sites and associated mine drainages will be carried out by personnel with appropriate safety training. Disposal of hazardous samples associated with this project will be carried out in accordance with all applicable laws and regulations.

IV. Costs and Schedule to Implement Proposed Project

a. Budget Costs

The costs for Phase One of the project cover a two year period and total $2,592,058, of which $1,701,471 is requested from CALFED. Budgeted costs are specified according to the eight tasks in this project and are broken down according to costs and funding sources in Table 1. In kind services by the USGS contribute to the cost of each of the eight tasks and total $781,587. In kind services from other sources total $79,000. Matching funds from the USGS State-Federal Cooperative Program total $30,000 for Phase One of this project, in the amount of $10,000 per year over three fiscal years. The USGS in kind services anticipate future budgeting levels for the USGS that are considered firm, but that are contingent on future Congressional appropriations. Without CALFED funding for this project the USGS funds are likely to be used on different projects that may or may not be related to the proposed work. Although the USGS has a strong interest in the completion of this project, USGS funding levels alone are not sufficient to provide the comprehensive, quantitative approach outlined in this proposal. CALFED funding is required at the proposed level to provide a sound technical basis for characterization of mercury sources in the Cache Creek watershed, and the critical information needed to ensure successful, cost-effective remediation.

Budget notes for specific tasks:

Task 5A) Stream-Gage Construction

Total cost for construction of 6 gaging stations in the Cache Cr. Watershed is $214,000. The cost of the construction of the gage along lower Bear Cr. ($19,000) will be paid by the Yolo County Flood Control District (agreement with USGS pending, expected in Aug. 1997). Construction costs ($195,000) for the other 5 gaging stations are requested from CALFED.

Task 5B) Stream Gage Operation and Maintenance

Operation and maintenance (O&M) costs per gage are estimated at $20,000 per year. O&M costs for gage on Davis Cr. will be paid by Homestake Mining Co., and for the gage on lower Bear Cr. by Yolo County. O&M costs for the other 4 gages for one year ($80,000) are requested from CALFED.

Task 6) Water-quality monitoring at gaged sites in the Cache Creek watershed

Budget based on 84 water samples: 11 events at 7 gaged sites plus 3 events at Yolo Bypass and 2 events at inflow and outflow of Yolo Settling Basin. CALFED budget includes chemical analysis of Hg and Hg-methyl, dissolved organic carbon, nutrients, and suspended sediment concentration. USGS in kind services include chemical analyses of major and trace elements in whole waters, filtrates, and ultra-filtrates.

b. Schedule Milestones

For each of the eight tasks below, specific start and completion dates are discussed as well as key milestones and payment schedules. The start dates anticipate funding from CALFED on or after January 1998, as noted below. Although all the tasks in Phase 1 of this project are related, there is a staged development of work in each task.

Task 1) Location and distribution of mine waste and mine drainages

1/98-6/98: analysis and compilation of existing historical files and photography to establish the location and distribution of mine wastes. Milestone: completion of data file analysis-1/3 payment for task 1.

6/98-12/98: field checking of identified location and distribution of mine wastes and natural sources and corrections to historical files and aerial photographic analysis. Milestone: preliminary map of the distribution of mine wastes in the watershed-1/3 payment.

1/99-4/99: integration of historical data, field analysis, and AVIRIS maps in Task 2 to create a final map of mercury mine wastes and natural sources for the watershed. Milestone: final watershed map published as USGS Open-File Report in cooperation with CA Division of Mines and Geology-final 1/3 payment.

Task 2) Imaging spectroscopy of mine wastes, and natural sources

1/98-6/98: processing of AVIRIS data, ground truthing of mine waste anomalies using hand held imaging spectroscopy, and determination of mineralogic association. Milestone: completion of ground truth analysis-1/3 payment for task 2.

6/98-12/98: generation of preliminary mineralogic maps showing mineral anomalies and surrogate maps of mine wastes and thermal anomalies and natural alteration areas. Milestone: completion of preliminary map of the watershed showing mine wastes and natural sources based on AVIRIS data-1/3 payment.

