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7
8 STATE WATER RESOURCE CONTROL BOARD
9 STATE OF CALIFORNIA

10
11
12 In the Matter of

13 Richard Miller,

14 Petitioner

15 For Review of Technical and Monitoring
Reporting Order #R5-2010-0048 of the
16 California Regional Water Quality
Control Board, Central Valley Region

PETITION No.

**PETITION FOR REVIEW AND REQUEST
FOR EVIDENTIARY HEARING**

REQUEST FOR STAY AS TO PETITIONER

**REQUEST TO HOLD PETITION IN
ABEYANCE**

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18
19 Pursuant to California Water Code section 13320 and Title 23 of the California
20 Code of Regulations §§ 2050 *et seq.*, Petitioner Richard Miller ("Petitioner") hereby
21 petitions the State Water Resources Control Board ("State Board") for review of Technical
22 and Monitoring Reporting Order #R5-2010-0048 ("Order") adopted by California
23 Regional Water Quality Control Board, Central Valley Region ("Regional Board") on May
24 27, 2010.¹ The Order requires the submittal of certain technical reports for the Central,
25 Cherry Hill, Empire, Manzanita, and West End Mines ("Mines") located in Colusa County,
26

27
28 ¹ See Order attached as Exhibit A to Declaration of Richard Miller in Support of Petition for
Review and Request for Evidentiary Hearing, Request for Stay as to Petitioner, and Request to
Hold Petition in Abeyance ("Miller Decl."), submitted concurrently herewith,

1 California. The Order improperly names Petitioner a discharger and omits other relevant
2 parties and unnecessarily requires the submittal of technical reports without any rational
3 basis. Petitioner requests a hearing on this matter and a stay of the Order pending this
4 appeal.

5
6 **I. PETITIONER**

7 Petitioner is Dr. Richard Miller and should be contacted through his legal counsel
8 at the following address:

9 Dr. Richard Miller
10 c/o William D. Wick
11 WACTOR & WICK LLP
12 180 Grand Avenue, Suite 950
13 Oakland CA 94612-3572
14 Telephone: (510) 465-5750
15 Facsimile: (510) 465-5697

16
17 **II. ACTION OF THE REGIONAL BOARD TO BE REVIEWED**

18 Petitioner requests that the State Board review the Order, which requires the
19 preparation and submittal of technical reports, including *Mining Waste Characterization*
20 *Work Plan, Mining Waste Characterization Report, Surface and Ground Water Monitoring*
21 *Plan*, and a Water Supply Well Survey and Sampling Plan, and improperly identifies
22 Petitioner as a "discharger" with respect to the Mines. A copy of the Order is attached as
23 Exhibit A. This Petition is a protective filing, and pursuant to 23 Cal. Code Regs. §
24 2050.5(d),² Petitioner requests that this Petition be held in abeyance by the State Board
25 until further notice.

26
27 ² 23 Cal. Code Regs. § 2050(d) provides:

28 (d) A petition may be held in abeyance at the request or with the agreement of
the petitioner.

(1) A request or agreement to hold a petition in abeyance must be in writing and
shall be provided to the state board, the regional board, and the discharger, if not
the petitioner.

(2) Petitions may be held in abeyance unless the regional board provides
reasonable grounds for objection. For petitions challenging the assessment of

1 **III. DATE OF THE REGIONAL BOARD ACTION**

2 The Regional Board issued the Order on May 27, 2010.

3
4 **IV. STATEMENT OF REASONS WHY THE REGIONAL BOARD'S ACTION WAS**
5 **INAPPROPRIATE OR IMPROPER**

6 As set forth more fully below, the Regional Board should review and rescind the
7 Order because: (1) it improperly named Petitioner as a discharger in requiring
8 Petitioner to conduct work on all of the Mines where Dr. Miller was not—and is not—a
9 "discharger," in violation of law; (2) it failed to name all responsible parties since it
10 excludes historic owners and operators of the Site, American Land Conservancy ("ALC"),
11 Sunoco Energy Development Company, and the Bureau of Land Management; and (3) it
12 violates California Water Code § 13267(b)(1) by failing to provide Petitioner "with a
13 written explanation with regard to the need for the reports, and [fails to] identify the
14 evidence that supports requiring [Dr. Miller] to provide the reports" to establish that the
15 required technical reports "bear a reasonable relationship to the need for the report and
16 the benefits to be obtained from the reports." Thus, the Regional Board's action was not
17 supported by the record and was arbitrary, capricious, and in violation of law and policy.

18
19 **A. Background**

20 As stated in the Order: "The Central, Cherry Hill, Empire, Manzanita, and West
21 End Mines (hereafter "Mines") are inactive mercury and/or gold mines" located in the
22 Wilber Springs hydrothermal area of the Sulphur Creek Mining District of Colusa County
23 identified by Assessor's Parcel Numbers 018-200-002-000, 018-200-013-000, 018-200-
24 014-000, 018-200-015-000, 018-200-016-000, 018-200-017-000, 018-200-018-000, 018-

25
26 administrative civil liability or penalties, written agreement from the regional board
27 is required.

28 (3) The time limit for formal disposition shall be tolled during the time a petition is
held in abeyance, and shall recommence running when the petition is removed
from abeyance.

1 200-004-000, 018-200-005-000, and 018-200-007-000. [¶ 1 and 2]. The Order asserts
2 that mining wastes from the Mines have eroded into Sulphur Creek, which is a tributary
3 to Cache Creek, since the late 1800s. [¶ 1 and 3].

4 With regard to Petitioner, the Regional Board found: "Richard L. Miller is the
5 current owner of all parcels subject to this Order" that he purchased in 1974, 1999, and
6 2003 and therefore is "responsible for investigating and cleaning up waste that is
7 discharging from the property." [Order at p. 12, ¶ 55]. Notably, the Regional Board
8 provided no evidence that Petitioner actively mined the sites or actually caused any
9 discharges.

10
11 **B. The Regional Board's Action Was Inappropriate and Improper**

12 **1. Dr. Miller Was Inappropriately Named as a Discharger.**

13 The Order concludes: "In light of Dr. Miller's long ownership of and ability to
14 control the property [. . .], the Board finds that it is appropriate to name Dr. Miller as a
15 named discharger." [Order at p. 12, ¶ 55]. This conclusion is unsupported by the
16 record or the law. Under California Water Code Section 13267, Regional Boards are
17 required to "provide written explanation with regard to the need for the reports, and
18 *shall identify the evidence that supports requiring that person to provide the reports.*"
19 Cal. Water Code § 13267(b)(emphasis added). The Regional Board failed to include
20 evidence in the Order that establishes a causal connection between the alleged
21 contamination and Petitioner. The Order fails to identify *any* evidence in support of its
22 claim that Dr. Miller discharged any of the mining waste that is the subject of the Order,
23 basing his liability solely on his acquisition of various parcels and the terms of an
24 easement. [Order at p. 12, ¶ 55]. Thus, the Order fails to meet, and cannot meet, this
25 requirement of California Water Code § 13267(b) in light of the evidence. Therefore,
26 Petitioner not only challenges the failure of the Regional Board to include all relevant
27 evidence in the Order, but also challenges the findings in the Order.

28

1 Even if the Order contained sufficient evidence relating to Petitioner, the operative
2 facts and applicable legal authority would support designating Petitioner, at most, as a
3 secondary discharger or secondarily responsible party. The Order alleges that mercury
4 has impacted Sulphur Creek through runoff and erosion from mine waste piles and
5 sediment loads. [Order at p. 5, ¶ 27]. Petitioner never operated the Mines and had
6 nothing to do with the activity that caused the condition of the pollution. Indeed, the
7 Order recognizes that other parties actively engaged in the mining operations at the root
8 of the ongoing discharge but notes they are no longer in existence. [Order at p. 14, ¶
9 63].

10 Furthermore, Dr. Miller testified at the hearing that Sunoco Energy Development
11 Company conducted activities at the Mines that did or could have caused soil disturbance
12 leading to off-site migration of mercury-laden sediments, but the Regional Board declined
13 to name this entity in the Order. [Order at p. 17, ¶ 14]. Petitioner submits that the
14 Regional Board's refusal to identify and name historic mine owners and operators and
15 Sunoco as dischargers is an arbitrary and capricious decision unsupported by the record.
16 The Regional Board's action is also inconsistent with Regional Board orders designating
17 property owners as secondary dischargers. Petitioner is not appropriately named as a
18 discharger.

19 **2. *The Order Inappropriately Assumes Joint and Several***
20 ***Liability Among the Named Dischargers.***
21

22 The Order implicitly requires the named dischargers to comply with its terms, and
23 apparently declares them to be jointly and severally liable. [Order at p. 13, ¶ 57]. The
24 Order's requirements that Petitioner and the other named dischargers submit an
25 investigation work plan, an investigative report, and a monitoring plan for all of the
26 Mines, are substantially overbroad, since Petitioner did not operate any of the Mines and
27 did not produce any mercury or generate any waste piles. The Order acknowledges that
28

1 California Water Code § 13267 imposes investigation and reporting liability on "any
2 person who has discharged, dischargers, or is suspected of having discharged or
3 discharging, or who proposes to discharge waste." [Order at p. 10, ¶ 51]. The plain
4 language of the California Water Code reveals that a "discharger" is only liable for
5 investigating areas to which it discharged. A "discharger" is not liable for investigating
6 and remediating the geographically distant and unrelated discharges of other PRPs. This
7 legal principle means that the Regional Board cannot require Dr. Miller to investigate
8 sources of mercury contamination unrelated to Dr. Miller's activities.

9 The Order improperly requires Petitioner to prepare technical reports related to
10 Mines where Dr. Miller was not a "discharger." Although the Order notes "Owners of
11 mine property are dischargers with respect to mining waste that erodes, runs off or
12 otherwise dischargers from the property," Dr. Miller did not own all the Mines for a
13 contiguous time period, acquiring parcels in a piecemeal fashion for conservation
14 purposes in 1974, 1999, and 2003 (see Order at p. 12, ¶ 55). Dr. Miller therefore objects
15 to the Order's requirement that he submit work plans and a report concerning all of the
16 Mines since his ownership is divisible.

17
18 **3. The Regional Board Provides No Rational Basis for the**
19 **Required Work and the Schedule.**

20 The Regional Board is subject to the limitation in Water Code § 13267 that the
21 "burden, including costs, of [technical or monitoring program] reports shall bear a
22 *reasonable relationship* to the need for the report and the benefits to be obtained from
23 the reports." Here, the Regional Board fails to meet this standard. In fact, the Regional
24 Board admits that it did not do any type of cost/benefit analysis, stating that "no specific
25 cost for the required reports has been estimated." [Order at p. 10, ¶ 49].

26 Moreover, the schedule in the Order for the work required is unduly burdensome.
27 Petitioner is being required to undertake site characterization and technical work.
28 Resolution 92-49 directs Regional Boards to determine schedules for investigation and

1 cleanup considering "the financial and technical resources available to the dischargers."
2 [Resolution 92-49(iv)(c)]. Petitioner is an individual with limited assets. Therefore,
3 Petitioner requests that he not be designated a responsible party, or alternatively, that
4 the State Board stay the enforcement of the Order as to Petitioner.

5
6 **4. The Regional Board's Findings and Conclusions Are**
7 **Unsupported by the Evidence.**

8 The Regional Board relies primarily on the *CalFed-Cache Creek Study, Task 5C2:*
9 *Final Report – Final Engineering Evaluation and Cost Analysis for the Sulphur Creek*
10 *Mining District* ("the CalFed Report")³ as the rationale for the issuance of Order. [See
11 Order at p. 2, ¶ 7-31]. However, the findings and conclusions of the Regional Board
12 extrapolated from the CalFed Report and other reports⁴ are inconsistent with the site-
13 specific, technical data for the Mines. For example, the Regional Board assumes that the
14 water deposits into the Wilbur Hot Springs originate from three separate sources (see
15 Order at p. 7, ¶ 37, identifying Sulphur Creek, Bear Creek, and Cache Creek as
16 originating water bodies) and lists the mercury content for each of the Mines based on
17 the CalFed reports for these sources (see Order at p. 4, ¶ 20 and 21). In reality, all the
18 water for the Wilbur Hot Springs comes from the one source and thus must have the
19 same mercury concentrations. In addition, the mercury levels at Wilbur Hot Springs from
20 independent, recent testing indicate that the geothermal water at Wilbur Hot Springs
21 meets the state standard for allowable mercury for drinking water.⁵

22
23
24 ³ See Exhibit B to Miller Decl.: *CalFed – Cache Creek Study (Task 5A: Final Report) January*
25 *2000-July 2002, Mercury Loading and Source Bioavailability from Upper Cache Creek Mining*
Districts.

26 ⁴ See Exhibit C to Miller Decl.: *Mercury Assessment and Monitoring Protocol for the Bear Creek*
27 *Watershed, Colusa, California*, Prepared for the Bureau of Land Management, Scientific
Investigations Report 2010-5018, U.S. Department of Interior, U.S. Geological Survey.

28 ⁵ See Exhibit D to Miller Decl.: Laboratory Report from FGL Environmental for Wilbur Hot Springs
in Williams, CA 95987, Results for Mercury and Lithium, June 18, 2010.

1 Further, the Regional Board provides no rationale, other than "modeling" or
2 "estimating" for its belief that cleaning up the mine tailings will significantly reduce
3 mercury levels downstream. (See Order at p. 5, ¶ 27; see also 5/27/10 Board Meeting
4 Minutes at p.6, stating "Central Valley Water Board staff *estimates* that remediation of
5 the mine sites would reduce mercury loads from the mines to the creek by approximately
6 95% (this is not 100% because these sites likely were naturally mercury-enriched above
7 regional background prior to mining."). As noted, the Regional Board recognizes that the
8 Mines have significant background levels of naturally-occurring mercury, which could
9 account for the mercury detected in the watershed. [See 2007 Basin Plan Amendment
10 Staff Report – 5/27/10 Board Meeting Minutes at p. 5, stating: " Mercury in the Sulphur
11 Creek watershed is from both natural (springs and mercury enriched soils) and
12 anthropogenic (mine waste) sources. The water quality objective attempts to account
13 for and give credit to dischargers for the high natural background mercury concentration
14 in the watershed."].

15 However, the Regional Board does not have the critical baseline levels of
16 naturally-occurring mercury in the streams to differentiate between naturally occurring
17 mercury or discharges. [See e.g. Order at p. 4, ¶ 20, noting that "complete
18 characterization of background soils and mining wastes at the Central and Empire Mines
19 has not been performed"; Order at p. 1 ¶ 3, stating "Mining waste discharged onto
20 ground surface has not been evaluated for its potential impact to ground water"; and
21 Order at p.5 ¶ 24, stating, "Complete characterization of background soils and mining
22 waste at the Cherry Hill and West End mines has not been performed"]. In fact, as
23 noted in Comment 3 to Order in the Regional Board Meeting Minutes at p. 7, "Homestake
24 notes that the proposed Order does not dispute that a significant amount of mercury is
25 naturally occurring, and cites findings in the proposed Order stating that as much as 90%
26 of the total mercury load in Sulphur Creek is dissolved mercury from active hydrothermal
27 systems." *Id.*

28

1 Without knowing the naturally-occurring background baseline levels of mercury,
2 the Regional Board has no factual basis to determine what concentrations are naturally
3 occurring or a result of discharges.⁶ Thus, Petitioner challenges the Regional Board's
4 findings and conclusions as well as the sampling methods and measurements on which
5 the findings and conclusions were based.

6 **5. The Regional Board Failed to Provide Any Evidence Showing**
7 **Mining Wastes Are the Source of Mercury Discharges.**

8 The Regional Board summarily finds: "The Mines have discharged and continue to
9 discharge or threaten to discharge mining waste into waters of the state." [Order at p.
10 1, ¶ 1]. However, the Regional Board fails to demonstrate a causal relationship between
11 the mercury in runoff from the mine tailings as opposed to naturally occurring
12 contributions from all of the hot springs in the area because the Regional Board never
13 measured the flux of mercury in several media. For example, Suchanek et al (2010) in
14 the CalFed report states that the mercury in the watershed streams comes from both the
15 natural contribution from the many springs in the area and potentially from the mine
16 tailings.

17 Instead of providing evidence that mercury, if any, leaching from the tailings is
18 actually impacting the streams, the Regional Board relies on unpublished data from the
19 CalFed reports to substantiate its conclusion that anthropogenic sources are "significant."
20 [See Suchanek on page 1 of the CalFed report, stating, "All three tributaries [Bear Creek,
21 Cache Creek and North Fork of Cache Creek] are known to be significant sources of
22 anthropogenically derived [mercury] Hg from historic mines...."]. The first reference
23 provided for that statement is "D.G. Slotton, unpub. data, 1995". The Regional Board
24 provides no summary of the findings of that unpublished data and omits any verification

25 _____
26 ⁶ In fact, a USGS report has clearly stated that 130 years of sediment deposited in the miles of
27 streambeds down Cache Creek is the major contributing factor to the mercury levels downstream
28 (i.e., no amount of tailing clean up will make a difference, because the naturally- occurring
mercury plus the mercury in the stream beds is already well above the levels the State allows).
[See Exhibit E to Miller Decl.: *Mercury and Methylmercury Concentrations and Loads in the
Cache Creek Watershed, California*, by Joseph L. Domagalski, published in the *Science of the
Total Environment, International Journal for Scientific Research* 327 (2004) 215-237.

1 of its accuracy. The Regional Board fails to conduct any type of analysis to confirm that
2 the Mines are a source of dischargers to the Cache Creek watershed and fails to
3 authenticate any of the documents in which it relies.

4
5 **V. THE MANNER IN WHICH PETITIONER HAS BEEN AGGRIEVED**

6 Petitioner has been aggrieved by the Regional Board's actions because he will be
7 subjected to the provisions of an arbitrary and capricious Order unsupported by evidence
8 in the record. As a result of being named a discharger in connection with the Site,
9 Petitioner will be forced to incur significant costs of compliance, to bear a heavier burden
10 of regulatory oversight and to suffer other serious economic consequences. Further, by
11 naming Petitioner as a primary discharger and excluding other parties, the entity or
12 entities which actually caused the contamination and which has the financial capabilities,
13 will not be participating.

14
15 **VI. REQUEST FOR A STAY OF THE ORDER**

16 Pursuant to California Water Code § 13321 and 23 Cal. Code of Regs. §2053,
17 Petitioner hereby petitions the State Board to stay implementation of the Order as to
18 Petitioner. Water Code section 13321 authorizes the State Board to stay the effect of
19 Regional Board decisions. Title 23, CCR § 2053 requires that a stay shall be granted if a
20 petitioner alleges facts and produces proof of:

- 21 (1) Substantial harm to petitioner or to the public interest if a stay is not granted;
- 22 (2) A lack of substantial harm to other interested persons and to the public if a
23 stay is granted; and,
- 24 (3) Substantial questions of fact or law regarding the disputed action.

25 23 CCR § 2053 (a).

26 The State Board's granting of a stay is equivalent to a preliminary injunction. The
27 California Supreme Court has stated that the standard for a preliminary injunction is as
28 follows: In deciding whether to issue a preliminary injunction, a court must weigh two

1 "interrelated" factors: (1) the likelihood that the moving party will ultimately prevail on
2 the merits and (2) the relative interim harm to the parties from issuance or non-issuance
3 of the injunction. *Butt v. California* (1992) 4 Cal. 4th 668,678 (citation omitted). The trial
4 court's determination must be guided by a "mix" of the potential-merit and interim-harm
5 factors; the greater the plaintiffs showing on one, the less must be shown on the other
6 to support an injunction. *Id.*; citation omitted).

7 Here, Petitioner, as detailed below, has satisfied the requirements of both tests.
8 The Regional Board's adoption of the Order was an erroneous action that poses
9 substantial harm to Petitioner and the public interest for the following reasons. First, it
10 requires Petitioner to prepare work plans and investigation reports covering all of the
11 Mine Sites, which is unjustified and overbroad, and fails to identify the evidence on which
12 it relies to make the unjustified demands, as required by California Water Code § 13267.
13 Second, the Order incorrectly assumes Petitioner "discharged" mercury from all of the
14 Mine Sites identified, which is false. Thus, Dr. Miller has a high likelihood of success on
15 the merits of his appeal. Therefore, the State Board should grant a stay of the Order as
16 to Dr. Miller.

17
18 **A. Substantial and Irreparable Harm to Petitioner and the Public**
19 **Interest Will Result if the Order is Implemented Without**
20 **Modification.**

21 The public interest and Petitioner will be substantially harmed by requiring
22 Petitioner to implement the Order. A failure to stay the Order as to Dr. Miller pending
23 State Board review would unfairly and illegally burden Petitioner by obligating him to
24 conduct the extensive and expensive work required under the Order according to its
25 abbreviated schedule that may be vacated upon judicial review. Further, Dr. Miller may
26 have no means of recovering such costs since many of the parties having actual legal
27 liability for the discharges no longer exist or appear to be without sufficient financial
28 resources to reimburse Dr. Miller.

1 Furthermore, a stay is proper because there is a lack of substantial harm to other
2 interested persons and the public interest if it is granted. First, while a stay would
3 prevent enforcement of the overly broad Order against Dr. Miller, the Regional Board
4 could focus on its investigation of additional responsible parties (see Order at p. 17, ¶
5 15) and the other parties named in the Order having legal responsibility for operations
6 and discharges on the Mines themselves in the specific areas of concern to the Regional
7 Board. The Regional Board could thereby avoid protracted litigation and move closer to
8 achieving the response actions it seeks over all of the Mine Sites much sooner than it can
9 by attempting to require Dr. Miller to perform such work.

10

11 **B. A Stay of the Order as to Dr. Miller Will Not Result in Substantial**
12 **Harm to Other Interested Persons or the Public.**

13 There is not likely to be any delay in the performance of the investigations sought
14 by the Regional Board as a result of the requested stay, because: (1) the Regional Board
15 has named in the Order responsible parties to perform the studies sought to be furnished
16 and (2) the Regional Board has been generally aware of the site conditions it now seeks
17 to address given the Mines' historic operations beginning in the late 1800s (see Order at
18 p. 1, ¶ 3), without issuing any similar orders to any of the owners or operators until now,
19 to Dr. Miller's knowledge. Thus, there will be no ongoing environmental harm as a
20 consequence of using a stay as to Dr. Miller. Moreover, the public interest is well-served
21 by insuring that only fair and just orders, supported by facts and law, are issued by the
22 Regional Board.

23

24 **C. The Regional Board's Action Raises Substantial Questions of Law**
25 **on Which Petitioner Is Likely to Prevail.**

26 The Petition for Review sets forth Dr. Miller's arguments regarding the legal
27 questions on which he is likely to prevail. The Order violates requirements set forth in the
28 Porter-Cologne Water Quality Act and is wholly unsupported by existing law and the

1 factual record. The State Board should therefore stay the Order as to Dr. Miller and
2 prevent the implementation of a decision that is illegal and sets an inappropriate
3 precedent. The record on file with the State Board contains the relevant supporting
4 documents to this Request for Stay of Action, which Dr. Miller reserves the right to - and
5 will- supplement. Dr. Miller also hereby incorporates all of the facts and arguments set
6 forth in the Petition for Review and the accompanying declaration, including any and all
7 supplemental submissions made by Dr. Miller or any other party in support of its Petition
8 for Review.