1/99-6/99: integration AVIRIS data with maps of Task 1 to create a final map of mercury mine wastes and natural sources for the watershed. Milestone: final map of the watershed with accompanying explanation published as USGS Open-File Report in cooperation with the CA Department of Conservation, Division of Mines and Geology-final 1/3 payment.

Task 3) Mercury content and speciation of mine wastes, mine drainages

1/98-6/98 Initiate water sampling program of mine drainages and drainages from natural areas, analyze for total mercury and mercury speciation. Initiate sampling of solid mine waste, mine drainage and thermal spring precipitates, and analyze for total mercury, MeHg and provide samples to Task 4 for speciation analysis of solid mine wastes. Milestone: analysis of initial data set for the watershed- 1/4 payment.

6/98-6/99 Expand sampling program to mercury source areas identified by Tasks 1 and 2 and continue the analytical approach with modifications based on preliminary data analysis - provide solid mine wastes and drainage precipitates for analysis in Task 4. Milestone: preliminary analysis of second data to identify the major mercury sources using data sets and maps generated in Tasks 1, 2, 4, 6, 7 - 1/2 payment.

6/99-9/99 Complete sampling and analysis and initiate characterization of mercury sources in the watershed integrating data from this task, and tasks 1 ,2, 4, 6, and 7.

10/99-1/00 Complete characterization of mercury sources in the watershed in Phase 1 USGS Open-File Report. Milestone: Publication of Phase1 report-final payment.

Task 4) Speciation of mercury in solid phases and sorbed on particle surfaces

1/98-10/98: micro-analytical characterization of pure Hg model compounds to create database, collection of and initial inspection of natural samples using bulk characterization methods. Milestone: Completion of data base and initial natural samples analysis-1/2 payment -total task 2

11/98-12/99: micro-analytical characterization natural samples, laboratory synthesized samples recreating mine environments in simplified form, characterization of idealized laboratory samples

Milestone: Complete speciation analysis and integrate with final report of Task 3

Task 5A) Stream-Gage Construction

10/97-11/97 Construction of gage along lower Bear Cr. - payment by Yolo County.

1/98-6/98 Construction of the other 5 new gages in watershed. Milestone: completion of construction - full payment.

Task 5B) Stream Gage Operation and Maintenance

12/97-6/98 O&M of gage along Bear Cr. above Cache Cr. (funded by Yolo County).

7/98-6/99 O&M for 5 other new gages in watershed.

Milestones: Real-time data on flow and turbidity for will appear on the WWW beginning in 8/98. Streamflow and turbidity data for the period 7/98-6/99 will be published in a data report, available in 11/99 - full payment.

Task 6) Water-quality monitoring at gaged sites

1/98-6/98 Monthly sampling at 3 gaged sites: Clear Lake, Rumsey, lower Bear Cr.

7/98-6/99 Monthly sampling (bi-monthly in dry season) at 4 new gaged sites plus 3 old gaged sites. Synoptic sampling of peak flow and sediment transport.

7/99-1/00 Data evaluation, synthesis, and report preparation

Milestone: Preliminary data report with water-quality data and contaminant loading analysis through 6/98 - 1/3 payment; Milestone: Phase 1 Final Report, 12/99, full payment.

Task 7) Hydrogeologic characterization of abandoned/inactive mercury mine sites

1/98-6/98 Initiate hydrogeological program, site reconnaissance, drill site selection, weir construction.

7/98-6/99 Collection of water-quality and water-level data.

7/99-12/99 Compilation, interpretation and reporting of results - consequences of remedial alternatives.

Milestones: Data reports are planned for 10/98 (1/4 payment) and 10/99 (1/4 payment) and an interpretive report would be available in draft form in 8/99 and in final form in 12/99- full payment.

Task 8) Protocol for the environmental evaluation of mercury mine sites

6/99-9/99 Initiate analysis of all approaches used in all of the tasks in Phase 1 and evaluate their effectiveness for use at other mercury mine sites and outline the protocol

10/99-1/00 Complete protocol "Environmental evaluation of mercury mine sites and natural sources in watersheds"- Milestone: publication of USGS Open-File Report- full payment.

c. Third Party Impacts - None anticipated.