9

10 **VII. STATE BOARD ACTION REQUESTED BY PETITIONER**

11 **A. Request to Hold in Abeyance**

12 As discussed above, Petitioner requests that the State Board hold this Petition in
13 abeyance.

14

15 **B. Request for Stay as to Petitioner**

16 Petitioner requests that the Order be stayed as to Petitioner.

17

18 **C. Petition**

19 If it becomes necessary for Petitioner to pursue this appeal, he will request that
20 the State Board determine that the Regional Board's adoption of the Order was arbitrary
21 and capricious or otherwise inappropriate and improper, and will request that the State
22 Board amend the Order to delete Petitioner as a named discharger. If the State Board
23 declines to delete Petitioner as a named discharger, then Petitioner requests that: (1)
24 the State Board designates him as a secondary liable party rather than a primary liable
25 party with respect to the Site and (2) the State Board extend the timeline for submittal of
26 technical reports.

27

28

1 **VIII. STATEMENT OF POINTS AND AUTHORITIES IN SUPPORT OF LEGAL**
2 **ISSUES RAISED IN THE PETITION**

3 For purposes of this protective filing, the Statement of Points and Authorities is
4 subsumed in section IV of the Petition. If Petitioner elects to pursue this appeal, he
5 reserves the right to file a Supplemental Statement of Points and Authorities, including
6 references to the complete administrative record, which is not yet available. Petitioner
7 also reserves the right to supplement his request for a hearing to consider testimony,
8 other evidence and argument.

9
10 **IX. STATEMENT REGARDING SERVICE OF THE PETITION ON THE REGIONAL**
11 **BOARD**

12 A copy of this Petition is being sent to the Regional Board, to the attention of
13 Pamela C. Creedon, Executive Officer. By copy of this Petition, Petitioner also notifies the
14 Regional Board of Petitioner's request that the State Board hold the Petition in abeyance
15 and presents these substantive issues and objections to the Regional Board.

16
17 **X. STATEMENT REGARDING ISSUE PRESENTED TO THE REGIONAL BOARD**

18 The substantive issues and objections raised in this Petition, as stated above, were
19 raised before the Regional Board.

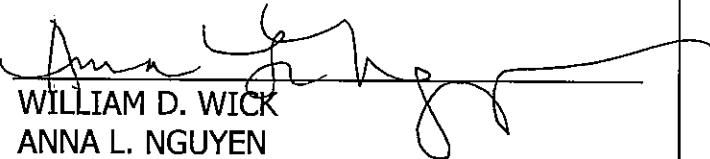
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21 **XI. CONCLUSION**

22 For all the foregoing reasons, if Petitioner pursues this appeal, he respectfully
23 requests that the State Board review the Order and grant the relief as set forth above.

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28

1 Dated: June 28, 2010

2 WACTOR & WICK LLP

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4 By: 
5 WILLIAM D. WICK
6 ANNA L. NGUYEN
7 Attorneys for Petitioner
8 Dr. Richard Miller
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12 In the Matter of
13 Richard Miller,
14 Petitioner
15 For Review of Technical and Monitoring
16 Reporting Order #R5-2010-0048 of the
California Regional Water Quality
17 Control Board, Central Valley Region

PETITION No.

**DECLARATION OF RICHARD MILLER IN
SUPPORT OF PETITION FOR REVIEW,
REQUEST FOR EVIDENTIARY HEARING,
REQUEST FOR STAY AS TO
PETITIONER, AND REQUEST TO HOLD
PETITION IN ABEYANCE**

18 I, Dr. Richard Miller, M.A., PhD., declare:

19 1. I am the petitioner in the above referenced matter. This declaration is
20 submitted pursuant to Title 23, Cal. Code of Regulations § 2053(a). I make this
21 declaration based upon my personal knowledge, and if called to testify in court on these
22 matters, I could and would testify as follows:

23 2. I am the Founder & President of Wilbur Hot Springs Health Sanctuary. I
24 began the present Wilbur Hot Springs Sanctuary for the Self in 1972 to revitalize the
25 ancient healing method of Balneology – the science of the therapeutic use of baths – and
26 to combine the safety and security of the Wilbur environment with a modern personal
27 health philosophy emphasizing dignity and respect for all. I have spent the last 40 years
28

1 studying, teaching, researching, administering and practicing psychology, health
2 education, psychotherapy and Executive Consulting.

3 3. On May 27, 2010, the Regional Water Quality Control Board, Central Valley
4 Region ("Regional Board") adopted the Technical and Monitoring Report Order No. R5-
5 2010-0048 for the Central, Cherry Hill, Empire, Manzanita, and West End Mines in Colusa
6 County ("the Order"). As stated in the Order: "The Central, Cherry Hill, Empire,
7 Manzanita, and West End Mines (hereafter "Mines") are inactive mercury and/or gold
8 mines" located in the Wilber Springs hydrothermal area of the Sulphur Creek Mining
9 District of Colusa County identified by Assessor's Parcel Numbers 018-200-002-000, 018-
10 200-013-000, 018-200-014-000, 018-200-015-000, 018-200-016-000, 018-200-017-000,
11 018-200-018-000, 018-200-004-000, 018-200-005-000, and 018-200-007-000. [Order at
12 p. 1, ¶ 1 and 2].

13 4. The Order states that I am the current owner of all of these parcels and
14 that I purchased the various parcels in 1974, 1999, and 2003. [Order at p. 12, ¶ 55].

15 5. I have never owned or operated any mines nor have I engaged in any
16 mining activities that may have caused discharges to the Cache Creek watershed, which
17 includes Sulphur Creek, Bear Creek, and Cache Creek.

18 6. The Order requires the named parties, including me, to perform certain
19 investigation, characterization, and monitoring activities to reduce existing loads of
20 mercury in the Cache Creek watershed.

21 7. The Order fails to name other responsible parties. At the May 27, 2010
22 hearing, I suggested that the Regional Board name Sunoco Energy Development
23 Company, which the Regional Board declined to do.

24 8. As of yet, no cleanup or abatement work has commenced on the Mines.
25 There is no indication that a stay of enforcement of the Order as to me, upon review of
26 the State Board, will cause substantial harm to the public or any other interested parties.

27 9. Conversely, if the implementation of the Order is not stayed as to me, the
28 Order places a significant financial burden on me for investigation, monitoring, and

1 cleanup of mercury contamination related to historic mining operations on the various
2 mines since the 1800s in which I was never involved. It also requires me to prepare
3 work plans and investigation reports covering all of the Mine Sites, which is unjustified
4 and overbroad, because it fails to identify the evidence on which the Regional Board
5 relies on to mandate the technical reports.

6 10. Attached as Exhibit A to this declaration is a true and correct copy of the
7 Technical and Monitoring Reporting Order #R5-2010-0048 ("the Order") adopted by
8 California Regional Water Quality Control Board, Central Valley Region ("the Regional
9 Board") on May 27, 2010.

10 11. Attached as Exhibit B to this declaration is a true and correct copy of the
11 *CalFed – Cache Creek Study (Task 5A: Final Report) January 2000-July 2002, Mercury*
12 *Loading and Source Bioavailability from Upper Cache Creek Mining Districts*, which the
13 Regional Board primarily relies on as the technical basis of the Order.

14 12. Attached as Exhibit C to this declaration is a true and correct copy of
15 *Mercury Assessment and Monitoring Protocol for the Bear Creek Watershed, Colusa,*
16 *California*, Prepared for the Bureau of Land Management, Scientific Investigations Report
17 2010-5018, U.S. Department of Interior, U.S. Geological Survey, which also serves as the
18 basis of the Regional Board's findings and conclusions in the Order.

19 13. Attached as Exhibit D to this declaration is a true and correct copy of the
20 Laboratory Report from FGL Environmental for Wilbur Hot Springs in Williams, CA 95987,
21 Results for Mercury and Lithium, June 18, 2010, which indicates that the geothermal
22 water at Wilbur Hot Springs meets the state standard for allowable mercury for drinking
23 water.

24 14. Attached as Exhibit E to this declaration is a true and correct copy of the
25 *Mercury and Methylmercury Concentrations and Loads in the Cache Creek Watershed,*
26 *California*, by Joseph L. Domagalski, published in the Science of the Total Environment,
27 International Journal for Scientific Research 327 (2004) 215-237, which states that 130
28 years of sediment deposited in the miles of streambeds down Cache Creek is the major

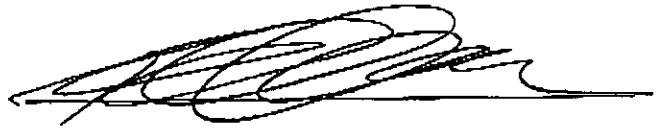
1 contributing factor to the mercury levels downstream (i.e., no amount of tailing clean up
 2 will make a difference, because the naturally- occurring mercury plus the mercury in the
 3 stream beds is already well above the levels the State allows).

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I declare under penalty of perjury under the laws of the State of California that
 the foregoing is true and correct. Executed on the date indicated below, in

Fort Bragg, California.

Dated: June 28, 2010



Dr. Richard Miller

Exhibit A

Technical and Monitoring Reporting Order #R5-2010-0048 ("the Order") adopted by California Regional Water Quality Control Board, Central Valley Region ("the Regional Board") on May 27, 2010.



**California Regional Water Quality Control Board
Central Valley Region**

Katherine Hart, Chair



Linda S. Adams
Secretary for
Environmental
Protection

11020 Sun Center Drive #200, Rancho Cordova, California 95670-6114
Phone (916) 464-3291 • FAX (916) 464-4645
<http://www.waterboards.ca.gov/centralvalley>

Arnold
Schwarzenegger
Governor

17 June 2010

To: See Attached Addressee List

TECHNICAL AND MONITORING REPORT ORDER R5-2010-0048, CENTRAL CHERRY HILL, EMPIRE, MANZANITA, AND WEST END MINES, COLUSA COUNTY

Enclosed is a copy of Technical and Monitoring Report Order No. R5-2010-0048 for the Central, Cherry Hill, Empire, Manzanita, and West End Mines in Colusa County. This Order was adopted by the Central Valley Regional Water Quality Control Board (Central Valley Water Board) at its meeting on 27 May 2010.

The Order requires the named parties to perform certain investigation, characterization, and monitoring activities to ensure protection of the waters of the state and to comply with the Central Valley Water Board's Water Quality Control Plan for the Sacramento River and San Joaquin River Basins, Fourth Edition (Basin Plan) requirement for responsible parties to develop plans to reduce existing loads of mercury from mining or other anthropogenic activities by 95% in the Cache Creek watershed.

In order to conserve paper and reduce mailing costs, a paper copy of the order has been sent only to the parties named in this Order. The full text of this order is available on the Regional Water Board's web site at http://www.waterboards.ca.gov/centralvalley/board_decisions/adopted_orders/.

Anyone without access to the Internet who needs a paper copy of the order can obtain one by calling Regional Water Board staff.

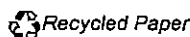
If you have any questions, please call Jeff Huggins at (916) 464-4639.

VICTOR J. IZZO
Senior Engineering Geologist
Title 27 Permitting and Mining

Enclosure: Technical and Monitoring Report Order R5-2010-0048

cc: Patrick Pulupa, Staff Counsel, Office of Chief Counsel, SWRCB, Sacramento

California Environmental Protection Agency



Addressee List
Central, Cherry Hill, Empire, Manzanita, and West End Mines

<p>Bailey Minerals Corporation, Represented by Michael J. Morrison 1495 Ridgeview Drive, Suite 220 Reno, NV 89510-6334</p>	<p>Gerald F. George, Attorney for Homestake Mining Company Pillsbury Winthrop Shaw Pitman LLP P.O. Box 7880 San Francisco, CA 94120-7880</p>
<p>Terhel Farms, Inc. Terri Harter P.O. Box 491 Colusa, CA 95932</p>	<p>Bonneville Industries, Inc. Richard Coombs, Agent for Service of Process 707 Commons Drive, #102 Sacramento, CA 95825</p>
<p>Richard L. Miller 4635 Paradise Drive Tiburon, CA 94920</p>	<p>Filiatra, Inc. Anthony Smernes 520 Hawkcrest Drive Sacramento, CA 95835</p>
<p>Holliday Foundation, Inc. Represented by Ralph W. Newcombe 513 SW C Ave Lawton, OK 73501</p>	<p>Asera Western Corporation Larry L. Asera Agent for Service of Process 164 Robles Drive, PMB 252 Vallejo, CA 94591</p>
<p>John D. Edgcomb Attorney for Cordero Mining Company and Sunoco Energy Development Company Edgcomb Law Group 115 Sansome Street, Suite 700 San Francisco, CA 94104</p>	<p>Magma Power Company Attention: Peter H. Weiner, Esq. Sanjay Ranchod, Esq. Paul, Hastings, Janofsky & Walker LLP 55 Second Street Twenty-Fourth Floor San Francisco, CA 94105-3441</p>
<p>Erinn Shirley Acting Abandoned Mine Lands / Hazmat Program Lead US Department of the Interior Bureau of Land Management California State Office 2800 Cottage Way, Suite W-1623 Sacramento, CA 95825</p>	<p>Gary Sharpe, Asst. Field Office Manager United States Bureau of Land Management, Ukiah Field Office 2550 North Street Ukiah, California 95482</p>

**CALIFORNIA REGIONAL WATER QUALITY CONTROL BOARD
CENTRAL VALLEY REGION**

**TECHNICAL AND MONITORING REPORT
ORDER R5-2010-0048**

**FOR
TERHEL FARMS, INC., RICHARD L. MILLER, HOLLIDAY FOUNDATION INC.,
HOMESTAKE MINING COMPANY, BONNEVILLE INDUSTRIES, INC.,
FILIATRA, INC., ASERA WESTERN CORPORATION**

**CENTRAL, CHERRY HILL, EMPIRE, MANZANITA, AND WEST END MINES
COLUSA COUNTY**

This Order is issued to Terhel Farms, Inc., Richard L. Miller, Holliday Foundation Inc., Homestake Mining Company, Bonneville Industries, Inc., Filiatra, Inc., and Asera Western Corporation (hereafter collectively referred to as Dischargers) based on provisions of California Water Code (CWC) section 13267, which authorizes the Central Valley Regional Water Quality Control Board (Central Valley Water Board or Board) to require the submittal of technical and monitoring reports.

The Central Valley Water Board finds:

1. The Central, Cherry Hill, Empire, Manzanita, and West End Mines (hereafter "Mines") are inactive mercury and/or gold mines. Mining waste from the Mines erodes into Sulphur Creek, which is tributary to Cache Creek. The Sulphur Creek streambed and flood plain directly below the Mines contain mining waste. The Mines have discharged and continue to discharge or threaten to discharge mining waste into waters of the state. These discharges have affected water quality, and continuing erosion of mining waste into Sulphur Creek will further affect water quality.
2. The Mines are located in the Wilber Springs hydrothermal area of the Sulphur Creek Mining District (District) of Colusa County, and about 20 miles west of Williams, California. The Mines are located within Colusa County Assessor's Parcel Numbers 018-200-002-000, 018-200-013-000, 018-200-014-000, 018-200-015-000, 018-200-016-000, 018-200-017-000, 018-200-018-000, 018-200-004-000, 018-200-005-000, and 018-200-007-000, in Sections 28 and 29, Township 14 North, Range 5 West, Mount Diablo Base and Meridian (MDBM), as shown in Attachment A, a part of this Order.
3. Mining waste has been discharged at the Mines since mining activities began in the late 1800s. Mining waste has been discharged onto ground surface where it has eroded into Sulphur Creek, resulting in elevated concentrations of metals within the creek. Mining waste discharged onto ground surface has not been evaluated for its potential impact to ground water. The Dischargers, own, have owned, or have operated the mining sites where the Mines are located and where mining waste has been discharged. In its current condition, mining waste is causing or threatens to cause a discharge of pollutants to waters of the state.

4. The Central Valley Water Board's *Water Quality Control Plan for the Sacramento River and San Joaquin River Basins, Fourth Edition* (hereafter Basin Plan) states: "By 6 February 2009, the Regional Water Board shall adopt cleanup and abatement orders or take other appropriate actions to control discharges from the inactive mines (Table IV-6.4) in the Cache Creek watershed." Mercury levels are already above applicable objectives in Sulphur Creek and Cache Creek, which constitutes a condition of pollution or nuisance.
5. The Prosecution Team conducted a title review of property records from the Colusa County Records Office. The parties named in this Order as Dischargers are known to presently exist or have viable successors. The basis of liability for each Discharger is addressed below under Dischargers' Liability.
6. This Order may be revised to include additional Dischargers as they become known, and may include additional current or former owners, leaseholders and operators.

Mining History

7. Copper, mercury, sulphur, and gold were all discovered in the District in the late 1800s, and the Mines were developed during that period. This information is described in the *CalFed-Cache Creek Study, Task 5C2: Final Report. Final Engineering Evaluation and Cost Analysis for the Sulphur Creek Mining District*, prepared by Tetra Tech EM Inc., September 2003 (hereafter CalFed Report).

The Central and Empire Groups

8. The Central and Empire mines are located near the Wilbur Springs resort. The Central Mine Group lies to the north of Sulphur Creek and is made up of the historic Central, Dewey, and Little Giant mining claims. The Empire Mine Group lies to the south of Sulphur Creek and is made up of the historic Empire, Mercury Queen, Mercury King, and Hidden Treasure lode mining claims (CalFed Report).
9. Mining started at the Empire mine in the 1870s and at the Central mine in 1891. In 1873, sixty-three flasks of mercury (one flask equals 76 pounds) were produced from ore mined at the Empire mine, but processed at the Wide Awake mine. Sometime between the 1890s and the early 1900s, the Central and Empire groups were operated in conjunction with the Abbott mine. Therefore, it is possible during this time that ore from Central and Empire groups was processed at the Abbott mine facilities. After this period, no significant production from the Central Group occurred until 1926 when \$10,000 worth of mercury (about 107 flasks) was produced. After that, the mines were idle until a small production was reported in 1942. No information was found on any operations after 1942. Total production was approximately 170 flasks. (CalFed Report).
10. The workings of the Central and Empire mines are now caved but are reported to include several hundred feet of underground drifts and crosscuts. The workings of the Central Mine consisted of four short adits, the highest about 400 feet above Sulphur Creek. The Empire Mine may have included at least three adits that where up to 150 feet long (Moisseeff 1966).

A small processing facility remains at Central Mine, and a small retort remains at Empire Mine (CalFed Report).

**The Manzanita Mine Group
(including the Cherry Hill, West End and Manzanita Mine Sites)**

11. The Manzanita mine is located about one mile west of Wilbur Springs resort. The Manzanita mine has been operated for both gold and mercury over its history. The Cherry Hill gold mine is located southwest of the Manzanita mine and on the south side of Sulphur Creek. The West End gold mine is located on the north side of Sulphur Creek west of the Manzanita mine (CalFed Report).
12. The Manzanita mine was discovered in 1863 and operated as a gold mine for many years (up to 1891). Cinnabar was recovered as a byproduct. From 1902 to 1942, it became primarily a mercury mine with intermittent operations by various companies and lessees, and yielded over 2,500 flasks of mercury. The mine may have been operated in conjunction with the Cherry Hill mine on the south side of Sulphur Creek in the 1920s. No records separating mercury and gold production are available prior to 1900 (CalFed Report).
13. The Manzanita mine consists of numerous tunnels and shafts, most of which are caved and inaccessible. Currently there is one open adit about 45 feet above the floodplain and there are several small open cuts, no more than 50 feet in depth between the adit and the top of the hill. Near the top of the hill is an open vertical shaft of unknown depth. Tailings appear to be exposed in the north stream bank of Sulphur Creek and there is a concrete foundation that may have been part of a crushing facility and stamp battery west of the adit (CalFed Report).
14. At the Manzanita mine, a ten-stamp mill was used to crush the ore, which was then concentrated in blanket sluices followed by two combination pans using sodium amalgam and bluestone amalgam. Three 5-foot Huntington mills, seven Victor concentrators, three 5-foot amalgamating pans, two 8-foot settlers, a No. 1 Gates crusher, and a 65 horse-power engine and boiler were reportedly operated for gold and mercury extraction (CalFed Report).
15. The Cherry Hill Mine workings consist of two short adits that have a maximum length of about 100 feet. The West End mine workings consist of three adits, the extent of which is unknown. The workings at the Cherry Hill Mine are open and accessible. The adits at the West End Mine are equipped with grates to prevent access by humans (CalFed Report).
16. Gold production records for the Cherry Hill Mine are incomplete. Gold production records are not available for West End Mine as this mine was likely operated in conjunction with Cherry Hill Mine. There is no evidence that either mine produced mercury (CalFed Report).
17. Ore processing facilities at the Cherry Hill mine consisted of a stamp mill with coarse gold recovery tables. There is no reported processing operation at the West End Mine. West End ore was reported to be very siliceous and similar in milling quality to Cherry Hill ore and it is inferred that processing of West End ore was done in the Cherry Hill stamp mill.

18. Currently, only various pieces of iron from the mill and concrete foundations remain at Cherry Hill Mine. The mill foundations may be of historical significance (CalFed Report).

Mining Waste Description and Characterization Central and Empire Group

19. Conspicuous waste rock piles with topographic relief are absent at the Central and Empire Mines. However, the slopes above and below the Central mine have a local hummocky appearance and are covered with thick grasses that may conceal small waste piles. In addition, the ground upon which the brick retort is located may contain up to 1,000 cubic yards (CY) of a mixture of tailings and waste rock. In addition, up to 1,000 CY of overburden or waste rock may be present below the cuts above the rotary furnace. Waste rock is also exposed in the slope below the retort at the Empire Mine but it is inconspicuous due to the vegetation. The total volume of this pile may be up to 5,600 CY (CalFed Report).

20. In 2002, Churchill and Clinkenbeard sampled solid materials at the Central and Empire mines. Mercury concentrations were measured at six locations at the Central Mine, and at two locations at the Empire Mine. Results showed mercury concentrations of 150 to 420 parts per million (ppm) in soil and waste materials near ore processing units, and 30 ppm in calcined tailings piles. Complete characterization of background soils and mining waste at the Central and Empire Mines has not been performed (CalFed Report).

21. Churchill and Clinkenbeard (2002) calculated that less than 3 kilograms (kg) of mercury remains in the small calcined tailings pile at the Central Mine, and 700 kg of mercury remains in two waste piles at the Empire Mine. The estimated mercury load from Central Mine is 0.003 to 0.03 kg/yr or 0.16 % of the total mine related mercury load of 4.4 to 18.6 kg/yr to Sulphur Creek. The estimated mercury load from Empire Mine is 0.04 to 0.06 kg/yr or 0.32 % of the total mine related mercury load of 4.4 to 18.6 kg/yr to Sulphur Creek (CalFed Report).

Mining Waste Description and Characterization Manzanita Mine Group (including the Cherry Hill and West End Mine Sites)

22. Waste rock piles at the Manzanita Mine are sparse and are limited to the lower portion of the hill below the area of argillic alteration. Tailings are not conspicuous at the surface near the mine but tailings appear to be exposed in the bank of Sulphur Creek above Jones Fountain of Life and may be buried in the flood plain along Sulphur Creek. The estimated mercury load from Manzanita Mine is 0.3 to 6.5 kg/yr or 34.9 % of the total mine related mercury load of 4.4 to 18.6 kg/yr to Sulphur Creek (CalFed Report).

23. Churchill and Clinkenbeard (2002) conducted solid materials sampling at the Manzanita Mine. Mercury concentrations were measured at 11 locations. Results showed mercury concentrations of 6 to 560 ppm in soil and waste materials near locations believed to be former ore processing units, and 25 to 260 ppm in background soils and sediments. Analysis of solid samples showed sediment in Sulphur Creek adjacent to Manzanita Mine had a

pH of 7, and mine site soils had a pH of approximately 4 to 5. Complete characterization of background soils and mining waste at the Manzanita Mine has not been performed (CalFed Report).