CACHE CREEK MERCURY FLUXES

Table 1 - Costs and Schedule to Implement Phase One of Proposed Project

	Direct Labor hours	Direct Salary and benefits	Overhead (on all direct costs)	Service Contracts	Material & Acquisition Contracts	Misc. & other Direct Costs	Total Cost
Task 1	**Location and distribution of mine waste and mine drainages**						
CALFED funds requested	643	$42,076	$17,691			$19,000	$78,767
USGS in kind services	296	$31,700	$14,455			$9,600	$55,755
Total - Task 1	939	$73,776	$32,146			$28,600	$134,522
Task 2	**Imaging spectroscopy of mine wastes, thermal springs, and mineralized areas**						
CALFED funds requested	224	$8,050	$5,488			$7,630	$21,168
USGS in kind services	224	$8,050	$5,488			$7,630	$21,168
Total - Task 2	448	$16,100	$10,976			$15,260	$42,336
Task 3	**Mercury speciation of mine drainages, thermal springs, and natural mineralized areas**						
CALFED funds requested	576	$63,400	$36,916			$42,075	$142,391
USGS in kind services	576	$63,400	$36,916			$42,075	$142,391
Total - Task 3	1152	$126,800	$73,833			$84,150	$284,783
Task 4	**Speciation of mercury in solid phases and sorbed on particle surfaces**						
CALFED funds requested	2080	$107,286	$86,030			$40,000	$233,316
USGS in kind services	0	$0	$23,364			$40,000	$63,364
Total - Task 4	2080	$107,286	$109,394			$80,000	$296,680
Task 5A	**Stream gage construction**						
CALFED funds requested	540	$20,000	$88,000			$68,000	$195,000
Yolo County	80	$3,000	$9,500			$6,500	$19,000
Total - Task 5A	620	$23,000	$97,500			$74,500	$214,000
Task 5B	**Stream gage operation and maintenance**						
CALFED funds requested	400	$20,000	$40,000			$20,000	$80,000
Yolo County	200	$10,000	$20,000			$10,000	$40,000
Homestake Mining Co.	100	$5,000	$10,000			$5,000	$20,000
Total - Task 5B	700	$35,000	$70,000			$35,000	$140,000

Table 1 - Costs and Schedule to Implement Phase One of Proposed Project (continued)

	Direct Labor hours	Direct Salary and benefits	Overhead (on all direct costs)	Service Contracts	Material & Acquisition Contracts	Misc. & other Direct Costs	Total Cost
Task 6A	**Water-quality monitoring at gaged sites in the Cache Creek watershed**						
CALFED funds requested	4900	$153,300	$201,300			$48,000	$402,600
USGS matching funds	167	$5,000	$5,000			$0	$10,000
USGS in kind services	1500	$60,000	$81,000			$21,000	$162,000
Total - Task 6A	6567	$218,300	$287,300			$69,000	$574,600
Task 6B	**Evaluation and reporting of water-quality monitoring data**						
CALFED funds requested	3050	$110,400	$130,400			$20,000	$260,800
USGS matching funds	167	$5,000	$5,000			$0	$10,000
USGS in kind services	1500	$60,000	$80,000			$20,000	$160,000
Total - Task 6B	4717	$175,400	$215,400			$40,000	$430,800
Task 7	**Hydrogeologic characterization of abandoned/inactive mercury mine sites**						
CALFED funds requested	2460	$79,420	$145,420			$66,000	$290,840
USGS matching funds	167	$5,000	$5,000			$0	$10,000
USGS in kind services	200	$7,000	$12,000			$5,000	$24,000
Total - Task 7	2827	$91,420	$162,420			$71,000	$324,840
Task 8	**Protocol for the environmental evaluation of mercury mine sites and thermal springs**						
CALFED funds requested	272	$11,225	$6,904			$8,500	$26,629
USGS in kind services	112	$4,025	$4,384			$8,500	$16,909
Total - Task 8	384	$15,250	$11,288			$17,000	$43,538

	Total Costs	% of total
Total funds requested from CALFED	**$ 1,701,471**	**67.7%**
USGS matching funds	**$ 30,000**	**1.2%**
USGS in kind services	**$ 781,587**	**31.1%**
Other stakeholders	**$ 79,000**	**3.1%**
Total project cost	**$ 2,513,058**	**100%**

I-006115

V. Applicant Qualifications:

Planned organization of staff

Dr. Rytuba and Dr. Alpers as principal investigators will oversee all aspects of technical, administrative, and project management and will be the main liaisons with other mercury- related projects sponsored by CALFED as well as other mercury projects within the USGS and outside agencies. Dr. Rytuba will have the primary responsibility for management of Tasks 1, 2, 3, 4 and 8 and will provide technical oversight of all activities within these Tasks. Dr. Alpers will have the primary responsibility for management of Tasks 5, 6, and 7 and provide technical oversight of all activities within these Tasks. Administrative costs will be managed by the existing administrative division within the USGS and monitoring of funds and expenses will follow established USGS administrative protocols. Quarterly administrative expenses and payment reports will be provided and yearly summaries of expenses and payments provided.

Dr. Rytuba and Dr. Churchill will have the primary technical responsibility for implementing Task 1 and completing the proposed maps and accompanying descriptive text. They will closely collaborate with related activities being carried out by staff at the CA Department of Conservation, Division of Mines and Geology under the supervision of Dr. Churchill. Dr. King has the primary responsibility of implementing the technical aspects of Task 2 and to produce the proposed AVIRIS maps and accompanying analysis. Dr. King will work closely with Task 1 to integrate efforts within both of these tasks. AVIRIS data processing will occur within the USGS in collaboration with USGS support staff and facilities. Dr. Rytuba and Chris Kim will have the primary technical responsibility for Task 3 for assessing mercury content of various mine wastes and natural sources. Analytical support for this approach uses existing USGS staff and facilities and Stanford University facilities. Dr. Brown and Dr. Parks are the lead technical investigators in Task 4, the determination of mercury speciation in solid mine wastes and mine drainage products, in collaboration with staff at the Stanford Synchrotron Radiation Laboratory and within the Department of Geological and Environmental Sciences. Mr. Kim and a postdoctoral student will participate in all aspects of this task. All technical equipment necessary for this task is available at Stanford University with collaboration provided by existing support staff for each of the facilities such as microprobe and SEM. Dr. Alpers will take the technical lead in organizing and implementing Task 5 for the establishment of gages as well as Task 6, monitoring studies. Experienced USGS staff will be used to establish the gages and implement the monitoring program. Dr. Taylor and Dr. Roth will provide the technical lead in analysis of mercury and other constituents for Task 6 using existing USGS analytical facilities. Dr. Alpers will have the primary responsibility of implementing the technical aspects of Task 7 and will work in collaboration with USGS staff to perform the ground-water studies of this task. Task 8 will be managed by Dr. Rytuba who will oversee the synthesis the results of all tasks that will be incorporated into the final protocol for the environmental assessment of mercury mine sites and natural mercury sources.

Dr. James J. Rytuba (Geologic Division, U.S. Geological Survey, Menlo Park, CA) is the Chief of the USGS Mercury and Arsenic Cycling Project. He has been the USGS mercury commodity specialist since 1979 and in this capacity he has investigated mercury deposits throughout the world including several of the worldÕs largest deposits. His research interests include the environmental geochemistry of Hg and As. He received his Ph.D. degree from Stanford University with dissertation research on mercury geochemistry.

Dr. Charles N. Alpers (Water Resources Division, U.S. Geological Survey, Sacramento, CA) received a Ph.D. in geochemistry from the University of California, Berkeley in 1986, and has been involved in numerous water-quality investigations involving trace-element geochemistry and the transport of trace elements in surface- and ground-water systems. Dr. Alpers has been involved in research concerning acid mine drainage at the Iron Mountain Superfund site since joining the USGS as a post-doctoral fellow in 1987. Since joining the USGS California District in 1991, Dr. Alpers has been Project Chief for an investigation of acid mine drainage in ground-water at Penn Mine, a project that received cooperative funding totaling more than $900,000 from the USGS, the State Water Resources Control Board and the East Bay Municipal Utility District. Dr. Alpers is actively involved as Project Chief of the Sacramento River Trace Metals Transport Project, characterizing the geochemistry of trace elements, including mercury, in the Sacramento River along a reach of the river between Shasta Lake and Freeport, with cooperative funding and in-kind services in excess of $600,000 from the USGS, the State Water Resources Control Board, the Sacramento County Regional Sanitation District, the U.S. Environmental Protection