24. Mercury concentrations were measured at six locations at Cherry Hill Mine, and at three locations at West End mine. Results showed mercury concentrations of 47 to 300 ppm in waste piles, and less than 1 to 280 ppm in background soils and sediments. A study by Percy and Petersen (1990) found background mercury concentrations of up to 6,000 ppm. Complete characterization of background soils and mining waste at the Cherry Hill and West End mines has not been performed (CalFed Report).
25. Currently, there is no mine waste rock pile outside of the short adits at Cherry Hill. There is small waste rock pile (about 578 CY) on the Sulphur Creek floodplain about 500 feet northeast of the adits. This pile is of unknown origin. There is currently a waste rock pile at the West End Mine that may contain up to 3,600 CY of waste rock. Assays obtained during this study indicated gold concentrations of up to 0.30 ounces per ton (CalFed Report).
26. The estimated mercury load from Cherry Hill Mine is up to 1 kg/yr or 5.4 % of the total mine related mercury load of 4.4 to 18.6 kg/yr to Sulphur Creek. The estimated mercury load from West End Mine is 0.002 to 1.1 kg/yr or 5.9 % of the total mine related mercury load of 4.4 to 18.6 kg/yr to Sulphur Creek (CalFed Report).

Mercury and Sediment Loads to Sulphur Creek

27. Mine site investigations within the District have estimated mercury and sediment loads from the individual mine sites. Mercury is transported primarily through erosion of mercury-bearing mine wastes, soils, and sediments during storm runoff events. Though natural processes have enriched sediments with mercury, mining activities have increased sediment generation, resulting in increased potential for mercury mobilization from the mine sites (CalFed Report).
28. Annual mercury load estimates from the Mines range from 4.4 to 18.6 kg/yr. Annual sediment load estimates from the Mines range from 5,700 to 60,100 kg/yr (CalFed Report).
29. Aqueous mercury concentrations in Sulphur Creek are among the highest in the Cache Creek watershed, and remain elevated during non-peak flow periods. Active hydrothermal springs constantly discharge into Sulphur Creek, with mercury concentrations ranging from 700 to 61,000 nanograms per liter (ng/L) (CalFed Report).
30. Particulate bound mercury in Sulphur Creek comes mostly from sediments and mercury-bearing mine waste mobilized into the creek during storms. All the mines together are estimated to contribute about 78% of the total mercury load. The Central Mine sub watershed is estimated to contribute about 16 % of the total mercury load. Similar to total and dissolved concentrations, methyl mercury concentrations in Sulphur Creek are among the highest reported for the Cache Creek watershed. Methyl mercury concentrations were as

high as 20.64 ng/L in Sulphur Creek above the confluence with Bear Creek. (*Sulphur Creek TMDL for Mercury, Final Staff Report, January 2007.*¹).

31. Mercury is a toxic substance, which can cause damage to the brain, kidneys, and to a developing fetus. Young children are particularly sensitive to mercury exposure. Methylmercury, the organic form of mercury that has entered the biological food chain, is of particular concern, as it accumulates in fish tissue and in wildlife and people that eat the fish. Mine waste present at this Mine may also pose a threat to human health due to exposure (dermal, ingestion, and inhalation) through recreational activities (hiking, camping, fishing, and hunting) or work at the site.

Regulatory Considerations

32. Section 303(d) of the Federal Clean Water Act requires states to identify waters not attaining water quality standards (referred to as the 303(d) list). Since 1990, Sulphur Creek has been identified by the Central Valley Water Board as an impaired water body because of high aqueous concentrations of mercury.
33. The Basin Plan designates beneficial uses of the waters of the state, establishes Water Quality Objectives (WQOs) to protect these uses, and establishes implementation policies to achieve WQOs.
34. Studies were conducted that demonstrated that the municipal and domestic supply (MUN) beneficial use and the human consumption of aquatic organisms beneficial use did not exist and could not be attained in Sulphur Creek from Schoolhouse Canyon to the mouth, due to natural sources of dissolved solids and mercury. The Central Valley Water Board, in Resolution R5-2007-0021, adopted a basin plan amendment that de-designated these uses in Sulphur Creek from Schoolhouse Canyon to the mouth. The remaining beneficial uses for Sulphur Creek, a tributary of Cache Creek, are: agricultural supply; industrial service supply; industrial process supply; water contact recreation and non-contact water recreation; warm-freshwater habitat; cold fresh water habitat; spawning, reproduction, and/or early development; and wildlife habitat.
35. The beneficial uses of underlying groundwater, as stated in the Basin Plan, are municipal and domestic supply, agricultural supply, industrial service supply, and industrial process supply.
36. The Central Valley Water Board adopted site-specific water quality objectives for Sulphur Creek in Resolution R5-2007-0021. The WQOs now listed in the Basin Plan for Sulphur Creek state that waters shall be maintained free of mercury from anthropogenic sources such that beneficial uses are not adversely affected. During low flow conditions, defined as flows less than 3 cfs, the instantaneous maximum total mercury concentration shall not exceed 1,800 ng/L. During high flow conditions, defined as flows greater than 3 cfs, the instantaneous maximum ratio of mercury to total suspended solids shall not exceed 35

¹ The report is available at http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/sulphur_creek_hq/sulphur_creek_tmdl.pdf

mg/kg. Both objectives apply at the mouth of Sulphur Creek. Exceedances of the water quality objective in Sulphur Creek during high flow events are documented in Appendix C (page 24) of the *Staff Report for the Amendment to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins to Determine Certain Beneficial Uses are Not Applicable in and Establish Water Quality Objectives for Sulphur Creek*,² dated March 2007, which is part of the administrative record of this Order.

37. Sulphur Creek is tributary to Bear Creek, which is tributary to Cache Creek. Beneficial uses of Bear and Cache Creeks are municipal and domestic supply, agriculture – irrigation and stock watering, contact and non-contact recreation, industrial process and service supply, warm freshwater habitat, spawning – warm and cold, wildlife habitat, cold freshwater habitat, and commercial and sport fishing. Cache Creek is impaired for mercury and therefore has no assimilative capacity. Any discharges of mercury or mercury-laden sediments that reach Cache Creek therefore threaten to cause or contribute to a condition of pollution or nuisance. Cache Creek drains to the Cache Creek Settling Basin, which discharges to the Yolo Bypass and flows into the Sacramento-San Joaquin Delta Estuary. Data documenting exceedances of water quality objectives in Cache and Bear Creeks are found in Table 3.2 (page 9) of the October 2005 staff report entitled *Amendments to the Water Quality Control Plan for the Sacramento River and San Joaquin River Basins for the Control of Mercury in Cache Creek, Bear Creek, Sulfur Creek, and Harley Gulch*, which is part of the administrative record of this Order.³

38. The Cache Creek Watershed Mercury Program, included in the Basin Plan, requires responsible parties to develop plans to reduce existing loads of mercury from mining or other anthropogenic activities by 95% in the Cache Creek watershed (i.e., Cache Creek and its tributaries). The Basin Plan, Chapter IV, page 33.05 states that,

Responsible parties shall develop and submit for Executive Officer approval plans, including a time schedule, to reduce loads of mercury from mining or other anthropogenic activities by 95% of existing loads consistent with State Water Resources Control Board Resolution 92-49. The goal of the cleanup is to restore the mines to premining conditions with respect to the discharge of mercury. Mercury and methylmercury loads produced by interaction of thermal springs with mine wastes from the Turkey Run and Elgin mines are considered to be anthropogenic loading. The responsible parties shall be deemed in compliance with this requirement if cleanup actions and maintenance activities are conducted in accordance with the approved plans. Cleanup actions at the mines shall be completed by 2011.

39. The Basin Plan, Chapter IV, page 33.05 states that,

The Sulphur Creek streambed and flood plain directly below the Central, Cherry Hill, Empire, Manzanita, West End and Wide Awake Mines contain mine waste. After mine cleanup has been

² This report is available at
http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/sulphur_creek_hq/sulphur_creek_staff_final.pdf

³ This report is available at
http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/central_valley_projects/cache_sulphur_creek/cache_crk_hq_final_rpt_oct2005.pdf

initiated, the Dischargers shall develop and submit for Executive Officer approval a cleanup and abatement plan to reduce anthropogenic mercury loading in the creek.

40. Under CWC section 13050, subdivision (q)(1), "mining waste" means all solid, semisolid, and liquid waste materials from the extraction, beneficiation, and processing of ores and minerals. Mining waste includes, but is not limited to, soil, waste rock, and overburden, as defined in Public Resources Code section 2732, and tailings, slag, and other processed waste materials...." The constituents listed in Findings No. 19, 22, and 25 are mining wastes as defined in CWC section 13050, subdivision (q) (1).
41. Because the Mines contain mining waste as described in CWC sections 13050, closure of Mining Unit(s) must comply with the requirements of California Code of Regulations, title 27, sections 22470 through 22510 and with such provisions of the other portions of California Code of Regulations, title 27 that are specifically referenced in that article.
42. Under CWC section 13050, subdivision (m) a condition that occurs as a result of disposal of wastes, is injurious to health, or is indecent or offensive to the senses, or is an obstruction to the free use of property, and affects at the same time any considerable number of persons, is a nuisance.
43. Affecting the beneficial uses of waters of the state by exceeding applicable WQOs constitutes a condition of pollution as defined in CWC section 13050, subdivision (l). Mine waste has been discharged or deposited where it has discharged or threatens to discharge to waters of the state and has created, and continues to threaten to create, a condition of pollution or nuisance.
44. CWC section 13304(a) states that:

Any person who has discharged or discharges waste into the waters of this state in violation of any waste discharge requirement or other order or prohibition issued by a Regional Water Board or the state board, or who has caused or permitted, causes or permits, or threatens to cause or permit any waste to be discharged or deposited where it is, or probably will be, discharged into the waters of the state and creates, or threatens to create, a condition of pollution or nuisance, shall upon order of the Regional Water Board, clean up the waste or abate the effects of the waste, or, in the case of threatened pollution or nuisance, take other necessary remedial action, including, but not limited to, overseeing cleanup and abatement efforts. A cleanup and abatement order issued by the state board or a Regional Water Board may require the provision of, or payment for, uninterrupted replacement water service, which may include wellhead treatment, to each affected public water supplier or private well owner. Upon failure of any person to comply with the cleanup or abatement order, the Attorney General, at the request of the board, shall petition the superior court for that county for the issuance of an injunction requiring the person to comply with the order. In the suit, the court shall have jurisdiction to grant a prohibitory or mandatory injunction, either preliminary or permanent, as the facts may warrant.
45. The State Water Resources Control Board (State Board) has adopted Resolution No. 92-49, the *Policies and Procedures for Investigation and Cleanup and Abatement of Discharges Under CWC Section 13304*. This Resolution sets forth the policies and procedures to be used during an investigation or cleanup of a polluted site and requires that cleanup levels be consistent with State Board Resolution No. 68-16, the *Statement of Policy With Respect to*

Maintaining High Quality of Waters in California, Resolution No. 92-49 and the Basin Plan establish cleanup levels to be achieved. Resolution No. 92-49 requires waste to be cleaned up to background, or if that is not reasonable, to an alternative level that is the most stringent level that is economically and technologically feasible in accordance with California Code of Regulations, title 23, section 2550.4. Any alternative cleanup level to background must: (1) be consistent with the maximum benefit to the people of the state; (2) not unreasonably affect present and anticipated beneficial use of such water; and (3) not result in water quality less than that prescribed in the Basin Plan and applicable Water Quality Control Plans and Policies of the State Board.

46. Chapter IV of the Basin Plan contains the *Policy for Investigation and Cleanup of Contaminated Sites*, which describes the Central Valley Water Board's policy for managing contaminated sites. This policy is based on CWC sections 13000 and 13304, California Code of Regulations, title 23, division 3, chapter 15; California Code of Regulations, title 23, division 2, subdivision 1; and State Water Board Resolution Nos. 68-16 and 92-49. The policy addresses site investigation, source removal or containment, information required to be submitted for consideration in establishing cleanup levels, and the basis for establishment of soil and groundwater cleanup levels.

47. The State Board's *Water Quality Enforcement Policy* states in part:

At a minimum, cleanup levels must be sufficiently stringent to fully support beneficial uses, unless the Central Valley Water Board allows a containment zone. In the interim, and if restoration of background water quality cannot be achieved, the Order should require the discharger(s) to abate the effects of the discharge (Water Quality Enforcement Policy, p. 19).

48. CWC section 13267 states that:

- (a) A regional board, in establishing or reviewing any water quality control plan or waste discharge requirements, or in connection with any action relating to any plan or requirement authorized by this division, may investigate the quality of any waters of the state within its region.
- (b) (1) In conducting an investigation specified in subdivision (a), the regional board may require that any person who has discharged, discharges, or is suspected of having discharged or discharging, or who proposes to discharge waste within its region, or any citizen or domiciliary, or political agency or entity of this state who has discharged, discharges, or is suspected of having discharged or discharging, or who proposes to discharge, waste outside of its region that could affect the quality of waters within its region shall furnish, under penalty of perjury, technical or monitoring program reports which the regional board requires. The burden, including costs, of these reports shall bear a reasonable relationship to the need for the report and the benefits to be obtained from the reports. In requiring those reports, the regional board shall provide the person with a written explanation with regard to the need for the reports, and shall identify the evidence that supports requiring that person to provide the reports.

49. The technical reports required by this Order are necessary to ensure the protection of the waters of the state, ensure the protection of the waters of the state, comply with the Basin Plan's requirement for responsible parties to develop plans to reduce existing loads of mercury from mining or other anthropogenic activities by 95% in the Cache Creek watershed

(Basin Plan, Chapter IV, page 33.05, see Finding 37), to further characterize the location of mining wastes, to complete a conceptual site model for the eventual cleanup of the mining sites and determine what cleanup measures are necessary, and to provide additional information about suspected past or future discharges. The Dischargers either own or have owned, leased, or operated the mining sites subject to this Order. Additional findings establishing the liability of each Discharger pursuant to CWC section 13267 are set forth below. While no specific cost for the required reports has been estimated, the need for cleanup is well established. (See, e.g., the Basin Plan's Cache Creek Watershed Mercury Program.) The technical or monitoring report is necessary to accomplish the cleanup. (See, State Water Board Resolution 92-49.) The investigation is as limited as possible, and is consistent with orders requiring investigation or cleanup at other sites.

50. The issuance of this Order is an enforcement action taken by a regulatory agency and is exempt from the provisions of the California Environmental Quality Act (CEQA) (Pub. Resources Code, section 21000 et seq.), pursuant to California Code of Regulations, title 14, section 15321(a) (2). The implementation of this Order is also an action to assure the restoration of natural resources and/or the environment and is exempt from the provisions of the CEQA, in accordance with California Code of Regulations, title 14 sections 15307 and 15308. The implementation of this Order also constitutes basic data collection, research and/or resource evaluation activities which do not result in a serious or major disturbance to an environmental resource, and is exempt from the provisions of the CEQA, in accordance with California Code of Regulations, title 14 sections 15306.

Dischargers' Liability

51. CWC section 13267 imposes investigation and reporting liability on "any person who has discharged, discharges, or is suspected of having discharged or discharging, or who proposes to discharge waste ..." Owners of mine property are dischargers with respect to mining waste that erodes, runs off or otherwise discharges from the property. (Opinion 55-116, 26 Ops. Cal. Atty. Gen. 88 (1955); see also, Order WQ 90-3 (*San Diego Unified Port District*)). "Evidence" for purposes of CWC section 13267 "means any relevant evidence on which responsible persons are accustomed to rely in the conduct of serious affairs, regardless of the existence of any common law or statutory rule which might make improper the admission of the evidence over objection in a civil action" (CWC § 13267, subd. (e).) There is adequate evidence in the record to support at least a suspicion that each Discharger discharged waste.
52. As established under the findings regarding *Mercury and Sediment Loads to Sulphur Creek*, above, mercury is mobilized by storm water runoff, slope failure, or water-rock interaction from mine waste. In addition, disturbed sediments can migrate across the property and be deposited where they are later discharged to waters of the state. Each of the Dischargers owned the property in question for at least twelve months. The Board takes official notice that there are no years on record during the relevant period of time when it did not rain at all.
53. The Board considered whether interim landowners and lessees should be held liable for passive discharges to surface waters even though the specific discharges during the time of interim ownership may have in the intervening years left the Sulphur Creek/Cash Creek

watersheds. The Board finds that such interim landowners are liable under this Order. As a preliminary matter, the migration of pollutants from soil in one area of the property to soil in another area, from where it may later be discharged into the surface waters, is a discharge for which an interim owner may be liable. Additionally, in accordance with *City of Modesto Redevelopment Agency v. Superior Court* (2004) 119 Cal.App.4th 28, the Board may look to the law of nuisance to interpret liability in the context of a section 13304 clean-up order. California Civil Code section 3483, which codified the common law duty of successive owners to abate a continuing nuisance, states that every successive owner of property who neglects to abate a continuing nuisance created by a former owner, is liable in the same manner as the one who first created it. In accordance with this principle, interim owners could have been named in a section 13304 order and it is even more appropriate to name them in this section 13267 Order where the Board need only establish that the interim owners are "suspected" of discharging waste.

54. AMERICAN LAND CONSERVANCY (ALC) is not named in this Order. There are two potentially applicable bases of ALC's liability: (i) ALC's Grant of Easement for Conservation Purposes, 10/27/99 ("Easement") in APNs 018-200-005-000, 018-200-007-000, 018-200-013-000, 018-200-014-000, 018-200-015-000, 018-200-016-000, 018-200-017-000, 018-200-018-000 and 018-200-006-000; and (ii) ALC's fee interest in APNs 018-200-005-000 and 018-200-007-000 from June 25, 1999 to October 26, 1999. The Prosecution Team presented no evidence that any activities under the Easement caused or permitted a discharge of mining waste and testified that the Easement was not a basis for liability. With respect to ALC's fee interest, the Board declines to exercise its discretion to require ALC to undertake investigation based on ALC's brief fee interest. The Prosecution Team presented no evidence of rain events during ALC's period of ownership, and presented no other evidence that ALC caused or permitted a discharge during its ownership. In addition, the *Water Quality Enforcement Policy* (2002) requires that regional water boards *should* (not *shall*) "name all dischargers for whom there is sufficient evidence of responsibility as set forth in California Water Code section 13304." The Enforcement Policy includes no similar policy statement for section 13267 orders.

The State Water Board has determined that it is inappropriate to require certain dischargers to participate in a cleanup, even though the dischargers have some legal responsibility for cleanup. (See, State Water Board Order WQ 92-13 (*Wenwest*). Although *Wenwest* was a cleanup order and not a site investigation order, the same reasoning applies to this Order. A consideration of the *Wenwest* factors weighs against requiring ALC to participate in investigation or cleanup of this site. ALC purchased the property solely for the purposes of conveying it to Dr. Miller; the ownership period was brief (four months); Dr. Miller is named in the Order; ALC had nothing to do with the activity that caused the condition of pollution; ALC never engaged in any activity that exacerbated the problem; ALC had incomplete knowledge of the pollution; and numerous other dischargers are named in this Order. Although no cleanup is proceeding, there are other parties named in this Order who are now required to begin site investigation. The Board makes no finding about whether ALC should have known about mercury pollution, or whether mercury pollution was just beginning to become known when ALC acquired the property, but finds that these factors are less significant because ALC acquired the property solely to facilitate the conservation easement and immediate property transfer. In addition to the *Wenwest* factors, in determining not to name

ALC, the Board considered that ALC acquired the property solely to facilitate its acquisition of the conservation easement; holding ALC liable may prevent or discourage ALC's or other entities' future conservation efforts; and ALC's period of ownership was during the summer and early fall, and not during the wet season. The Board will therefore exercise its discretion not to name ALC in this Order.

55. RICHARD L. MILLER is the current owner of all parcels subject to this Order. He purchased various parcels in 1974, 1999 and 2003. He is therefore responsible for investigating and cleaning up waste that is discharging from the property, or that has been or may be deposited where it will discharge from the property. Dr. Miller asserted that he is not responsible because he granted the Easement to ALC. However, Dr. Miller explicitly reserved the obligation to comply with environmental laws (Easement, paragraph 3) and all rights of ownership not prohibited by the Easement (Easement, paragraph 4). The reserved rights of ownership include soil stabilization and erosion control. (Easement, Attachment C, paragraph 4.) Dr. Miller also agreed to comply with laws (Easement, paragraph 9), agreed that ALC would not become an owner or operator (Easement, paragraph 13(b)), and warranted compliance with environmental laws (*ibid*). Although ALC has the right to conduct certain erosion control activities at its sole discretion (Easement, paragraph 2), ALC has no obligation to do so.

Dr. Miller also contended that Regional Water Board staff advised him before he purchased the property that he would not be held liable. This assertion is contradicted by the evidence, including a the Phase I Preliminary Evaluation and Site Assessment (Erler & Kalinowski, 9/18/97) which states that the Central Valley Water Board might require formal closure (i.e., remediation) of the site; mine waste from inactive mines along Sulphur Creek might be a potential source of mercury in Cache Creek; testing was incomplete; and Sulphur Creek flows through the site.

Finally, Dr. Miller contended that holding him responsible for discharges from the site would deter other landowners from granting conservation easements. In light of Dr. Miller's long ownership of and ability to control the property, and the speculative nature of this contention, it is questionable whether the Board has discretion to relieve Dr. Miller of responsibility to investigate or clean up the site on this basis. Even if such discretion is available, the Board finds that it is appropriate to name Dr. Miller named as a discharger for the reasons stated in this paragraph.

56. [This paragraph intentionally left blank.]

57. HOMESTAKE MINING COMPANY owned or leased APNs 018-200-013-000, 018-200-014-000, 018-200-015-000, 018-200-016-000, 018-200-017-000, 018-200-018-000 and 018-200-006-000 from January 6, 1978 until 1999. There is no evidence that Homestake actively mined the site. Homestake provided evidence that its activity on the site was limited to mining exploration activity, including drilling. These activities might have caused discharges due to soil disturbance from equipment moving or drill cuttings. The Board need not determine whether these activities caused discharges, because Homestake's ownership and control over the property is a sufficient basis to require additional investigation. The lease provided that Homestake had exclusive possession of the property for mining purposes and

the lease's scope included control of tailings and waste piles on the mining property. Homestake asserted that its activities did not significantly cause or contribute to the discharge of mining wastes. Under the terms of its lease, Homestake exercised control over the property and had the ability to prevent mine materials and enriched mercury soil from entering waterways or migrating across the sites. Homestake, by holding a leasehold interest giving it control over the property during a time when mining waste was present, assumed responsibility for managing the discharges from the waste. In addition, Homestake owned the property for over ten years. As these wastes were eroding or are suspected of eroding into surface waters during the time that Homestake controlled the property, Homestake is a person who has discharged, discharges, or is suspected of having discharged or discharging wastes into waters of the state.

Homestake asserted that other sources, including naturally occurring conditions, contribute to mercury contamination, and that waste rock located farther from streams discharges only during very heavy rain events. Neither claim is sufficient to overcome the considerable evidence supporting Homestake's status as a discharger or suspected discharger.

Homestake asserted that its liability is divisible and that joint and several liabilities are not appropriate. All dischargers are jointly and severally liable for the discharge of waste. (State Board Order WQ 90-2 [*Union Oil Company*]). At this stage, the Board has not determined the relative mercury contributions of various sources or the relative contributions of various dischargers at any given site. Even were the Board inclined to apportion responsibility, which it is not, apportionment would be premature at this time.