Agency, and the National Marine Fisheries Service. Dr. Alpers is a member of several technical advisory committees involved with the remediation of inactive and abandoned mine sites in California and other states, and has published extensively on the topics of the environmental geochemistry of sulfide oxidation (e.g. Alpers and Blowes, 1994; Nordstrom and Alpers, 1995, 1997), ground-water characterization at mine sites (e.g. Hamlin and Alpers, 1995, 1996), and the effects of efflorescent salts on mine drainage composition (Alpers et al., 1994a, 1994b; Alpers and Nordstrom, 1997).

Dr. Gordon Brown (Department of Geological and Environmental Sciences and Stanford Synchrotron Radiation Laboratory) is the D.W. Kirby Professor of Earth Sciences and Professor at the Stanford Synchrotron Radiation Laboratory, Stanford University. He has a Ph.D. degree from the Virginia Polytechnic Institute and State University and did post-doctoral work at the State University of New York at Stony Brook. Prior to joining the Stanford faculty in 1973, he was an Assistant Professor in the Department of Geological & Geophysical Sciences at Proneceton University for a two-year period. Brown brings extensive experience in the chemistry and physics of minerals and amorphous materials to this project. He has utilized x-ray and neutron scattering, various spectroscopic methods (x-ray emission, XPS, Mossbauer, Raman, FTIR, XAFS, X-ray standing wave, photoemission, etc.), and STM/AFM in a wide variety of geochemical and mineralogical applications. During the past decade, he has had extensive experience with applications of synchrotron radiation to earth materials problems, with special emphasis on the application of X-ray absorption spectroscopy to the analysis of bonding environments and structures of metal sorption complexes on mineral surfaces and of metals in complex minerals, glasses, and environmental samples. Professor Brown's present research program includes spectroscopic studies of mineral surfaces, chemisorption reactions at mineral-water interfaces, heavy metal contaminants in environmental samples, and structural studies of silicate melts and glasses, using the spectroscopic methods listed above. He has had a long-term collaboration with Prof. George A. Parks (Stanford University) on the factors controlling heavy metal sorption on mineral surfaces and the speciation of heavy metals in environmental samples, including mine wastes and contaminated soils. In addition, Brown has active collaborations with a number of other scientists, including Dr. James Rytuba (USGS, Menlo Park, CA) on Hg and As speciation in mine wastes, Dr. Tetsu Tokunaga of LBNL on Se geochemistry, and Prof. Georges Calas (U. Paris) and Prof. Harvey Doner (U.C. Berkeley) on environmental geochemistry problems. Brown is the author or co-author of over 150 peer-reviewed publications. He is Past President and Fellow of the Mineralogical Society of America, a Fellow of the Geological Society of America, and recently received the Doctor Honoris Causa Degree from the University of Paris.

Dr. George A. Parks (Department of Geological and Environmental Sciences) has a long history of research experience with theoretical and experimental aqueous thermodynamics and the surface chemistry of oxides and silicates, the sorption behavior and environmental geochemistry of heavy metals, metallurgical process development, and computer simulation in these contexts. Professor Parks' present research program includes experimental and theoretical work on the cooperative adsorption of inorganic and organic solutes on oxide minerals and clays, on the hydrolysis and adsorption chemistry of mercury, uranium, and arsenic, and molecular descriptions of sorption complexes at oxide/water interfaces (in collaboration with Brown). Parks is author or co-author of many publications, including a U.S. Patent on Hg hydrometallurgy and a series of reports on the environmental geochemistry of Hg.

Chris Kim (Department of Geological and Environmental Sciences) is a first-year graduate student working on the environmental geochemistry of mercury with Professor Gordon Brown. Chris received his B.S. degree in Geological & Geophysical Sciences, summa cum laude, from Princeton University where he completed a senior thesis on the hosting of contaminant elements in magadiite, an evaporite mineral. He spent a year in Korea following graduation from Princeton teaching English. His Ph.D. project at Stanford University involves the speciation of mercury in soils and mining wastes in the California Coast Range.