58. TERHEL FARMS, INC., BONNEVILLE INDUSTRIES, INC., FILIATRA, INC. and ASERA WESTERN CORPORATION owned fee interest in owned APNs 018-200-005-000 and 018-200-007-000 between March 6, 1959 and an unknown date, as described below. Part of West End Mine was located on parcel APN 018-200-005-000. Mine waste and a portion of Sulphur Creek are located on parcel APN 018-200-007-000.
59. TERHEL FARMS, INC. owned APNs 018-200-005-000 and 018-200-007-000 from March 6, 1959 until March 3, 1986. Terhel Farms asserted that no mining was conducted during ownership. However, liability is based on the discharge or suspected discharge of mining waste to Sulphur Creek, which continued after active mining ceases. In addition, Terhel Farms, Inc. contended that it sold the entire "hill range" to Bonneville Industries in 1983. This contention is inconsistent with title records showing acquisition and sale on the above dates.
60. BONNEVILLE INDUSTRIES, INC. owned APNs 018-200-005-000 and 018-200-007-000 from March 3, 1986 until some time in 1999. Bonneville Industries asserted no defenses to the proposed Cleanup and Abatement Order presented to the Board on 7 October 2009.
61. FILIATRA, INC. owned APNs 018-200-005-000 and 018-200-007-000 from October 9, 1990 until June 30, 1992; after that, it appears Filiatra retained "all mineral rights, hydrocarbon rights, gravel rights, geothermal rights, water rights, all grazing rights, pasturing rights, hunting rights, and fishing rights" but transferred fee ownership. During the time Filiatra held fee title, mining waste was present on this property; discharged from the property to waters

of the State during rain events; and migrated to other locations from which it may have discharged to waters of the State. Filiatra asserted no defenses to the proposed Cleanup and Abatement Order presented to the Board on 7 October 2009.

62. ASERA WESTERN CORPORATION owned APNs 018-200-005-000 and 018-200-007-000 from June 30, 1992 until an unknown date. Asera Western asserted no defenses to the proposed Cleanup and Abatement Order presented to the Board on 7 October 2009.

63. HELEN HOLLIDAY FOUNDATION, INC. (Holliday Foundation) owned fee title to APN 018-200-004-000 from December 22, 1975 to March 25, 2003. During the time Holliday Foundation-owned fee title, mining waste was present on this property; discharged from the property to waters of the State during rain events; and migrated to other locations from which it may have discharged to waters of the State. Holliday Foundation denied liability based on its status as a charitable foundation. However, this does not provide a legal basis to avoid liability. In addition, Holliday Foundation owned the property for over 27 years.

Holliday Foundation contended that it should be secondarily liable for any cleanup requirements. In the context of clean-up orders (CWC section 13304), the Central Valley Water Board may find certain dischargers to be only secondarily liable for clean-up. (See State Board Order WQ 87-6 [*Prudential Ins. Co.*] and State Board Order WQ 86-18 [*Vallco Park, Ltd.*]). Even if the secondary liability concept can be applied in the section 13267 context, it is not appropriate here. The Central Valley Water Board considered whether any named Dischargers should be secondarily liable and has concluded that all Dischargers should be primarily liable. Here, the investigation and cleanup is not proceeding and the parties that actively engaged in the mining operations at the root of the ongoing discharge are no longer in existence. Accordingly, all named Dischargers to the Order stand on essentially the same footing and should be treated alike. (State Board Order WQ 93-9 [*Aluminum Company of America et al.*].)

64. The Executive Officer may add additional responsible parties to this Order without bringing the matter to the Central Valley Water Board for a hearing, if the Executive Officer determines that additional parties are liable for investigation of the mine waste. The Executive Officer may remove Dischargers from this Order if the Executive Officer receives new evidence demonstrating that such Dischargers did not cause or permit the discharge of waste that could affect water quality. All Dischargers named in this Order and any responsible parties proposed to be added shall receive notice of, and shall have the opportunity to comment on, the addition or removal of responsible parties.

IT IS HEREBY ORDERED that, the Dischargers, and their agents, assigns and successors, in order to meet the provisions contained in Division 7 of the California Water Code and regulations, plans and policies adopted thereunder, shall:

1. Conduct all work in conformance with the Regional Board's Water Quality Control Plan for the Sacramento River and San Joaquin River Basins (in particular the Policies and Plans listed within the Control Action Considerations portion of Chapter IV).

Waste Characterization

2. By **26 July 2010**, submit a *Mining Waste Characterization Work Plan* (hereafter *Characterization Plan*) for the mine sites. The Characterization Plan shall assess the nature and extent of mining waste at the site, the nature and extent of mining waste that is discharging or that has the potential to discharge from the site to Sulphur Creek, and the potential threat to water quality and/or human health. The Characterization Plan shall describe the methods that will be used to establish background levels for soil, surface water, and ground water at the site, and the means and methods for determining the vertical and lateral extent of the mining waste.

The Characterization Plan shall also address slope stability of the site and assess the need for slope design and slope stability measures to minimize the transport of mining waste-laden soils to surface water and ephemeral streams. The Characterization Plan shall adopt the time schedule as described below in items 3 through 13 below for implementation of the proposed work.

3. Within **30 days** of staff concurrence with the Characterization Plan, but no later than **27 September 2010**, begin implementing the Characterization Plan in accordance with the approved time schedule, which shall become part of this Order.
4. By **27 January 2011**, submit a *Mining Waste Characterization Report* (hereafter *Characterization Report*) for the Mine. The Characterization Report shall include:
 - a. A narrative summary of the field investigation;
 - b. A section describing background soil concentrations, mining waste concentrations, and the vertical and lateral extent of the mining waste;
 - c. Surface water and ground water sampling results;
 - d. A section describing slope stability and erosion potential and recommendations for slope stabilization;
 - e. An evaluation of risks to human health from site conditions, and;
 - f. A work plan for additional investigation, if needed, as determined by staff. If no additional investigation is needed, this report shall be the Final Characterization Report.
5. By **27 January 2011**, submit a *Surface and Ground Water Monitoring Plan* (hereafter *Monitoring Plan*) for the Mine. The Monitoring Plan shall describe the methods and rationale that will be used to establish background levels for surface water and ground water at the site. The Monitoring Plan shall also address long-term monitoring necessary to confirm the effectiveness of the remedies.

Water Supply Well Survey

6. By **27 September 2010**, submit the results of a water supply well survey within one-half mile of the site and a sampling plan to sample any water supply well(s) threatened to be polluted by mining waste originating from the site. The sampling plan shall include specific actions

and a commitment by the Dischargers to implement the sampling plans, including obtaining any necessary access agreements. If the Dischargers demonstrate that exceedances of water quality objectives in the water supply well survey discussed above are the result of naturally occurring hydrothermal sources, then the Dischargers may request a waiver of requirements No. 7 and 8 listed below.

7. Within 30 days of staff concurrence with the water supply well sampling plan, the Dischargers shall implement the sampling plan and submit the sampling results in accordance with the approved time schedule, which shall become part of this Order.
8. Within 30 days of staff notifying the Dischargers that an alternate water supply is necessary, submit a work plan and schedule to provide an in-kind replacement for any impacted water supply well. The Dischargers shall implement the work plan in accordance with an approved time schedule, which shall become part of this Order.

General Requirements

The Dischargers shall:

9. Pursuant to CWC section 13365, reimburse the Central Valley Water Board for reasonable costs associated with oversight of the investigation of the site. Within 30 days of the effective date of this Order, the Dischargers shall provide the name and address where the invoices shall be sent. Failure to provide a name and address for invoices and/or failure to reimburse the Central Valley Water Board's oversight costs in a timely manner shall be considered a violation of this Order. If the Central Valley Water Board adopts Waste Discharge Requirements (WDRs), review of reports related to writing of the WDRs and all compliance measures thereafter would be subject to the fees required by issuance of the Order and the reimbursement under this requirement would no longer apply.
10. Submit all reports with a cover letter signed by the Dischargers. In the cover letter, the Dischargers shall express their concurrence or non-concurrence with the contents of all reports and work plans.
11. Notify staff at least three working days prior to any onsite work, testing, or sampling that pertains to environmental investigation and is not routine monitoring, maintenance, or inspection.
12. Obtain all local and state permits and access agreements necessary to fulfill the requirements of this Order prior to beginning work.
13. Continue any investigation, reporting or monitoring activities until such time as the Executive Officer determines that sufficient work has been accomplished to comply with this Order. The Executive Officer, with concurrence from the Prosecution Team, and after soliciting comments from the remaining named parties, may determine that a party named to this Order has satisfied or will satisfy their obligations under this Order by performing or agreeing to perform substantial work that results in a more complete understanding of the scope of the problems present at the Site, consistent with the obligations imposed by this 13267 Order. After such a determination has been made, the Prosecution Team will be

directed to compel the remaining named parties to fulfill the remaining obligations under this Order.

Investigation of Additional Responsible Parties

14. Dr. Miller testified at the hearing that Sunoco Energy Development Company conducted activities at the site that did or could have caused soil disturbance leading to off-site migration of mercury-laden sediments. However, the Prosecution Team declined to name this entity in the proposed order.
15. The Prosecution Team shall complete its investigation of other entities that are or may be responsible for investigation or cleanup of the Mine. This investigation shall include, without limitation, the Bureau of Land Management and Sunoco Energy Development Company. The Prosecution Team may issue subpoenas, or may request the Executive Officer to issue orders under section 13267, as appropriate. This directive is without prejudice to any rights of any person to contest such subpoena(s) or order(s). Any person may provide evidence relevant to liability (or lack thereof), whether or not that person is the subject of a subpoena or section 13267 order. The Prosecution Team shall report the results of its investigation to the Executive Officer, with a copy to all parties and interested persons, by 30 November 2010. The Executive Officer may extend this deadline.

Any person signing a document submitted under this Order must make the following certification:

"I certify under penalty of law that I have personally examined and am familiar with the information submitted in this document and all attachments and that, based on my knowledge and on my inquiry of those individuals immediately responsible for obtaining the information, I believe that the information is true, accurate, and complete. I am aware that there are significant penalties for submitting false information, including the possibility of fine and imprisonment."

In accordance with California Business and Professions Code sections 6735, 7835, and 7835.1, engineering and geologic evaluations and judgments must be performed by or under the direction of registered professionals competent and proficient in the fields pertinent to the required activities. All technical reports specified herein that contain work plans for, that describe the conduct of investigations and studies, or that contain technical conclusions and recommendations concerning engineering and geology must be prepared by or under the direction of appropriately qualified professional(s), even if not explicitly stated. Each technical report submitted by the Dischargers must contain the professional's signature and, where necessary, his stamp or seal.

The Executive Officer may extend the deadlines contained in this Order if the Dischargers demonstrate that unforeseeable contingencies have created delays, provided that the Dischargers continue to undertake all appropriate measures to meet the deadlines and make the extension request in advance of the expiration of the deadline. The Dischargers shall make any deadline extension request in writing prior to the compliance date. An extension may be

denied in writing or granted by revision of this Order or by a letter from the Executive Officer. Any request for an extension not responded to in writing by the Board shall be deemed denied.

If, in the opinion of the Executive Officer, the Dischargers fail to comply with the provisions of this Order, the Executive Officer may issue a complaint for administrative civil liability. Failure to comply with this Order may result in the assessment of an Administrative Civil Liability of up to \$1,000 per violation per day pursuant to the California Water Code section 13268. The Central Valley Water Board reserves its right to take any enforcement actions authorized by law.

Any person aggrieved by this action of the Central Valley Water Board may petition the State Water Board to review the action in accordance with CWC section 13320 and California Code of Regulations, title 23, sections 2050 and following. The State Water Board must receive the petition by 5:00 p.m., 30 days after the date of this Order, except that if the thirtieth day following the date of this Order falls on a Saturday, Sunday, or state holiday, the petition must be received by the State Water Board by 5:00 p.m. on the next business day. Copies of the law and regulations applicable to filing petitions may be found on the Internet at:

http://www.waterboards.ca.gov/public_notices/petitions/water_quality

or will be provided upon request.

I, Pamela Creedon, do hereby certify that the foregoing is a full, true, and correct copy of an Order issued by the Central Valley Water Board on 27 May 2010.



PAMELA C. CREEDON, Executive Officer

EXHIBIT B

CalFed – Cache Creek Study (Task 5A: Final Report) January 2000-July 2002, Mercury Loading and Source Bioavailability from Upper Cache Creek Mining Districts

**CALFED – CACHE CREEK STUDY
(TASK 5A: FINAL REPORT)
January 2000 to July 2002**

**MERCURY LOADING AND SOURCE BIOAVAILABILITY
FROM THE UPPER CACHE CREEK MINING DISTRICTS**

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ABSTRACT

Mercury (Hg) loading from upstream mining and geothermal spring sites in the Upper Cache Creek region may contribute significantly to Hg bioaccumulation in the San Francisco Bay-Delta Complex. The goal of this study was to evaluate Hg concentrations in upstream waters and estimate potential loading from both anthropogenic mining related sites and natural geothermal springs in the Upper Cache Creek region. Potential methyl Hg production from sediments or in-stream flocculent precipitates was also evaluated in a series of laboratory based slurry and microcosm experiments.

In order to estimate maximum potential Hg loading, water from streams and geothermal springs was collected during February (the winter rainy season) in both 2000 and 2001 from two regions: (1) the Harley Gulch Mining Region, and (2) the Sulphur Creek Mining Region. Total Hg and methyl Hg was analyzed from RAW (unfiltered) and FILTERED (0.45 µm pore size) water samples. Stream flow was typically two times higher in Sulphur Creek compared with Harley Gulch and was 5-10 fold lower on the sampling dates in 2001 than in 2000. Total Hg in RAW water ranged from 4-39,700 ng/L (parts per trillion), with the lowest concentrations obtained in the geothermal spring in the Harley Gulch region, and the highest concentrations obtained in the geothermal spring in the Sulphur Creek region. Stream waters that passed through or nearby abandoned mine sites typically ranged from ca. 1,000 – 6,800 ng/L total Hg in RAW water, whereas total Hg in FILTERED water ranged from ca. 100 – 2,000 ng/L from those same sites, with the dissolved fraction of the Hg comprising ca. 5-30% in the year 2000 and ca. 30-70% in 2001. Methyl Hg in RAW water (which was analyzed for only a subset of samples) ranged from 0.15-20.40 ng/L, with the highest values again obtained from the geothermal spring in the Sulphur Creek region. Methyl Hg in FILTERED water ranged from 0.12-14.40 ng/L with comparably high values at the geothermal spring in the Sulphur Creek region.

Hg loading (daily, monthly, annually) was calculated using the aqueous Hg concentrations (above) multiplied times stream flow rates for specific regions and sites within regions. Local stream flow rates from specific mining sites were obtained by hand, whereas regional flow rates were obtained from automated USGS gauging stations. Based on stream data collected in February 2000, Harley Gulch

produced projected total Hg loading estimates of up to ca. 0.02 kg/d, whereas estimated loading from 2001 data yielded only ca. 0.0013 kg/d. Using the USGS flow rates from the gauged stations, monthly and annual estimates of Hg loading from Harley Gulch yielded maximum values of ca. 0.65 kg/month and 1.2 kg/yr using 2000 data. Hg loading projected from Sulphur Creek sites using year 2000 data yielded a maximum monthly value of ca. 5 kg/month and a maximum annual value of ca. 10 kg/yr. Comparable data from year 2001 yielded maximum loading estimates of 0.1 kg/day, 9.5 kg/month and 16 kg/yr. Thus, estimates of Hg loading from the Sulphur Creek region were about 10 times greater than those from the Harley Gulch region. In the long-term context of watershed Hg loading influenced by erosion from rainfall events, the stream flow rates during the two years in this study were only 55% of the long-term average. Thus, during much heavier rainfall we might predict that more Hg-laden erodable materials would be mobilized and transported downstream. However, within the flow rates observed during this study, no statistically significant relationships were documented between flow rates and total Hg or methyl Hg in RAW water or FILTERED water. Thus, we do not have estimates of how those more extreme events would affect long-term Hg loading and cannot use other years' flow data to predict loading in higher precipitation years which would produce higher flow rates.

A 5-day laboratory microcosm experiment (used previously at Clear Lake), designed to test the potential of a flocculent precipitate found within Sulphur Creek to produce methyl Hg, yielded virtually no net production of methyl Hg.

Because mine-derived Hg-contaminated soils/sediments could become mobilized and transported downstream, ultimately contaminating distant stream and estuary sites, a series of laboratory-based methylation trials (using slurries) were designed to evaluate the potential of upstream SOURCE materials (e.g. mine-derived soils/sediments) to produce methyl Hg in downstream RECEIVING sediments. A preliminary trial conducted in November 2000 at U.C. Davis yielded encouraging results, suggesting potentially significant differences in methyl Hg production from different source materials such as mercuric chloride, Abbott Mine tailings and Sulphur Creek floc. These preliminary results provided the foundation for the development of a more in depth trial involving several mine-derived and geothermal spring related floc SOURCE materials and downstream sediments from Cache Creek. These laboratory trials were conducted at Frontier Geosciences laboratory in Seattle. Results of these trials can be found in N. Bloom's report.

INTRODUCTION:

Elevated mercury (Hg) in fishes has become a significant concern in many regions of the United States Wiener *et al.* (in press). Most of the studies to date have focused on the atmospheric deposition of Hg as the primary causative factor. In the western states, however, mining for Hg, gold and silver has resulted in the release of Hg, sulfate and acid mine drainage, factors which are known to promote Hg methylation. California, for instance, has 13 water bodies for which human health consumption advisories have been issued because of elevated Hg levels in fish tissues (Alpers and Hunerlach 2000). The San Francisco Bay Delta (Delta) and the upstream water sources of Clear Lake (within the Cache Creek Watershed) and Lake Berryessa (within the Putah Creek Watershed) are of particular concern. In addition, all three are listed on the state of California's 303d list of Impaired Water Bodies because of elevated Hg concentrations, and there are ongoing efforts to lower Hg in fish tissues by reducing Hg loading to these water bodies through the Total Daily Maximum Load (TMDL) process implemented by the U.S. Environmental Protection Agency (USEPA).

Hg loading to the Delta is driven by atmospheric deposition and upstream water-borne sources and processes. These sources are both natural (e.g. geothermal springs and soils naturally enriched in Hg) and anthropogenic (e.g. abandoned mines). We have focused our efforts on the contribution of the Cache Creek watershed to Hg loading in the Delta.

Our goal in this project was (1) to identify potential Hg minerals and precipitate-associations from upstream mining regions within the Cache Creek watershed that have the potential to be methylated, (2) to evaluate Hg loading from specific anthropogenic (mine-related) and natural (geothermal spring) sources and (3) with these data, work with the team from Task 5C to identify and evaluate sites that have the potential for effective remediation of Hg source materials. We have not attempted to quantify or estimate atmospheric Hg deposition from upstream watersheds that feed into Cache Creek.

Specifically, we have attempted to:

- Quantify Hg loading, in both particulate and dissolved form, from specific/selected anthropogenic (abandoned mine sites) and natural (geothermal springs) sites that have a significant potential to contribute to Hg loading in downstream Cache Creek.
- At selected mining-related and natural inorganic Hg "hotspots" in the watershed above Cache Creek, evaluate inorganic Hg source materials as potential substrates for the production of on-site methyl Hg, which could be transported downstream to the Sacramento-San Joaquin Delta. This objective has been accomplished via laboratory experiments.

Our hypotheses are:

- Abandoned mining (primarily mercury and/or gold) sites contribute significant inorganic and/or methyl Hg loading to Cache Creek, which transports this loading downstream to the Bay-Delta.

- Natural geothermal springs contribute significant inorganic Hg loading to Cache Creek, which transports this loading downstream to the Bay-Delta.
- Physical, chemical and/or biological processes present at mining sites and/or natural geothermal spring sites methylate Hg locally and transport this bioavailable Hg downstream into Cache Creek.

METHODS:

Collaborations/Integration:

Task 5A has been conducted in close coordination with:

- (1) R. Churchill *et al.* (CA Div. Mines & Geology - Task 5C1, C2) to evaluate potential sites and feasibility for mine waste remediation,
- (2) N. Bloom (Frontier Geosciences) to conduct selective extraction trials on specific mine waste source materials to evaluate the chemical form of Hg present at mining sites,
- (3) N. Bloom (Frontier Geosciences) to develop a protocol for evaluating the methylation potential of mine source materials when mixed with or added to downstream sediments to provide a proxy for the evaluation of relative potential for production of bioavailable meHg,
- (4) D. Slotton *et al.* (UC Davis - Task 5B) to evaluate Hg bioaccumulation and trophic transfer of Hg within the Cache Creek watershed as a function of aqueous Hg loading, and
- (5) J. Domagalski and C. Alpers (USGS - Task 1C) to quantify bulk loading from Cache Creek to the Sacramento-San Joaquin Delta.

Mining Regions under investigation:

Figures 1A and 1B show the location of the mining regions in relation to the Cache Creek Watershed region. The primary sites where intensive investigations have taken place are:

- (1) Sulphur Bank Mercury Mine at Clear Lake [feeds directly into Cache Creek];
- (2) Harley Gulch Mining Region [includes Abbott and Turkey Run Mines and feeds into Cache Creek];
- (3) Sulphur Creek Mining Region (mercury and gold mines) [feeds through Sulphur Creek, into Bear Creek and on to Cache Creek].

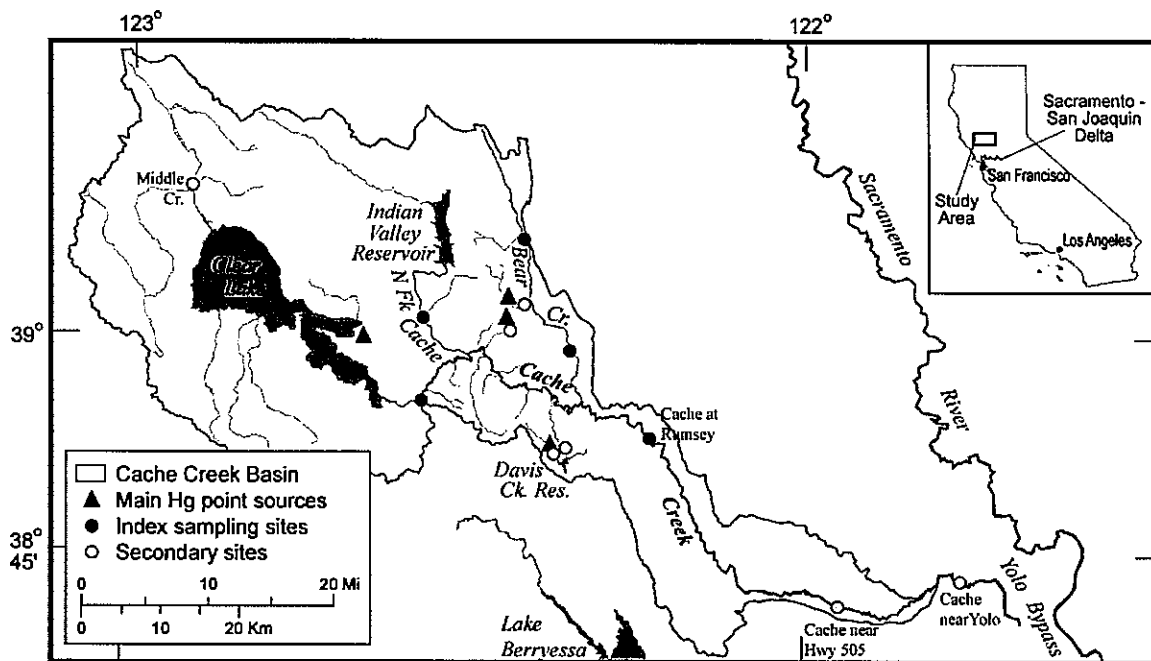


Figure 1A. Regional map showing the Cache Creek watershed and its relationship to Clear Lake, Cache Creek, Bear Creek and the downstream reaches into the Sacramento Valley at the Yolo Bypass. *Modified from a USGS base map.*

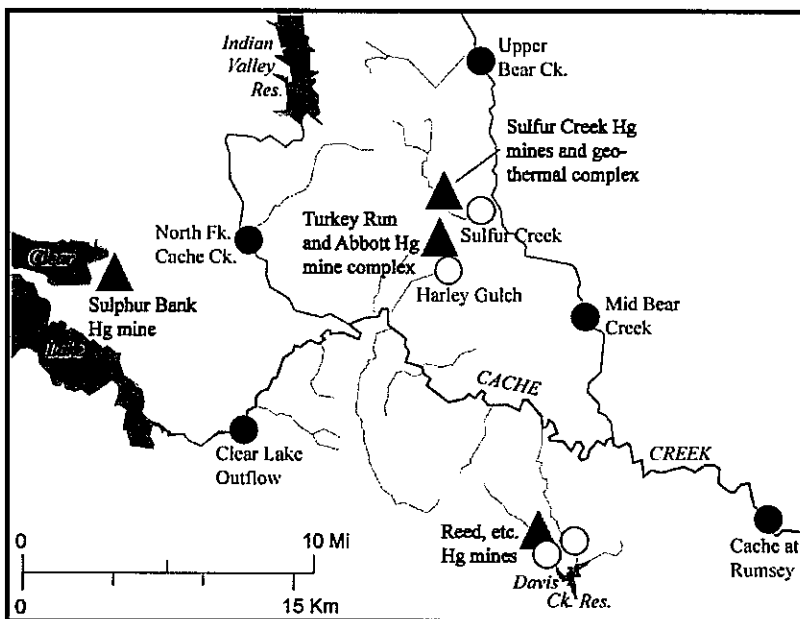


Figure 1B. Local map showing the location of the Harley Gulch Mining Region (including the Turkey Run and Abbott Hg Mines), and the Sulphur Creek Mining Region. *Modified from a USGS base map.*

Harley Gulch sampling locations

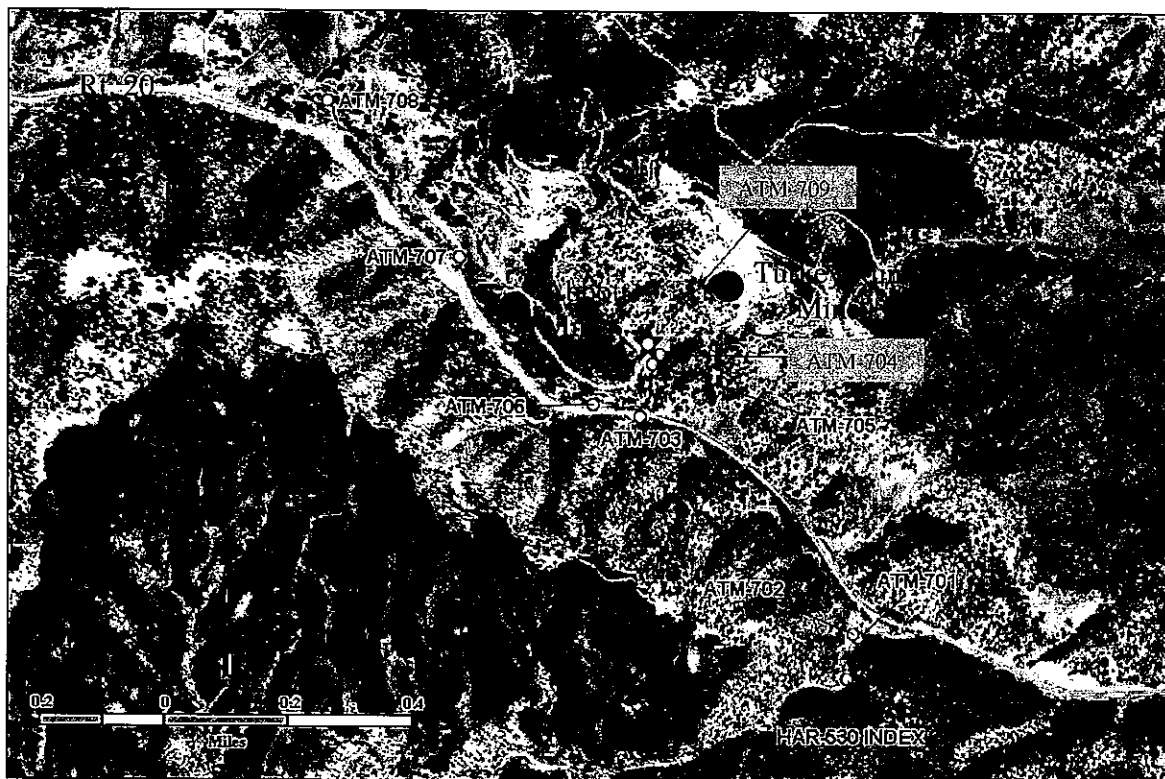


Figure 2. Aerial photograph indicating sampling locations for the Harley Gulch Mining Region, including collection sites from the Abbott and Turkey Run mines. The curved white line running from NW to SE is Rt. 20. Star at ATM-709 represents site of a geothermal spring.

Sulphur Creek Sampling Locations

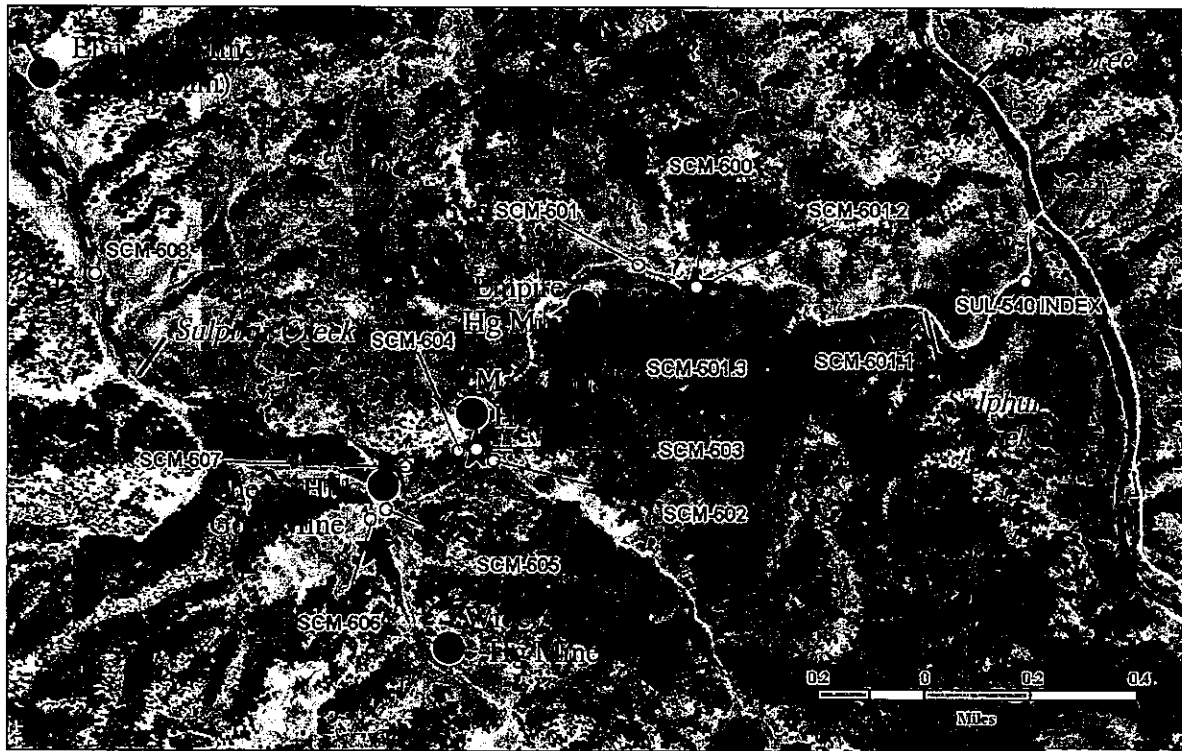


Figure 3. Aerial photograph of the Sulphur Creek Mining Region indicating the sampling sites along Sulphur Creek. The curvilinear feature in the NE region of the photograph is Bear Creek. Stars represent sites of geothermal springs.

Figures 4a and 4b provide more detailed relationships between the location of each mine and small tributaries and geothermal springs for the Harley Gulch and Sulphur Creek region respectively.

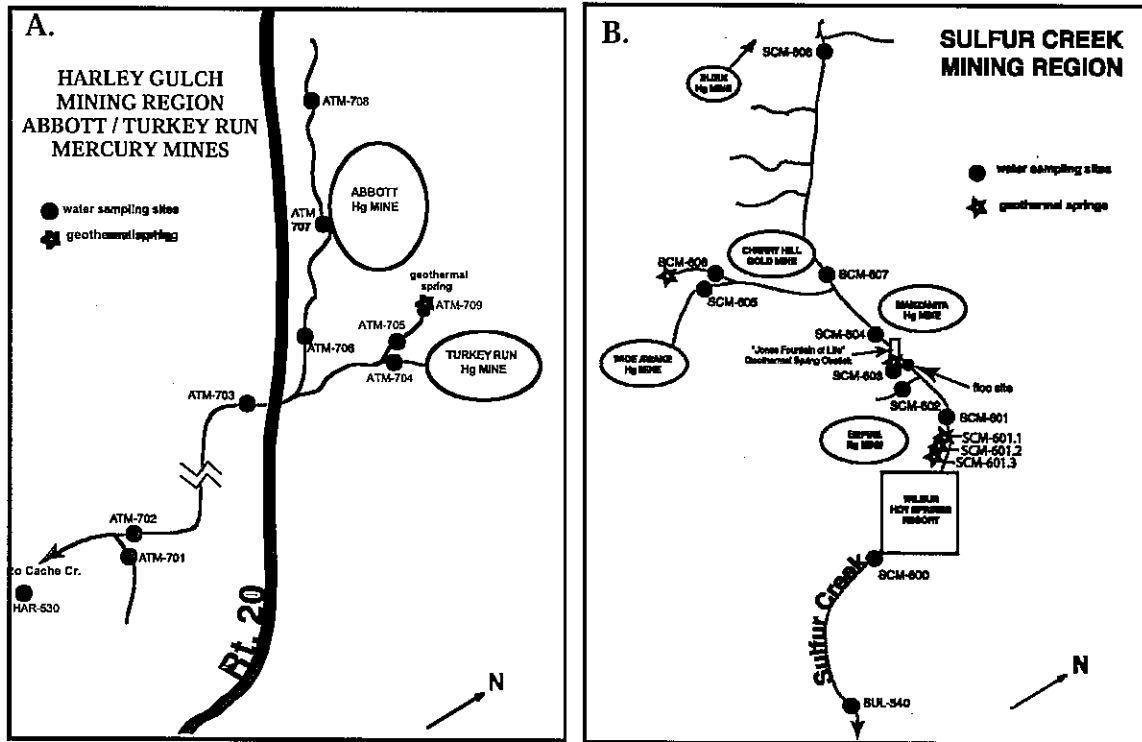


Figure 4. Detailed map of Harley Gulch region sampling sites in relation to local tributaries and geothermal springs. A = Harley Gulch, B = Sulphur Creek.

Quantifying Hg Concentrations and Loading:

Calculations of total Hg loading from this region were derived from daily flow rates (obtained primarily from USGS gauging stations on Harley Gulch and Sulphur Creek, and in some cases flow rates calculated by hand) and aqueous Hg concentrations from each of the individual sampling sites from these regions. Water collections took place on the following dates: Harley Gulch Mining Region (2/14/00 and 2/21/01) and Sulphur Creek Mining Region (2/14/00 and 2/22/01), which represented periods of elevated flow rates, although in 2001 we were not able to sample on the peak flow. Note that the USGS gauging station at Harley Gulch was not functional during this period in 2001, so the loading estimate for this stream was derived from flow measurements taken by hand at the site on 2/21/01 (= 4.0 cfs).

Water samples were collected from key tributary locations where previous mining activities were documented and from natural geothermal spring inputs to tributaries that flow eventually into Cache Creek. It was anticipated that the greatest transport of particulate material containing Hg-laden particles from the mining sites occurs during winter storm runoff. Thus, samples were collected during high flow periods that maximize the probability of quantifying maximum loading. Figures 5a and 5b show hydrographs for the USGS Harley Gulch and Sulphur Creek gauging stations for the water years

1999/2000 and 2000/2001 indicating that the annual storm samples were collected from Harley Gulch and Sulphur Creek mining regions during periods of peak flow in 2000 and in nearly peak flow in 2001. In 2001 GPS coordinates were recorded for each site (Table 1) and the following water quality parameters were quantified at each site using a YSI-6000 multi-probe water quality device: temperature, dissolved oxygen, conductivity, specific conductivity, pH and oxidation/reduction potential.

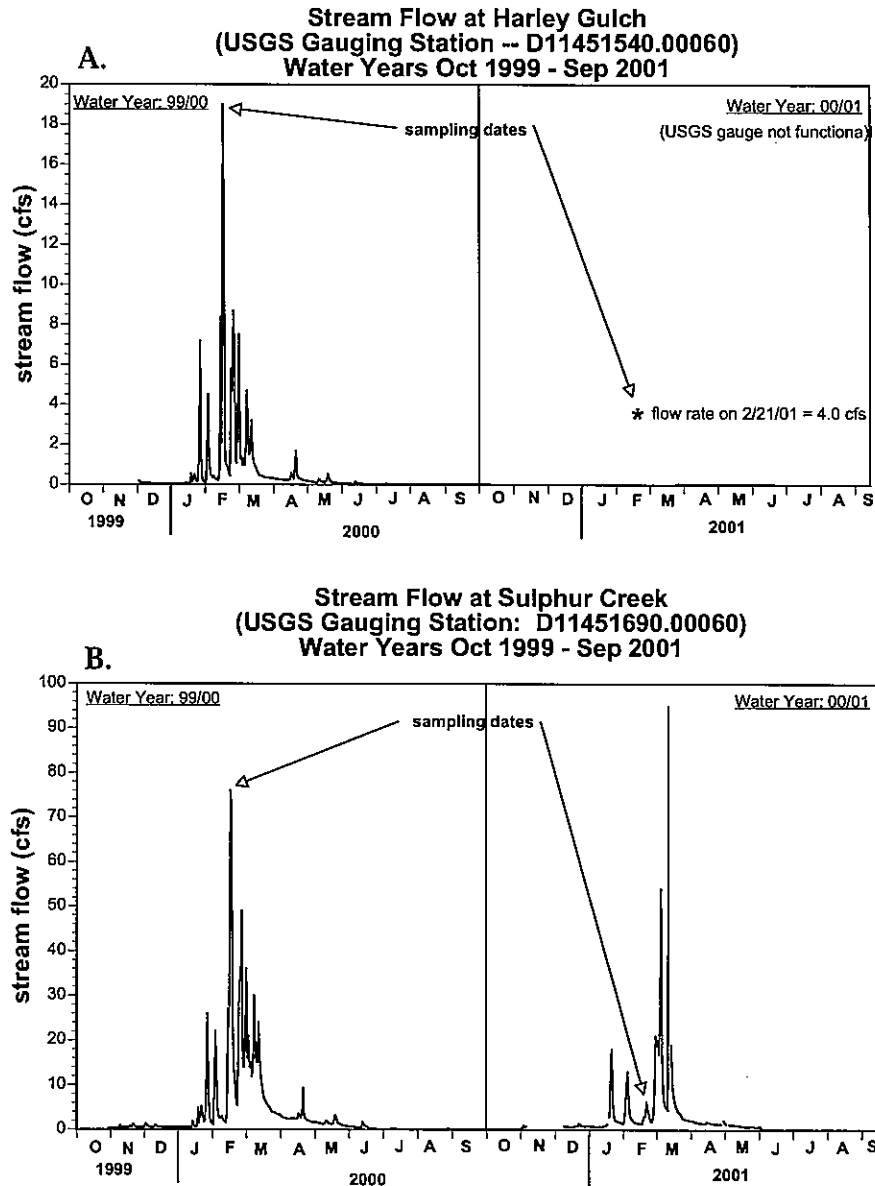


Figure 5. Hydrographs (derived from USGS gauging stations) from Harley Gulch (Station D11451540.00060) and Sulphur Creek (Station D11451690.00060) indicating the dates in water years 1999/2000 and 2000/2001 when aqueous Hg samples were collected at these sites.

At each site water for Hg analysis was collected into trace metal clean glass bottles (using standard ultra-clean techniques -- Gill and Bruland 1990 and Watras *et al.* 1991) to be analyzed for raw (unfiltered) and filtered (0.45µm pore size) total Hg, and a subset of those samples analyzed for methyl Hg. In addition, sulfate and total suspended solids (TSS) were analyzed on all samples. At a selected subset of these sites in 2001, additional samples were collected for USGS analysis of the following analytes on unfiltered and filtered (0.45 µm pore size) water: aluminum, antimony, arsenic, barium, beryllium, bismuth, boron, cadmium, calcium, cerium, cesium, chromium, cobalt, copper, dysprosium, erbium, europium, gadolinium, holmium, iron, lanthanum, lead, lithium, lutetium, magnesium, manganese, molybdenum, neodymium, nickel, potassium, praseodymium, rhenium, rubidium, samarium, selenium, silica (as SiO₂), silver, sodium, strontium, sulfur, tellurium, terbium, thallium, thorium, thulium, uranium, vanadium, ytterbium, yttrium, zinc and zirconium. At each site ancillary data on temperature, pH, conductivity, specific conductivity, oxidation/reduction potential and oxygen concentration was also collected using a YSI 6000 multiprobe water quality meter.

TABLE 1. Coordinates for sampling sites in Harley Gulch and Sulphur Creek Mining Regions.

SITE	LATITUDE	LONGITUDE
HAR-530 INDEX	39 00 33.045	122 26 03.421
ATM-701	39 00 36.609	122 26 02.285
ATM-702	39 00 36.963	122 26 02.74
ATM-703	39 00 55.357	122 26 25.623
ATM-704	(~ 50 m SE of #709)	(~ 50 m SE of #709)
ATM-705	39 00 59.72	122 26 24.272
ATM-709	39 01 1.59	122 26 24.722
ATM-706	39 00 56.39	122 22 30.665
ATM-707	39 01 8.804	122 26 45.033
ATM-708	39 01 22.03598	122 26 59.18805
SUL-540 INDEX	39 02 18.475	122 24 31.872
SCM-600	39 02 17.91	122 25 13.378
SCM-601.1	39 02 17.90152	122 25 13.37446
SCM-601.2	39 02 17.90152	122 25 13.37446
SCM-601.3	39 02 17.90152	122 25 13.37446
SCM-601	39 02 20.27289	122 25 20.1194
SCM-602	39 02 01.19305	122 25 38.44962
SCM-603	39 02 02.56097	122 25 40.36111
SCM-604	39 02 02.14366	122 25 42.82273
SCM-606	39 01 55.50114	122 25 53.93905
SCM-605	39 01 56.49658	122 25 51.9659
SCM-607	39 02 00.64045	122 25 49.5448
SCM-608	39 02 19.58823	122 26 28.20043

Water samples were kept cool (to 4°C), shipped overnight FedEx and analyzed for Hg by Battelle Marine Sciences Laboratory, Sequim, WA, for sulfate and TSS by Columbia Analytical (Kelso, WA) and for the elemental suite by USGS (Sacramento, CA).

U.S.G.S. Methods for Analyzing the Aqueous Elemental Suite:

Major Cations: Inductively coupled plasma emission spectrometry

Elements present at concentration levels in the milligram per liter range, including Ca, K, Mg, Na, and some selected trace elements, such as Fe, were determined by inductively coupled plasma-atomic emission spectrometric (ICP-AES) techniques utilizing a Perkin Elmer Optima 3300DV, multichannel emission spectrometer at the USGS research laboratory in Boulder, Colorado, under the direction of Howard E. Taylor. A general description of the analysis conditions and procedures are reported by Garbarino and Taylor (1979). Details of the operational conditions are described by Mitko and Bebek (1999, 2000).

Trace Elements: Inductively coupled plasma-mass spectrometry

Trace element determinations (excluding Hg) were performed with a Perkin Elmer Elan Model 6000, inductively coupled plasma-mass spectrometer (ICP-MS) at the USGS research laboratory in Boulder, Colorado. Aerosols of acidified aqueous samples were introduced into the spectrometer with a cone-spray pneumatic nebulizer. Multiple internal standards (indium, iridium and rhodium), covering the entire mass range of measured isotopes were used to normalize the system for drift. Details of the specific analysis techniques, procedures and instrumental settings are described elsewhere (Garbarino and Taylor, 1996).

QA/QC procedures for the elemental suite analyses are detailed in Appendix 11.

Stream Flows:

Stream flow rates were measured directly at USGS gauging stations at the Clear Lake dam outflow, on Harley Gulch (Abbott/Turkey Run Mining Region) and Sulphur Creek (Sulphur Creek Mining Region). At all sites, including the gauged sites, we also calculated independent estimates of flow by hand to compare with the automated gauges and to estimate flow and loading from each specific mine sub-site or sub-watershed. Hand measurements of flow involved timing a near-neutral density floating object (orange) over a straight section of stream reach.

The points at which these tributaries flow into Cache Creek or other tributaries that eventually flow into Cache Creek (i.e.- where water from the Sulphur Creek Mines flow into Bear Creek, and where water from the Abbott/Turkey Run Mines flow into Harley Gulch) were included in the sampling schedule for both Task 5A and Task 5B (water Index Stations). Thus, we were able to quantify loading from specific mine sites and from the major tributaries that integrate all of those mine sites by sampling the high-flow events at the mines in Task 5A and the seasonal Index Stations sampled in Task 5B, which provided integration between these two tasks and allowed comparisons of the maximal loading potential as well as the seasonal variability in loading.

Monthly and annual Hg loading estimates were calculated as follows. Stream flow data (in cubic feet per second = cfs) were obtained as daily averages from each USGS gauging station for the water years 1999/2000 (Oct 1999 to Sep 2000) and 2000/2001 (Oct 2000 to Sep 2001). The minimum, mean and maximum daily flow rates for each month were multiplied times the Hg concentrations for raw and filtered total Hg and methyl Hg to obtain minimum, mean and maximum projected monthly Hg loading estimates. The cumulative minimum, mean and maximum values for each month were used to estimate annual Hg loading.

Hg Methylation from In-Situ Sediments: (Sediment/Floc Microcosm Experiment)

Annually, a characteristic mass of Hg-rich flocculent precipitate (possible methyl Hg-rich floc) accumulates below the *Jones Fountain of Life*, which could become mobilized and transported downstream, thus contaminating significant stretches of Sulphur Creek, Bear Creek and possibly Cache Creek with total Hg and/or methyl Hg. In order to test whether this floc had a significant potential to produce methyl Hg, we conducted a laboratory microcosm experiment. This trial was conducted from November 10-15, 2000 (before winter rains began) under the direction of Professor Doug Nelson, Microbiology, UC Davis. Earlier comparable experiments were conducted at Clear Lake, indicating significant differences in sediment methyl Hg production between different regions within the lake. Results obtained for the methylation of Sulphur Creek Hg source materials were compared with those obtained from Clear Lake. This CALFED microcosm experiment utilized Hg-rich flocculent material from Sulphur Creek, immediately below the input from a geothermal spring (*Jones Fountain of Life*) with extremely high total Hg concentrations (~24,000-39,000 ng/L unfiltered total Hg and ~5,800-9,800 ng/L filtered total Hg). Our intent was to evaluate the potential of this flocculent material to produce methyl Hg under comparable conditions which had been tested previously at Clear Lake.