Dr. Ron Churchill (CA Department of Conservation, Division of Mines and Geology) received a Ph.D. in economic geology from the University of Minnesota in 1980, and has been involved in numerous economic geology investigations involving the assessment of mineral deposits. Dr. Churchill is presently a Senior Geologist Specialist who is leading a program to evaluate the environmental hazards of historic and abandoned mines with an emphasis on the mercury mines in CA. He is a technical advisor to the USGS study of Metal Transport in the Sacramento River" and was a technical advisor to the "Sacramento River Mercury Control Planning Project".

Dr. Trude V. King (Geologic Division, U.S. Geological Survey, Denver, CO) is a specialist in the assessment of mineral deposits using imaging spectroscopy. Dr. King has pioneered the development of techniques for processing AVIRIS data for use in the assessment of environmental effects from mines and mine drainages. Dr. King is currently lead scientist on the USGS project to evaluate Coast Range mercury deposits using imaging spectroscopy.

Dr. Howard Taylor (Water Resources Division, U.S. Geological Survey, Boulder, CO) is a senior geochemist and analytical chemist for the U.S. Geological Survey with over 25 years of investigations of trace metal chemistry in large river and ground water systems throughout the United States. Dr. Taylor is a senior scientist on the comprehensive USGS study of trace metals in the Mississippi River system that began in 1987 (Garbarino et al., 1996), and during 1996-1997 has an active collaboratory on the USGS Sacramento River Metals Transport Study. Dr. Taylor has performed pioneering development work in field sampling and processing, and in the laboratory technology of the determination of ultra-low concentration levels of trace metals, including mercury, in environmental applications.

Dr. David Roth (Water Resources Division, U.S. Geological Survey, Boulder, CO) received his Ph.D. in 1994 from Colorado State University; his dissertation work involved ultra-trace analysis of mercury in environmental samples. Dr. Roth is a frequent collaborator with Dr. Howard Taylor on mercury studies (e.g. Roth et al., 1996; Roth and Taylor, 1995, 1997). Dr. Roth is currently involved with Dr. Alpers in the preparation, isolation, and analysis of colloidal material from the Sacramento River for mercury and trace metals as part of the Sacramento River Trace Metals Transport Project.

VI. Compliance with standard terms and conditions

All terms and conditions listed in the Request for Proposals (RFP), Attachment D, are agreeable with the exception of item 9 (p. 35 of RFP). As a Federal agency, the U.S. Geological Survey requires instead a statement such as the following:

> "The USGS agrees to cooperate to the extent allowed by federal law, in submittal of all claims for alleged loss, injuries, or damage to persons or property arising from the acts of USGS employees, agents, subcontractors, or assigns, acting within the scope of their employment in connection with the performance of this agreement, pursuant to the Federal Tort Claims Act (28 U.S.C. &2671, et seq.)."

According to Table D-1 in the RFP, the only form required at the proposal stage for "Services/Consulting/Preconstruction/Research" proposals is item 8, "Non-discrimination compliance." A statement regarding the USGS position on non-discrimination compliance is attached.

NONDISCRIMINATION COMPLIANCE STATEMENT

COMPANY NAME

U.S. Geological Survey

The company named above (hereinafter referred to as "prospective contractor") hereby certifies, unles specifically exempted, compliance with Government Code Section 12990 (a-f) and California Code o Regulations, Title 2, Division 4, Chapter 5 in matters relating to reporting requirements and th development, implementation and maintenance of a Nondiscrimination Program. Prospective contracto agrees not to unlawfully discriminate, harass or allow harassment against any employee or applicant fo employment because of sex, race, color, ancestry, religious creed, national origin, disability (includin HIV and AIDS), medical condition (cancer), age, marital status, denial of family and medical care leav and denial of pregnancy disability leave.