Hg source material (floc from below the *Jones Fountain of Life*) was collected in teflon core tubes from the site. Each core tube was plugged with a rubber stopper on the bottom (beneath the sediment/floc) and one on the top (Figure 6). The test material (in this case floc) with a fixed level of overlying water (relatively low Hg water from the Upper Arm of Clear Lake was used in order to compare with earlier production experiments in Clear Lake), was incubated under oxic (sparged with air) and anoxic (sparged with nitrogen) conditions over a five day period. Water from each core tube was drawn off and replaced with a syringe at 0.5 and 2.5 days, then harvested after 5.0 days of total incubation time. Samples were FedExed overnight to Battelle Marine Science Laboratories, where they were filtered (0.45 µm) and analyzed for methyl Hg concentrations. Methyl Hg concentrations for each treatment and time interval were quantified. Two replicate samples of floc and a water blank were incubated for each treatment (oxic and anoxic).

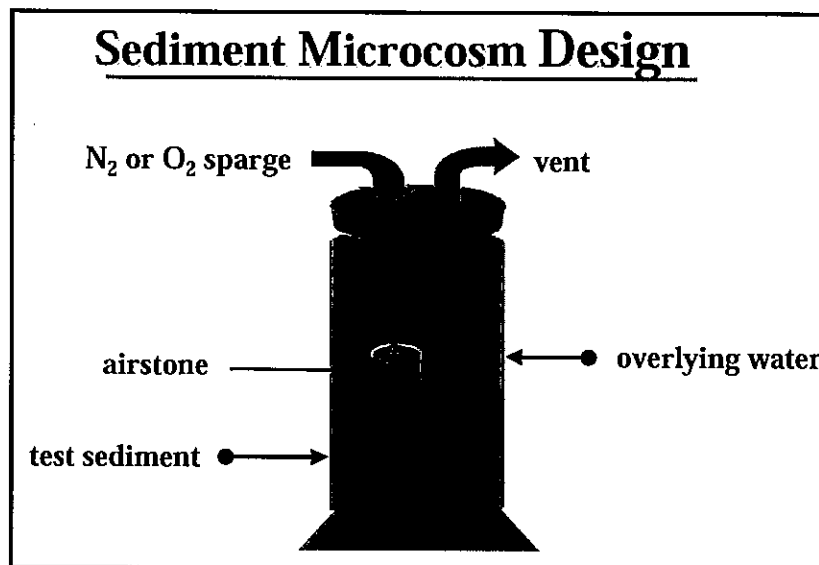


FIGURE 6. Microcosm laboratory trial core tube design.

Quantifying Hg Methylation Potential of Mine-Derived Source Sediments: (Slurry Experiments)

The focus of these laboratory trials was to differentiate the relative potential of selected mine-derived, inorganic Hg source materials to produce methyl Hg. Based on data compiled by our group and the mining geology team (Task 5C1), representative samples of relatively homogeneous, erodeable materials were collected for additional Hg analysis and laboratory trials. These upstream mine-derived source materials were added to downstream sediments from Cache Creek, where these materials can be transported naturally, especially during high winter flow regimes.

Because developing a consistent mixture of point source materials and downstream sediments was key to this work, we chose a slurry experimental design, as opposed to more natural intact core approaches, and analyzed the homogeneous slurry mixture over time for methyl Hg production. The intent was to include a variety of source and receiving sediments that would be characteristic of the wide range of upstream source materials derived from mines and geothermal springs and downstream sediment characteristics found in the receiving waters of the Yolo Bypass and the Sacramento-San Joaquin Delta. The plan for this experiment involved the following possible Source and Receiving sediments:

SOURCE Sediments:

- 1) Abbott Mine tailings pile fine grained sieved particulate material from the main waste pile.
- 2) Turkey Run Mine waste material that appeared to have the potential to become mobilized during precipitation events
- 3) Floc precipitate material from below geothermal spring on Sulphur Creek
- 4) Local native soils that had the potential to become mobilized during precipitation events

RECEIVING Sediments:

- 1) Yolo Bypass sediments (more sandy sediments, low in organics)
- 2) Peat sediments from Frank's Tract and/or Venice Cut (sediments high in organics)
- 3) West Delta sites (west of the Entrapment Zone): e.g. - Grizzly Bay, Honker Bay, where high meHg concentrations have been documented in other phases of this project
- 4) Accumulated sediments from the depositional environment of Cache Creek immediately upstream of the Capay Dam

QA/QC Protocols:

Duplicate field samples were collected and analyzed identically for approximately 10% of all total Hg samples for each site on each date and the identity of those samples were not revealed to the analytical laboratory. The comparability between the two replicates ranged from 15.4-21.7%, with exception of one replicate sample that was 65.9% different than the original sample.

RESULTS:

Within the Cache Creek watershed region, we have the most extensive and long-term data for the Sulphur Bank Mercury Mine (SBMM) at Clear Lake. Water collections at the SBMM over the past 10 yrs indicate methyl Hg production is enhanced by the formation of an alumino-silicate floc precipitate produced from acid mine drainage in regions near-shore to the mine and transported downstream to Cache Creek especially during summer/fall months. More of these data can be obtained by referencing several other publications (e.g. Suchanek et al. 1993, 1997, 1998, 2000a, 2000b).

At the other two mining regions studied (i.e. Harley Gulch and Sulphur Creek), inorganic particulate Hg loading occurs primarily during winter storm seasons. Inorganic Hg export from the Abbott/Turkey Run mine complex clearly derives from slumping of some of the large tailings piles at Abbott Mine. A large, hot geothermal spring at the Turkey Run Mine, however, contains extremely low concentrations of Hg and thus does not likely contribute to significant Hg loading.

Hg IN WATER

Hg in water was sampled in February 2000 and 2001 at both the Harley Gulch and Sulphur Creek mining regions. Table 2 provides data for total Hg and methyl Hg in both raw (unfiltered) and filtered water samples analyzed for those dates. Appendix 1 gives the water quality data for each site for 2000 and 2001.

Table 2. Data for aqueous total Hg and methyl Hg from raw (unfiltered) and filtered water samples and TSS and SO₄ from Harley Gulch and Sulphur Creek mining regions from February 2000 and February 2001. Dashed lines and gray areas indicate no data available.

2000		Total Mercury (ng/L)			Methyl Mercury (ng/L)			
	tot Hg RAW	tot Hg FILT	% dissolved	meHg RAW	MeHg FILT	% dissolved		
Harley Gulch (2/14/00)								
Harley Gulch INDEX STATION (combined flow) • HAR-530	500	42	8	0.35	0.30	84		
South Side tributary (non-mine) • ATM-701	135	21	15	--	--	--		
Mine Site tributary above confluence of #701 • ATM-702	2,066	128	6	--	--	--		
Wetland tributary from mine, W of Hwy 20 • ATM-703	1,928	86	4	--	--	--		
Turkey Run S Fk, from piles • ATM-704	6,800	74	1	--	--	--		
Turkey Run N Fk, from spring • ATM-705	404	43	11	--	--	--		
Turkey Run spring above #705 • ATM-709	4	3	60	--	--	--		
Tributary from Abbott above TR Mine input • ATM-706	1,648	89	5	--	--	--		
Tributary below main Abbott piles • ATM-707	1,911	78	4	--	--	--		
Tributary below main Abbott piles • ATM-707 (duplicate)	1,528	84	5	--	--	--		
Tributary above all main Abbott piles • ATM-708	181	30	16	--	--	--		
Sulphur Creek (2/14/00)								
Sulfur Creek INDEX STATION • SUL-540	973	100	10	0.48	0.45	94		
Sulfur Ck above Wilbur Springs Resort • SCM-601	620	83	13	--	--	--		
Side Stream to Sulfur Cr. • SCM-602	673	88	13	--	--	--		
Side Stream to Sulfur Cr. • SCM-602 (duplicate)	229	36	16	--	--	--		
"Jones Fountain of Life" geothermal spring • SCM-603	24,262	8,552	35	--	--	--		
Sulfur Ck above "Jones Fountain" geyser • SCM-604	350	81	23	--	--	--		
Creek from Wide Awake mine • SCM-605	2,454	1,416	58	--	--	--		
sulfurous creek by Cherry Hill • SCM-606	1,113	224	20	--	--	--		
Sulfur Ck above 605/606 input • SCM-607	230	64	28	--	--	--		
Sulfur Ck above all mines except Elgin • SCM-608	341	226	66	--	--	--		
2001								
	tot Hg RAW	tot Hg FILT	% dissolved	meHg RAW	MeHg FILT	% dissolved	TSS (mg/L) SO ₄ (mg/L)	
Harley Gulch (2/21/01)								
Harley Gulch INDEX STATION (combined flow) • HAR-530	92	48	52	0.34	0.22	65	13 268	
South Side tributary (non-mine) • ATM-701	22	10	45	--	--	--	17 107	
Mine Site tributary above confluence of #701 • ATM-702	385	256	66	0.15	0.08	52	1 773	
Wetland tributary from mine, W of Hwy 20 • ATM-703	933	484	52	0.25	0.12	48	4 675	
Turkey Run S Fk, from piles • ATM-704	--	--	--	--	--	--	-- --	
Turkey Run N Fk, from spring • ATM-705	87	40	46	--	--	--	1 1,140	
Turkey Run spring above #705 • ATM-709	6	2	33	--	--	--	1 1,350	
Tributary from Abbott above TR Mine input • ATM-706	283	124	44	0.30	0.28	94	5 515	
Tributary below main Abbott piles • ATM-707	180	66	37	--	--	--	5 207	
Tributary below main Abbott piles • ATM-707 (duplicate)	141	63	45	--	--	--	4 213	
Tributary above all main Abbott piles • ATM-708	62	26	42	--	--	--	7 87	
Sulphur Creek (2/22/01)								
Sulfur Creek INDEX STATION • SUL-540	1,340	160	12	0.49	0.08	17	56 51	
Sulfur Ck below Wilbur Springs Resort • SCM-600	1,110	177	16	--	--	--	43 50	
Geothermal Spring feeding hot baths #1 • SCM-601.1	3,460	2,300	66	3.73	3.24	87	5 81	
Geothermal Spring feeding hot baths #2 • SCM-601.2	7,250	1,900	26	2.01	2.27	113	6 54	
Geothermal Spring feeding hot baths #3 • SCM-601.3	3,970	2,750	69	1.28	0.59	46	12 59	
Sulfur Ck above Wilbur Springs Resort • SCM-601	465	117	25	--	--	--	22 33	
Side Stream to Sulfur Cr. • SCM-602	137	33	24	--	--	--	25 35	
"Jones Fountain of Life" geothermal spring • SCM-603	33,600	9,880	29	20.40	14.40	71	46 57	
"Jones Fountain of Life" geothermal spring • SCM-603 (duplicate)	39,700	5,470	14	--	--	--	13 42	
Sulfur Ck above "Jones Fountain" geyser • SCM-604	374	103	28	--	--	--	22 32	
Creek from Wide Awake mine • SCM-605	4,300	2,219	52	--	--	--	26 59	
sulfurous creek by Cherry Hill • SCM-606	2,110	959	45	--	--	--	135 88	
Sulfur Ck above 605/606 input • SCM-607	289	102	35	0.50	0.21	41	15 31	
Sulfur Ck above all mines except Elgin • SCM-608	330	87	26	--	--	--	15 29	

Harley Gulch - February 2000:

Data from the Harley Gulch mining region (location of Abbott and Turkey Run Mines) from February 2000 are presented in Figure 7. Hg concentrations for raw (unfiltered) water were typically quite elevated (1,000-2,000 ng/L = parts per trillion) in nearly all samples collected from mine run-off, but considerably reduced in (1) the tributary above the Abbott/Turkey Run mines, (2) the geothermal spring outflow at the Turkey Run Mine, and (3) in the tributary to the south that originated from a non-mining source region. The highest raw (unfiltered) water total Hg concentration (6,350 ng/L) was recorded in water from the Turkey Run Mine run-off (ATM-704), and the lowest Hg concentration (4.32 ng/L) was recorded from the geothermal spring at the Turkey Run Mine (ATM-709). These values compare with water from Clear Lake, which is under the influence of the Sulphur Bank Mercury Mine and average about 1-2 ng/L for raw (unfiltered) water total Hg concentrations. Nearly all total Hg (typically > 95%) from terrestrial mine run-off was in particulate form. However, total Hg in the Turkey Run geothermal spring was 61% dissolved. The single sample that was analyzed for methyl Hg exhibited relatively low concentrations of methyl Hg at 0.35 ng/L for unfiltered water and 0.29 ng/L for filtered water.

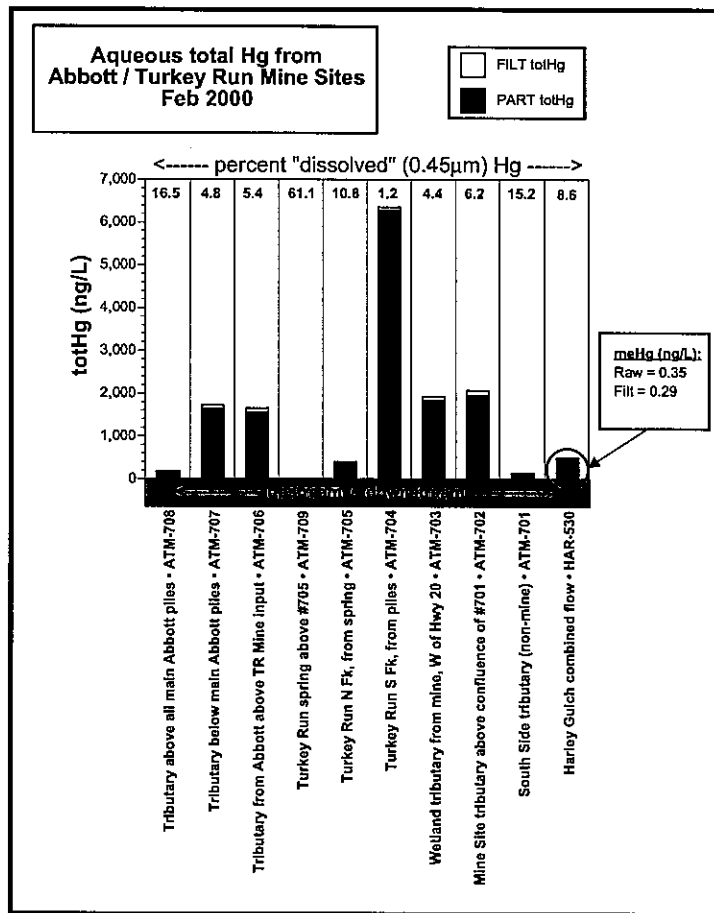


Figure 7. Total Hg in water from the Harley Gulch Mining Region sites in 2000. Dark portions of bars represent total Hg in raw (unfiltered) water and the light portions of the bars indicate total Hg in the dissolved fraction (0.45 µm pore size).

Total aqueous Hg in the dissolved fraction ranged from ca. 2.6-128 ng/L, with the lowest Hg concentration found in the geothermal spring water (ATM-709) and the highest documented at a run-off site below the Abbott Mine tailings piles (ATM-702).

QA/QC data, including results from laboratory spikes, splits, equipment blanks, etc. for Hg in RAW and FILTERED water samples are provided in Appendix 4 and Appendix 5.

Harley Gulch - February 2001:

Data from the Harley Gulch mining region from February 2001 are presented in Figure 8. Hg concentrations for raw (unfiltered) water ranged from 6-933 ng/L and were elevated at mine run-off sites, but were not as high as those values obtained in 2000. However, as in the previous year, Hg concentrations were considerably reduced in (1) the tributary above the Abbott/Turkey Run mines (62 ng/L), (2) the geothermal spring outflow at the Turkey Run Mine (6 ng/L), and (3) in the tributary to the south that originated from a non-mining source region (22 ng/L). The highest Hg concentration (933 ng/L) was recorded in water from a site (ATM-703) just below the confluence of the streams that collect run-off from both the Abbott Mine and the Turkey Run Mine. The lowest Hg concentration (6 ng/L) was comparable to the previous year's value (4.3 ng/L) recorded from the geothermal spring at the Turkey Run Mine (ATM-709). In contrast to the data from 2000 in which 80-95% of total Hg was in particulate form, only about 40-60% of the aqueous Hg was in the particulate form. Four samples were analyzed for methyl Hg in 2001 and ranged from 0.15-0.34 ng/L, with the highest values for both raw and filtered water being documented at the downstream Harley Gulch Index Station (HAR-530) that receives all of the flow from both the Abbott and Turkey Run Mines and then flows through a wetland before reaching that site.

Hg in filtered water ranged from ca. 2-484 ng/L, with the lowest Hg concentration found in the geothermal spring water (ATM-709) and the highest documented at a run-off site below both mines (ATM-703), which is comparable to the raw water results.

Ancillary data on the total and dissolved elemental concentrations in waters collected from Harley Gulch (analyzed by USGS) are provided in Appendix 2.

QA/QC data, including results from laboratory spikes, splits, equipment blanks, etc. for Hg in RAW and FILTERED water samples are provided in Appendix 6 and Appendix 7.

QA/QC data, including results from laboratory spikes, splits, equipment blanks, etc. for TSS and SO₄ are provided in Appendix 8.

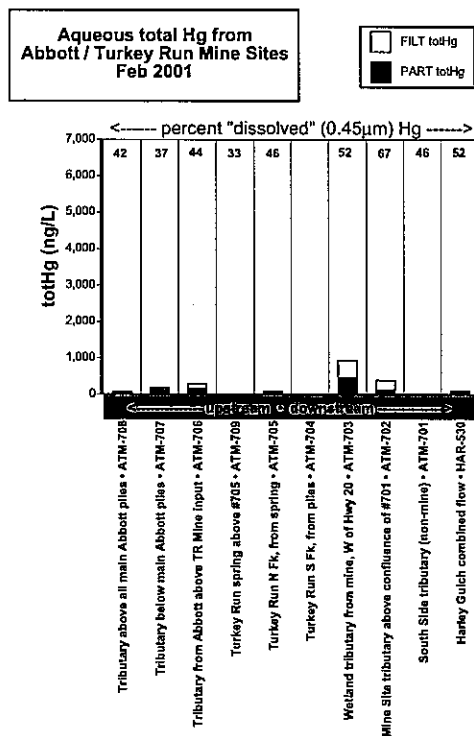


Figure 8. Hg in water from the Harley Gulch Mining Region sites in 2001, using the same scale as the 2000 data shown in Figure 7 for comparison.

Sulphur Creek - February 2000:

Sulphur Creek mining region Hg data from February 2000 are presented in Figure 9 and Table 2. Hg in raw water ranged from 229 ng/L (at a site with no identified mining sources – SCM-602), to 24,300 ng/L. The three most elevated samples were (1) a sulfurous creek with likely geothermal spring origin above the Cherry Hill Gold Mine at SCM-606 (1,110 ng/L), (2) the run-off tributary from the Wide Awake Hg Mine at site SCM-605 (2,450 ng/L) and (3) the *Jones Fountain of Life* geothermal spring (with significantly elevated total Hg at 24,300 ng/L). Most sites had Hg in varying percentages (35-85%) in particulate form. Even water above this mining region, with only the Elgin Hg Mine influence (at site SCM-608), had 340 ng/L Hg. The downstream Sulphur Creek Index Station (also sampled in Task 5B), was also significantly elevated at 974 ng/L unfiltered total Hg (ca. 90% of which was in particulate form), and 0.48 ng/L unfiltered methyl Hg (ca. 16% of which was in particulate form).

Filtered water yielded Hg concentrations of 35.8-8,120 ng/L with the minimum and maximum values corresponding exactly to those same sites as reported for raw water (see above).

QA/QC data, including results from laboratory spikes, splits, equipment blanks, etc. for Hg in RAW and FILTERED water samples are provided in Appendix 4 and Appendix 5.

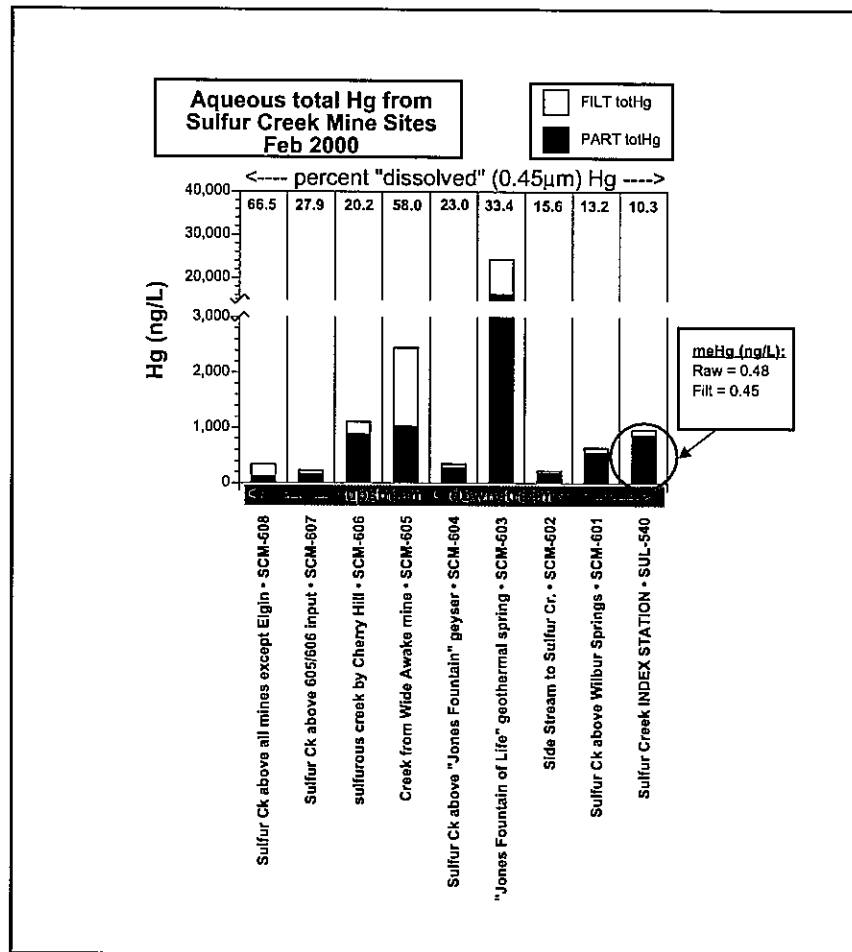


Figure 9. Hg in water from the Sulphur Creek Mining Region sites in 2000.

Sulphur Creek - February 2001:

Sulphur Creek mining region Hg data from February 2001 are presented in Figure 10 and Table 2. Hg in raw water ranged from 137 ng/L (at a site with no identified mining sources – SCM-602), to 24,300 ng/L. Comparing these values with those for the same sites in the year 2000, the three most elevated samples were again: (1) a sulphurous creek with likely geothermal spring origin above the Cherry Hill Gold Mine at SCM-606 (2,110 ng/L), (2) the run-off tributary from the Wide Awake Hg Mine at site SCM-605 (4,300 ng/L) and (3) the *Jones Fountain of Life* geothermal spring (with significantly elevated total Hg at 39,700 ng/L). Similar to the previous year’s results, most sites contained Hg in about 35-85% particulate form. Water derived from above this mining region, with only the Elgin Hg Mine influence (at site SCM-608), had virtually identical Hg concentrations as the previous year, at 330 ng/L. And, again as in the previous year, the downstream Sulphur Creek Index Station (also sampled in Task 5B), was significantly elevated at 1,340 ng/L unfiltered total Hg (88% of which was in particulate form), and

0.49 ng/L unfiltered methyl Hg (ca. 17% of which was in particulate form). These results indicate strongly that the Sulphur Creek Mining region (which includes both mines and geothermal spring inputs of Hg) adds significant Hg to Sulphur Creek, which is then transported down into Bear Creek.

Four additional sites were added in 2001 (one site immediately below the Wilbur Hot Springs Resort – SCM-600, and three sites at geothermal springs that provide the source water for the hot baths at the Resort: SCM-601.1, SCM-601.2 and SCM-601.3). The latter three sources are contained within cement enclosures covered by wooden boards and/or styrofoam. SCM-601.1 represents a geothermal spring that historically fed the baths, but is not currently used. SCM-601.2 (larger cement enclosure) and SCM-601.3 (smaller cement enclosure) currently provide hot geothermal spring water for the Resort baths. At 1,110 ng/L total Hg in raw water and 177 ng/L total Hg in filtered water, the site below the Resort was comparable to the Sulphur Creek Index Station (which contained 1,340 ng/L and 160 ng/L Hg respectively). At 3,460 ng/L, 7,250 ng/L and 3,970 ng/L total Hg in raw water for SCM-601.1, SCM-601.2 and SCM-601.3 respectively, all three geothermal spring sources were about an order of magnitude lower than those values obtained from the upstream *Jones Fountain of Life* (39,700 ng/L Hg for raw water). Particulate Hg ranged from 31-74% in those samples.

Total Hg in filtered water was measured at 33 – 9,880 ng/L with the minimum and maximum values corresponding to the same sites reported for maximum and minimum values in raw water (see above).

Ancillary data on the total and dissolved elemental concentrations in waters collected from Sulphur Creek sites (analyzed by USGS) are provided in Appendix 3.

QA/QC data, including results from laboratory spikes, splits, equipment blanks, etc. for Hg in RAW and FILTERED water samples are provided in Appendix 6 and Appendix 7.

QA/QC data, including results from laboratory spikes, splits, equipment blanks, etc. for TSS and SO₄ are provided in Appendix 8.

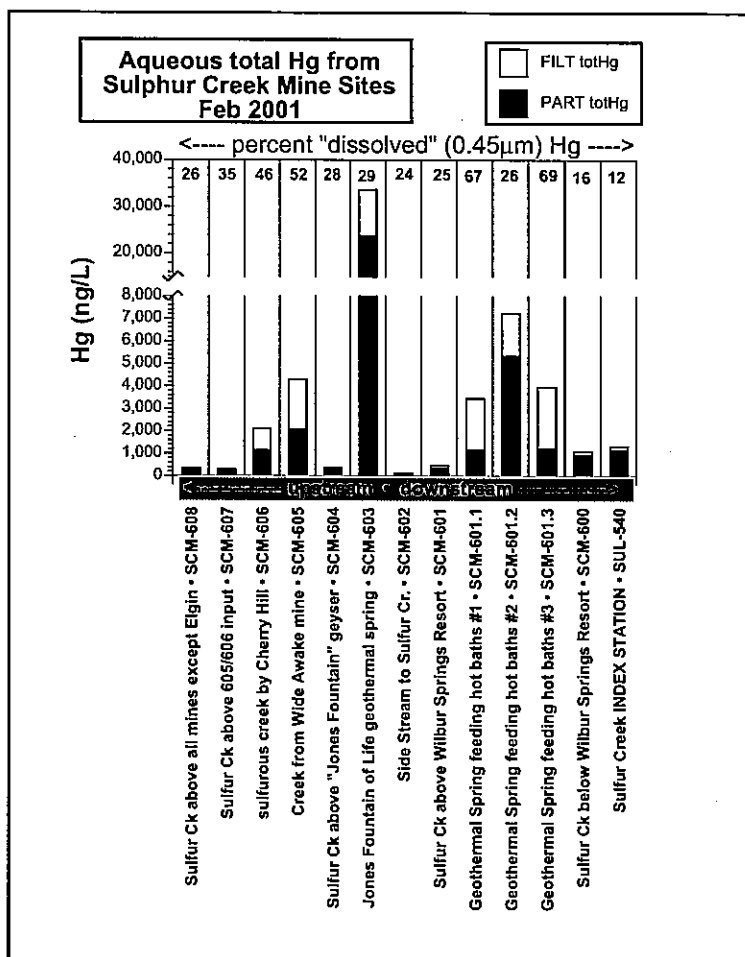


Figure 10. Hg in water from the Sulphur Creek Mining Region sites in 2001, using the same scale as the 2000 data shown in Figure 9 for comparison.

Hg LOADING:

Hg loading was calculated for each mining region (Harley Gulch and Sulphur Creek) as well as for each sampling site (such as tailings piles, waste rock piles, geothermal springs, etc.) within each mining region. This enabled us to assign either relative or quantitative values to different mine sites and/or different local features within each mining region. Below we report these loading estimates for each region separately.

Harley Gulch - 2000:

From the flow rates measured at each stream station by hand, together with the aqueous Hg concentrations, we calculated loading rates for specific local stretches of the streams in each region.

Figure 11A and 11B provide both stream flow (in cfs) and loading estimates (in kg/d) for sites within the Harley Gulch region based on the data collected on February 14, 2000 (the sampling date).

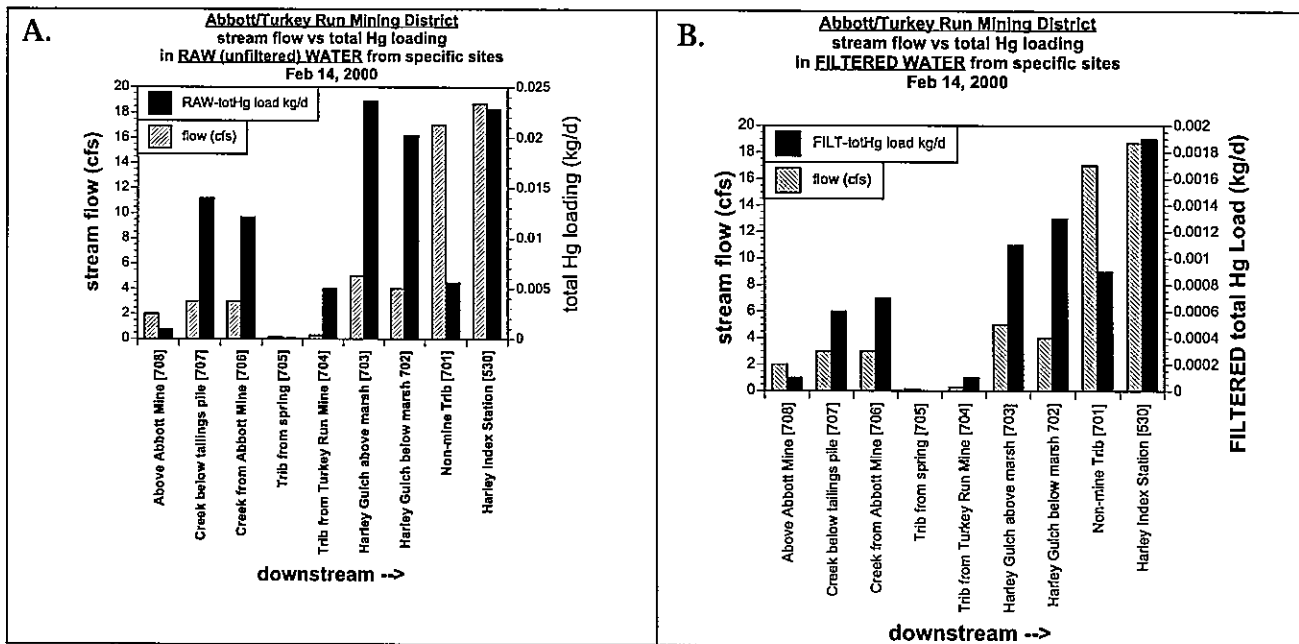


Figure 11. Stream flow and estimated daily total Hg loading from specific stream sites in the Harley Gulch Mining Region based on water collections and Hg analyses from Feb. 14, 2000. (A). Estimates derived from RAW water samples. (B). Estimates derived from FILTERED water samples. Note the different scale for the Hg concentrations in B.

A comparison of total Hg and methyl Hg loading from specific Harley Gulch sites is based on those water samples collected on a very rainy day in February. Obviously, those daily loading rates would not be sustained throughout the year and likely not sustained during precipitation events of lesser magnitude either, both because the flow rates would be lower and because the mobilization/erosion rates of particulate materials would be less during less stormy periods. So these values represent maximum values relative to that magnitude of storm/precipitation event, resulting in that magnitude of stream flow rates.

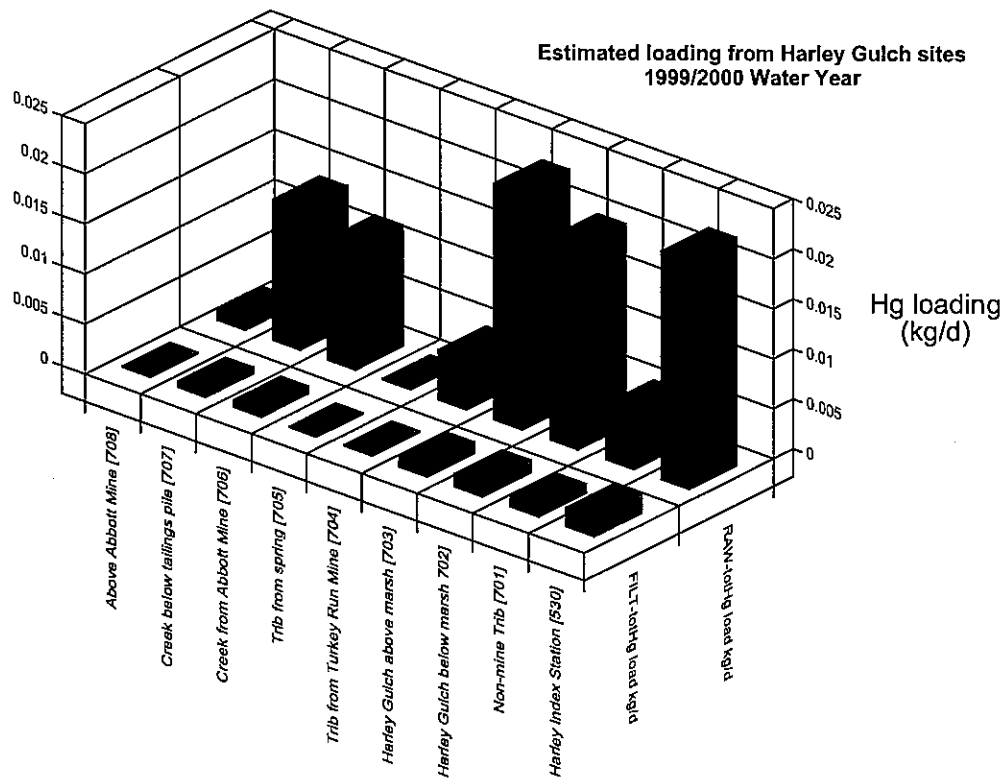


Figure 12. Comparison of daily total Hg loading for RAW (unfiltered) and FILTERED water from specific sites within the Harley Gulch Mining Region. Based on hand collected flow measurements and aqueous Hg analyses from Feb 14, 2000. Note: sites are arranged from left to right in relation to their upstream to downstream locations, with the Index Station (HAR-530) representing the furthest site downstream.

Using additional daily flow data from the USGS gauging station at Harley Gulch, we were also able to calculate a range of loading estimates. Figure 13 provides estimated maximum, mean and minimum monthly total Hg loading from the Harley Gulch Mining Region in the 1999/2000 water year, indicating that the greatest Hg loading occurred from January through March 2000, with the highest loading occurring in February with an estimated maximum total Hg loading of 0.67 for that month. Figure 14 provides an estimate of annual maximum, mean and minimum total Hg loading from this region for the water year 1999/2000, with estimates of total Hg loading ranging from 0.03-1.22 kg/yr. Nearly all of this loading is believed to be derived from mining wastes.

Harley Gulch Mining Region, CA - 1999/2000

Estimated Maximum, Mean, and Minimum Monthly Total Mercury Load

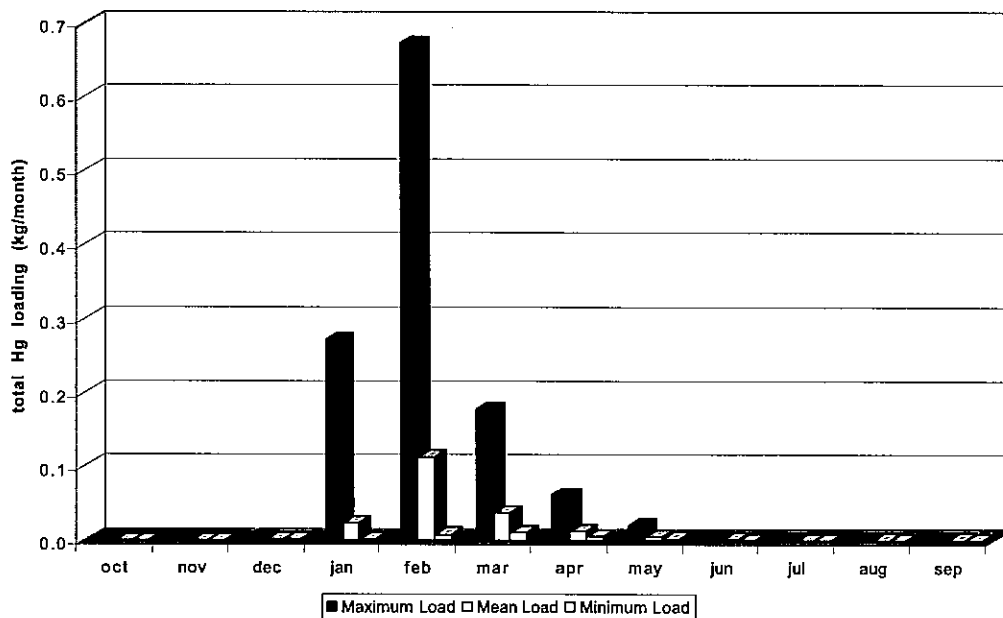


Figure 13. Estimated maximum, mean and minimum monthly loading of total Hg (kg/month) from the Harley Gulch mining region for the 1999/2000 water year.

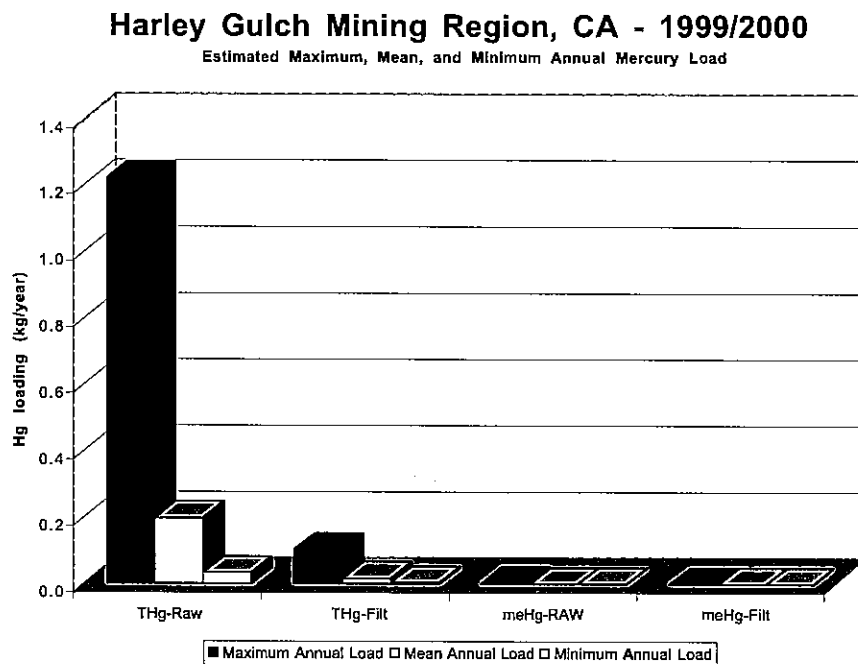


Figure 14. Estimated maximum, mean and minimum annual loading of total Hg and methyl Hg (kg/yr) from the Harley Gulch Mining Region for the 1999/2000 water year only.

Harley Gulch - 2001:

Figure 15A and 15B provide both stream flow (in cfs) and total (RAW and FILTERED) Hg loading estimates (in kg/d) for sites within the Harley Gulch region for February 21, 2001 (the sampling date). Figure 15C and 15D provide comparable methyl (RAW and FILTERED) Hg loading estimates (in kg/d) for these same sites on that sampling date.

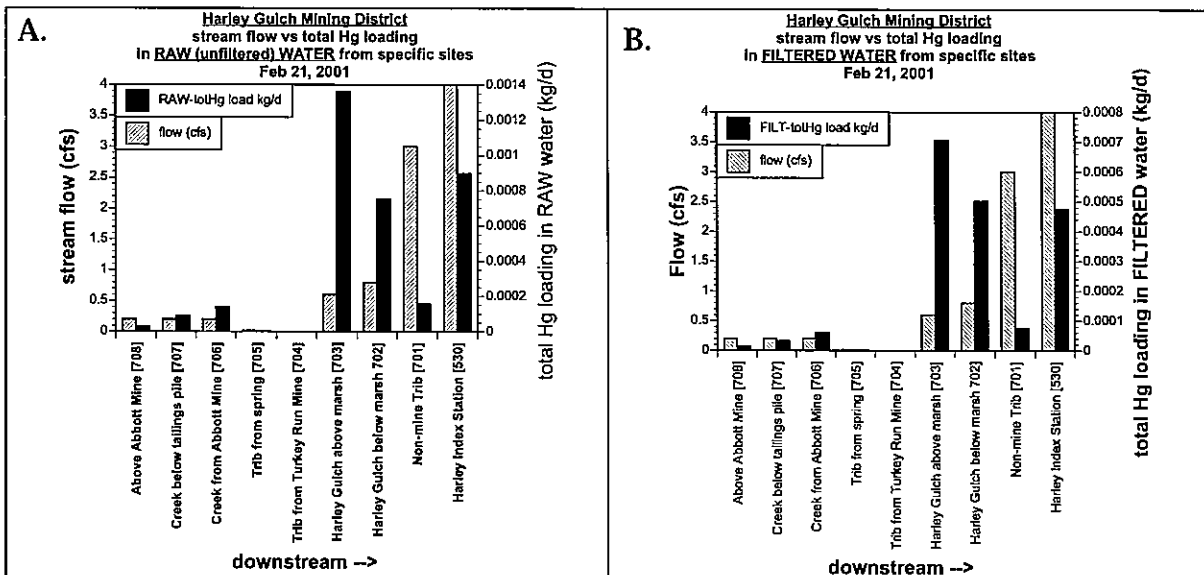


Figure 15A. Stream flow and estimated daily total Hg loading from specific stream sites in the Harley Gulch Mining Region derived from RAW water samples collected on Feb 21, 2001.

Figure 15B. Stream flow and estimated daily total Hg loading from specific stream sites in the Harley Gulch Mining Region derived from FILTERED water samples collected on Feb 21, 2001. Note the different scale for the Hg concentrations in B.

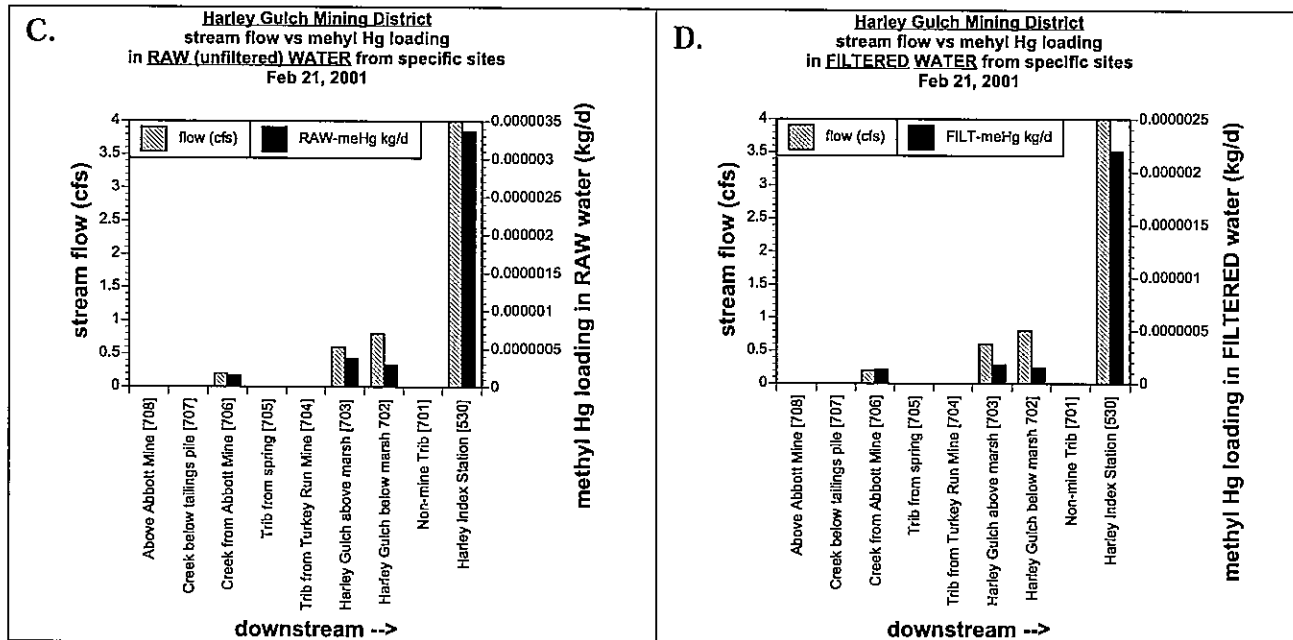


Figure 15C. Stream flow and estimated daily methyl Hg loading from specific stream sites in the Harley Gulch Mining Region derived from RAW water samples collected on Feb 21, 2001.

Figure 15D. Stream flow and estimated daily methyl Hg loading from specific stream sites in the Harley Gulch Mining Region derived from FILTERED water samples collected on Feb 21, 2001. Note the different scale for the Hg concentrations in B.

A comparison chart providing loading data for RAW and FILTERED total Hg as well as RAW and FILTERED methyl Hg is provided in Figure 16.