CERTIFICATION

I, the official named below, hereby swear that I am duly authorized to legally bind the prospectiv contractor to the above described certification. I am fully aware that this certification, executed on th date and in the county below, is made under penalty of perjury under the laws of the State of Californi

OFFICIAL'S NAME

Michael V. Shulters

DATE EXECUTED

July 25, 1997

EXECUTED IN THE COUNTY OF

Sacramento, California

PROSPECTIVE CONTRACTOR'S SIGNATURE

PROSPECTIVE CONTRACTOR'S TITLE

District Chief

PROSPECTIVE CONTRACTOR'S LEGAL BUSINESS NAME

U.S. Geological Survey

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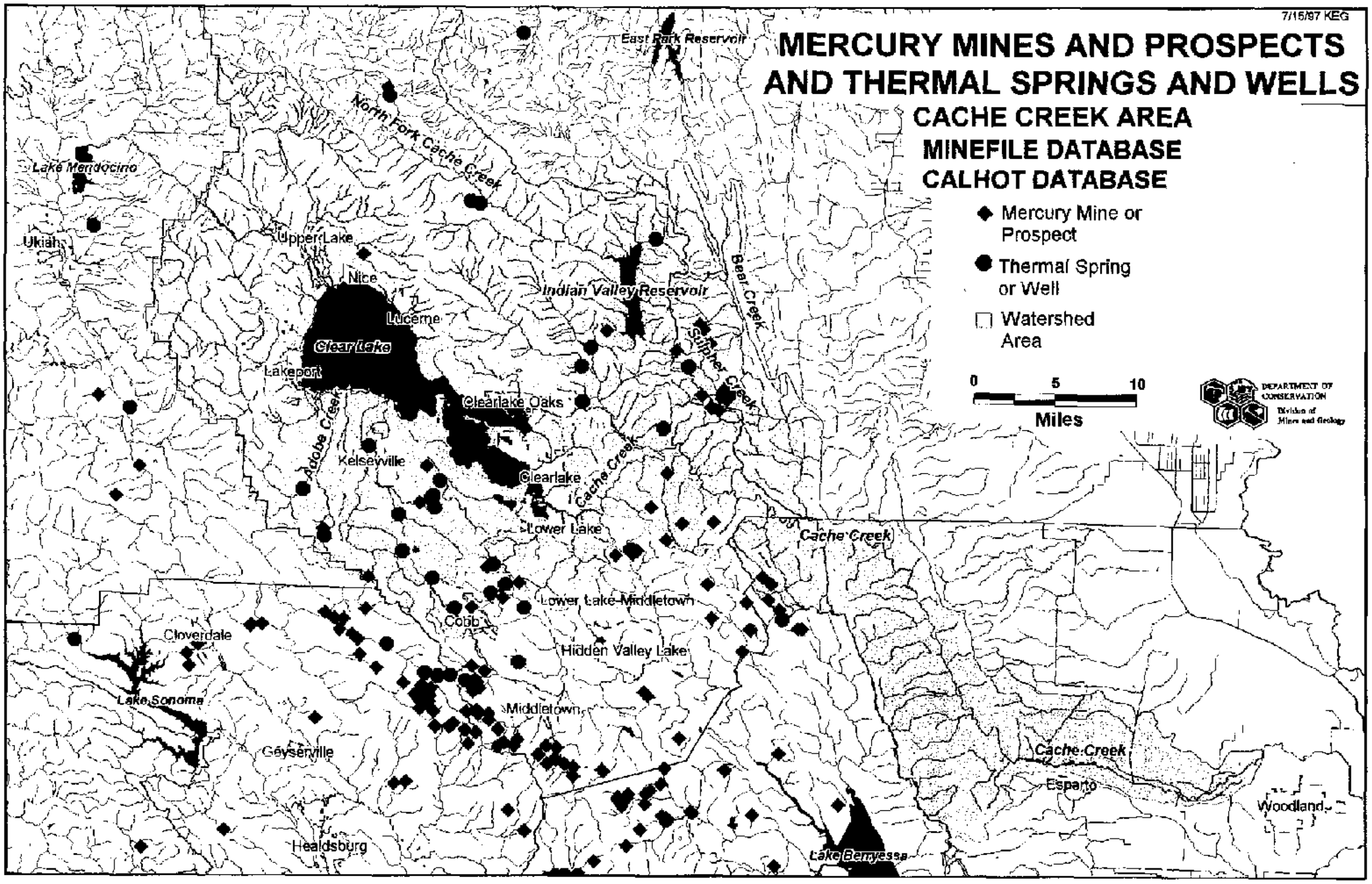

Figure 1. Location of mercury mines, prospects, and thermal springs in the Cache Creek Watershed.

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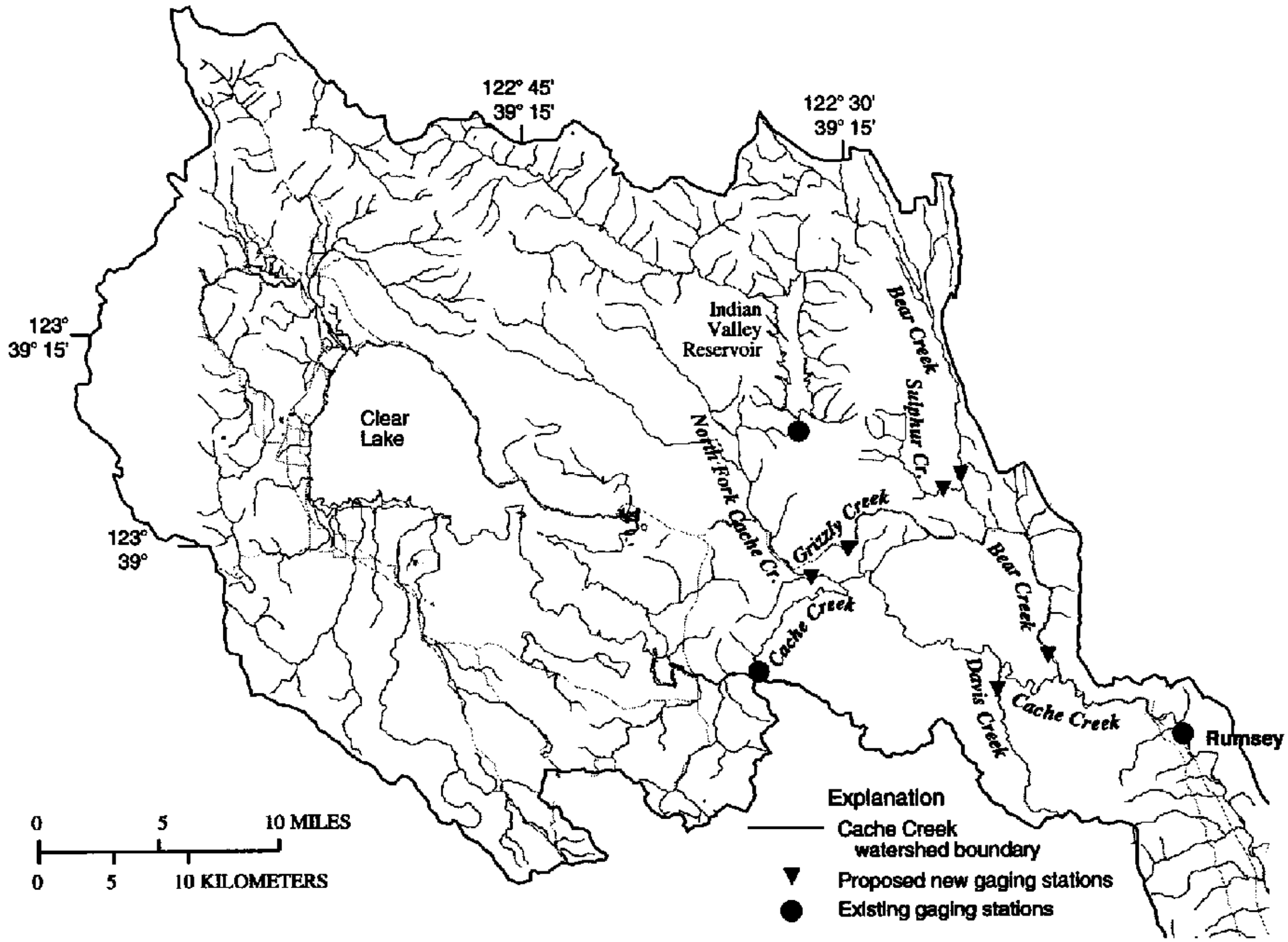

Figure 2. Location of existing and proposed gaging stations in the Cache Creek watershed.