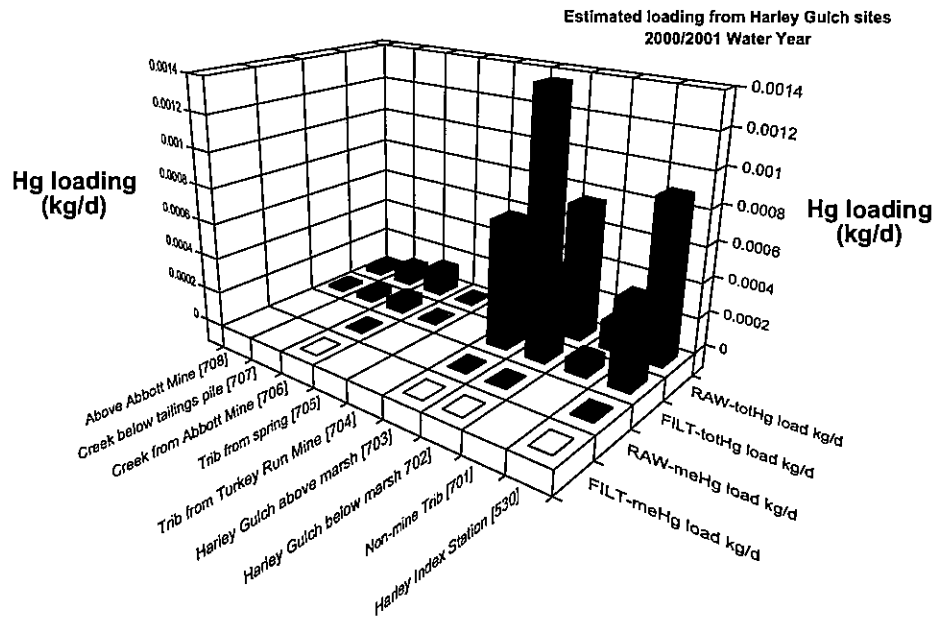


Figure 16. Comparison of daily total Hg and methyl Hg loading for RAW (unfiltered) and FILTERED water from specific sites within the Harley Gulch Mining Region. Based on hand collected flow measurements and aqueous Hg analyses from Feb 21, 2001. Note: sites are arranged from left to right in relation to their upstream to downstream locations, with the Index Station (HAR-530) on the right representing the furthest site downstream.

Because the USGS gauging station at Harley Gulch was not functional during the 2000/2001 water year, it was not possible to obtain daily or monthly flow estimates, which made it impossible to estimate monthly and annual Hg loading from the Harley Gulch Mining Region for that water year.

Sulphur Creek - 2000:

No specific local flow rates were quantified by hand for sites within the Sulphur Creek Mining Region in the year 2000. Therefore, no site-specific estimates of loading for local features was possible. However, flow rates from the Index Station at Sulphur Creek provided sufficient data to calculate projected monthly and annual loading projections for that year.

Figure 17 provides estimated monthly maximum, mean and minimum total Hg loading from the Sulphur Creek Mining Region for the 1999/2000 water year, indicating (and similar to the Harley Gulch system) that the greatest Hg loading occurred in the time period from January through April, with the highest monthly loading estimated for February at 5.25 kg/month. Figure 18 provides a cumulative estimate of maximum, mean and minimum annual Hg loading from this region for the 1999/2000 water year only, with average estimates ranging from 0.6-10.7 kg/yr. This loading is likely derived from a combination of mining wastes and geothermal spring activity.

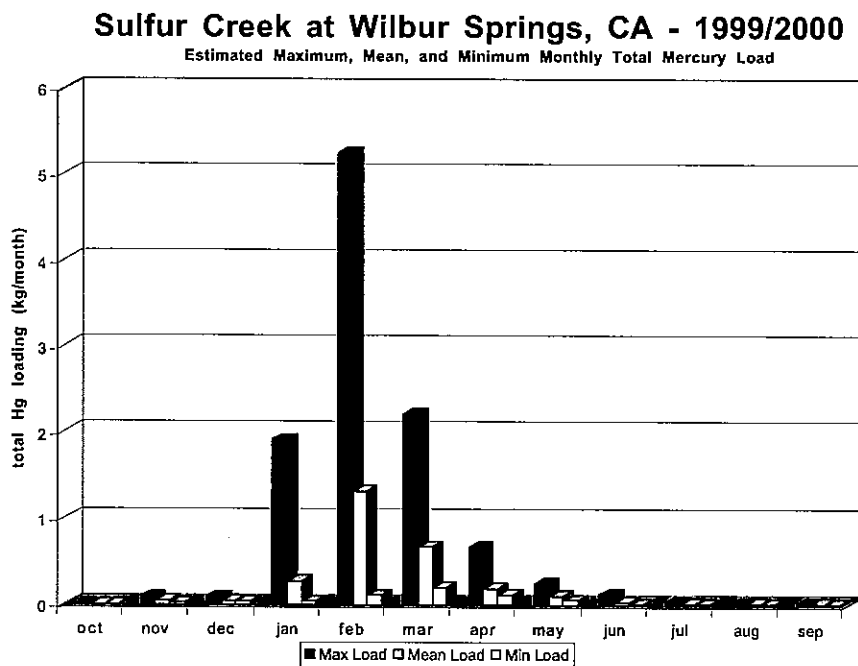


Figure 17. Estimated maximum, mean and minimum monthly loading of total Hg (kg/month) from the Sulphur Creek Mining District during the 1999/2000 water year.

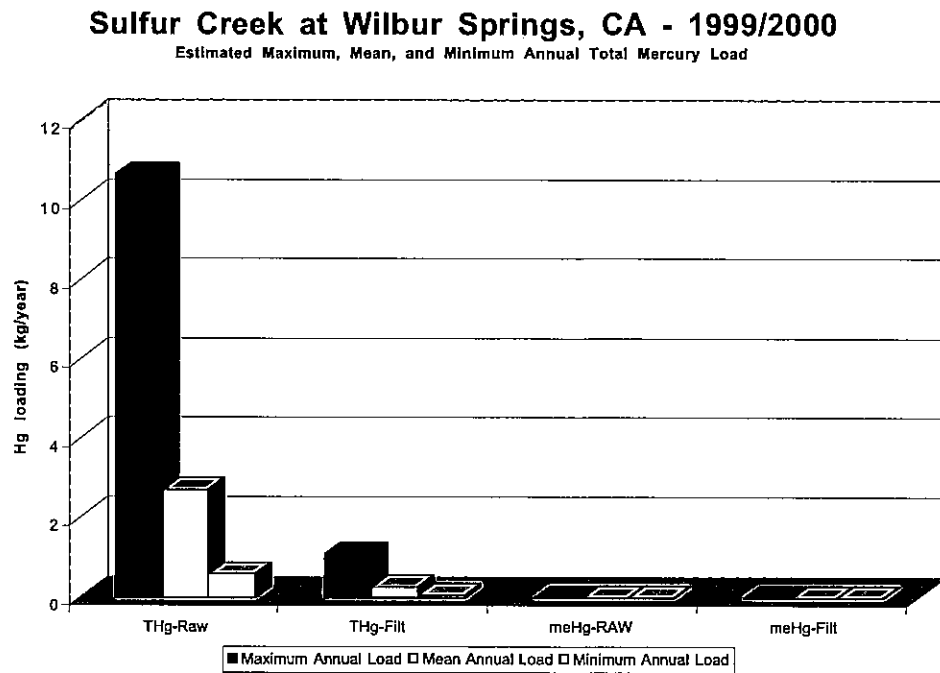


Figure 18. Estimated maximum, mean and minimum annual loading of total Hg and methyl Hg (kg/yr) from the Sulfur Creek Mining District during the 1999/2000 water year only.

Sulphur Creek - 2001:

From the flow rates measured at each stream station by hand, together with the aqueous Hg concentrations at those sites, we calculated daily loading rates for specific local stretches of the streams in each region. Figures 19A and 19B provide both stream flow (in cfs) and daily total Hg loading estimates (in kg/d) for sites within the Sulphur Creek region for February 22, 2001 (the sampling date).

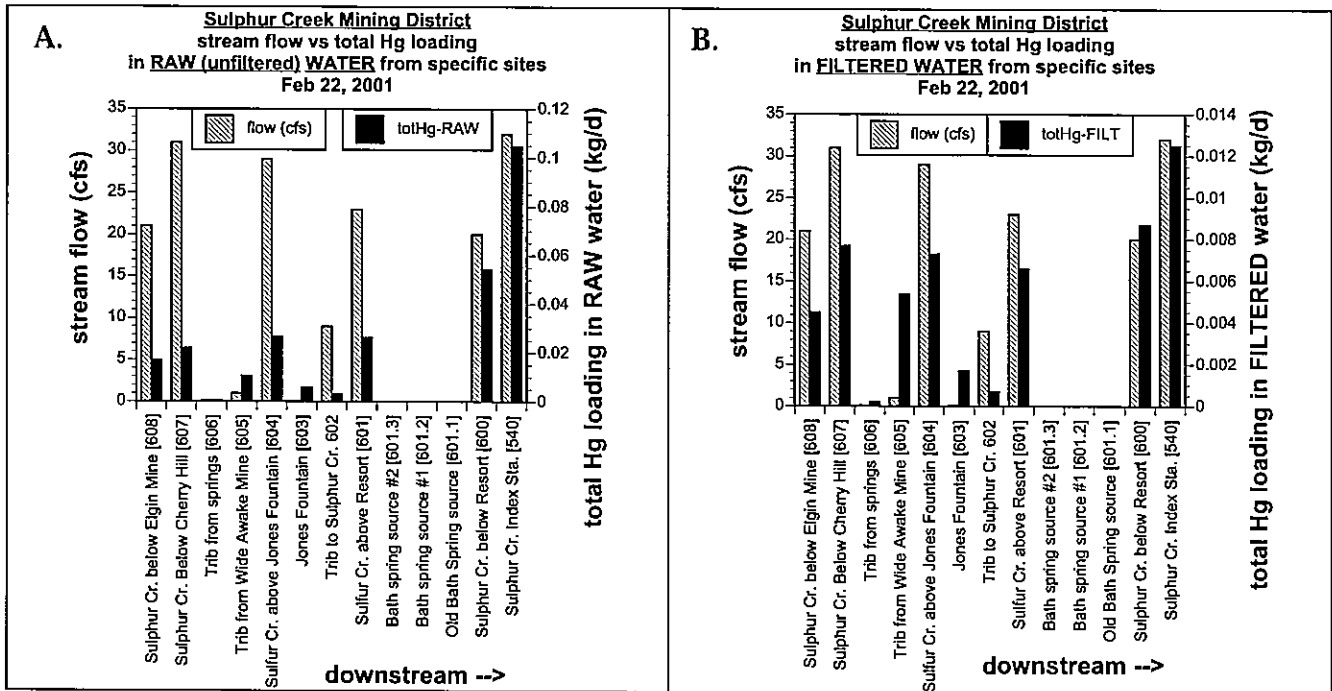


Figure 19A. Stream flow and estimated daily total Hg loading from specific stream sites in the Sulphur Creek Mining Region derived from RAW water samples collected on Feb 22, 2001.

Figure 19B. Stream flow and estimated daily total Hg loading from specific stream sites in the Harley Gulch Mining Region derived from FILTERED water samples collected on Feb 22, 2001. Note the different scale for the Hg concentrations in B.

Figure 19C and 19D provide both stream flow (in cfs) and daily methyl Hg loading estimates (in kg/d) for sites within the Sulphur Creek region for February 22, 2001 (the sampling date).

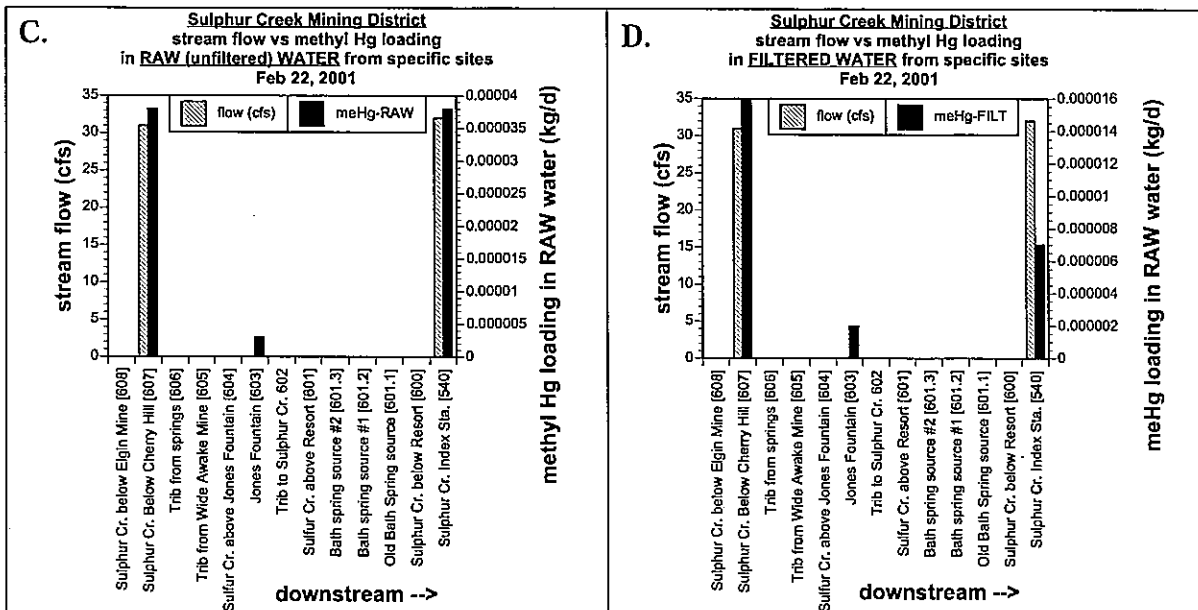


Figure 19C. Stream flow and estimated daily methyl Hg loading from specific stream sites in the Sulphur Creek Mining Region derived from RAW water samples collected on Feb 22, 2001.

Figure 19D. Stream flow and estimated daily methyl Hg loading from specific stream sites in the Sulphur Creek Mining Region derived from FILTERED water samples collected on Feb 22, 2001. Note the different scale for the Hg concentrations in B.

Figure 20 provides a comparison for daily total Hg and methyl Hg loading data derived from RAW and FILTERED water samples on Feb 22, 2001. Note that most loading is in particulate form.

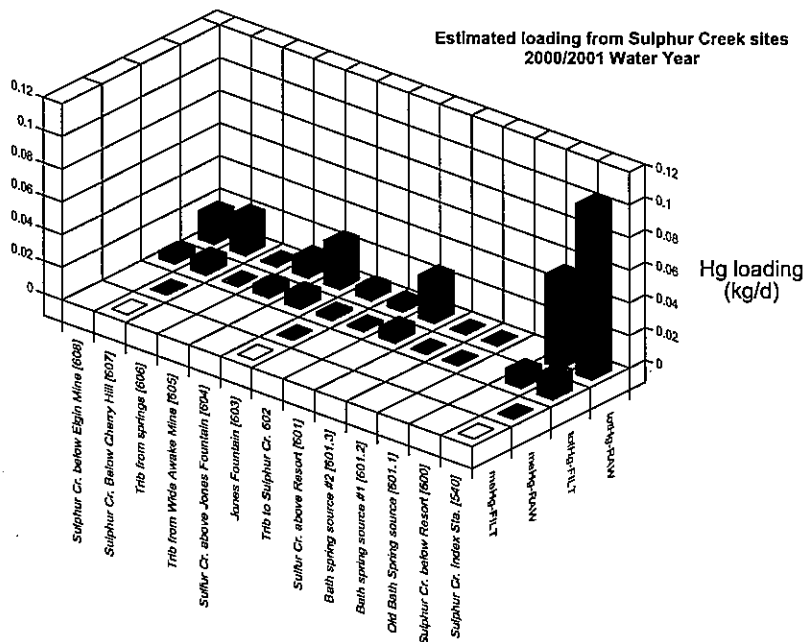


Figure 20. Comparison of daily total Hg and methyl Hg loading for RAW (unfiltered) and FILTERED water from specific sites within the Sulphur Creek Mining Region. Based on hand collected flow measurements and aqueous Hg analyses from Feb 22, 2001. Note: sites are arranged from left to right in relation to their upstream to downstream locations, with the Index Station (SUL-540) representing the furthest site downstream.

Figure 21 provides estimated monthly maximum, mean and minimum total Hg loading from the Sulphur Creek Mining Region for the 2000/2001 water year, indicating that the greatest Hg loading for this year occurred in the same general time period as the previous year (from January through April), with the range of total Hg loading estimated for March at 0.16-9.65 kg/month. Figure 22 provides a cumulative estimate of maximum, mean and minimum annual Hg loading from this region for the 2000/2001 water year only, with average estimates ranging from 0.6-17.1 kg/yr. This loading is likely derived from a combination of mining wastes and geothermal spring activity.

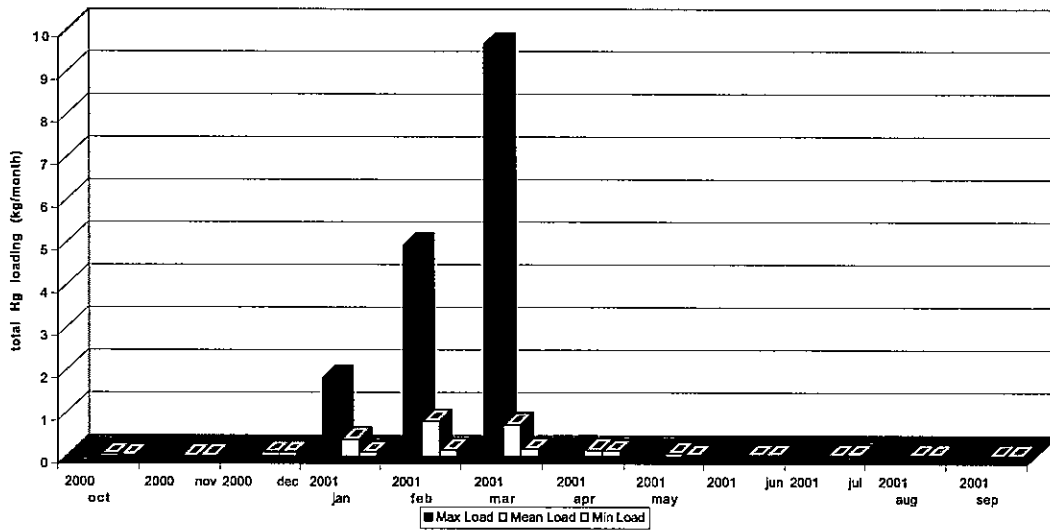


Figure 21. Estimated monthly loading of total Hg (kg/month) from the Sulphur Creek Mining Region during the 2000/2001 water year.

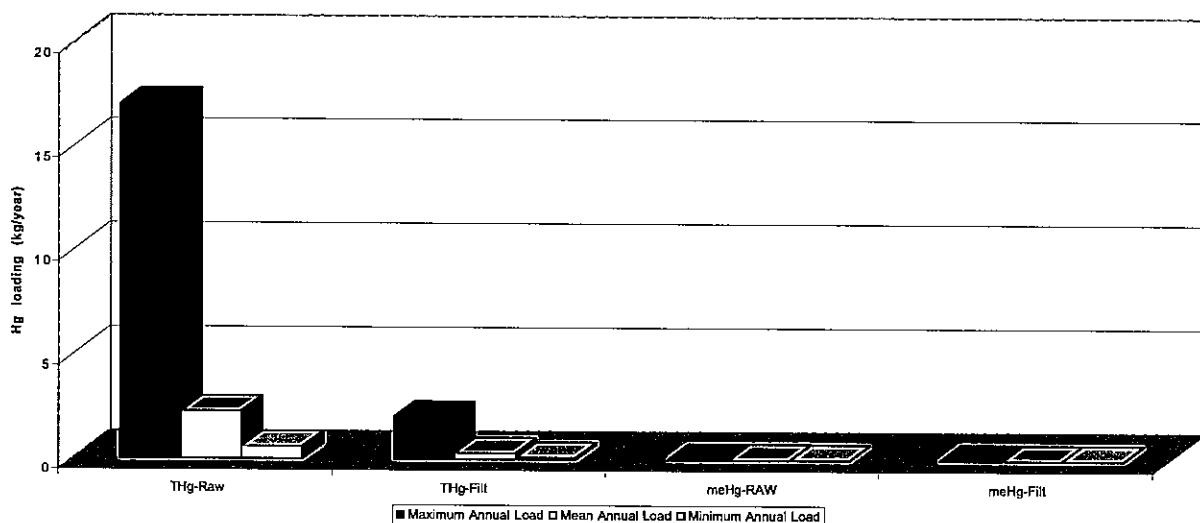


Figure 22. Estimated maximum, mean and minimum annual loading of total Hg and methyl Hg (kg/yr) from the Sulphur Creek Mining Region during the 2000/2001 water year only.

In summary, estimates of Hg loading from the Sulphur Creek mining and geothermal spring region were about 10 times greater than those from the Harley Gulch region. In the long-term context of watershed Hg loading influenced by erosion from rainfall events, the stream flow rates during the two years in this study were only about 55% of the long-term average. Thus, during much heavier rainfall we might predict that more Hg-laden erodable materials would be mobilized and transported downstream. However, within the flow rates observed during this study, plots of total Hg and methyl Hg versus flow rates for both RAW water and FILTERED water exhibited no statistically significant relationships. Thus, we do not have estimates or predictions of how those more extreme events would affect long-term Hg loading and cannot use other years' flow data to predict loading in higher precipitation years which would naturally yield higher flow rates.

SEDIMENT (FLOC) MICROCOSM EXPERIMENT:

Aqueous methyl Hg concentrations were quantified from the water in experimental teflon core tubes under oxic (air sparged) and anoxic (nitrogen sparged) treatments. Methyl Hg concentrations in all cases except one were below the minimum detectable level. Table 3 provides raw data for this test and shows that after a five day incubation period (November 10-15, 2000), the final methyl Hg concentrations were negligible. These results are in sharp contrast to those found in a comparable microcosm experiment at Clear Lake, where net production of methyl Hg ranged from 0.01-0.05 ng/cm². Because virtually all of the analytical results were below the detection level, it was not impossible to calculate net production from the sediments in this experiment. These data do suggest that the floc which accumulates immediately below the *Jones Fountain of Life* has a very low potential to produce methyl Hg.

Table 3. Raw data for aqueous methyl Hg and total Hg in water samples collected during the preliminary microcosm experiment. The “U” qualifier indicates values that were measured but were below the MDL (minimum detectable level) of the analytical instrument.

SAMPLE	TEST	Value	Qual	units	TEST	Value	units	
Water: Day 0	00-11-260	MeHg	0.0214	U	ng/L	Total Hg	0.822	ng/L
Oxic: Floc day 2.5 - Rep 1	00-11-261	MeHg	0.0365	U	ng/L			
Oxic: Floc day 2.5 - Rep 2	00-11-262	MeHg	0.0351	U	ng/L			
Oxic: Water Blank - Day 2.5	00-11-263	MeHg	0.0214	U	ng/L			
Anoxic: Floc day 2.5 - Rep 1	00-11-264	MeHg	0.0338	U	ng/L			
Anoxic: Floc day 2.5 - Rep 2	00-11-265	MeHg	0.0317	U	ng/L			
Anoxic: Water Blank - Day 2.5	00-11-266	MeHg	0.0217	U	ng/L			
Holding Water: Day 2.5	00-11-273	MeHg	0.0213	U	ng/L	Total Hg	0.612	ng/L
Oxic: Floc day 5.0 - Rep 1	00-11-267	MeHg	0.0217	U	ng/L			
Oxic: Floc day 5.0 - Rep 2	00-11-268	MeHg	0.0214	U	ng/L			
Oxic: Water Blank- day 5.0	00-11-269	MeHg	0.0214	U	ng/L			
Anoxic: Floc day 5.0 - Rep 1	00-11-270	MeHg	0.0209	U	ng/L			
Anoxic: Floc day 5.0 - Rep 2	00-11-271	MeHg	0.0501		ng/L			
Holding Water: Day 5.0	00-11-272	MeHg	0.0211	U	ng/L			

QA/QC data, including results from laboratory spikes, splits, equipment blanks, etc. for Hg analyzed in the microcosm experiment are provided in Appendix 9.

PRELIMINARY METHYLATION TRIALS:

As discussed briefly during the December 2000 CALFED Review Committee meeting in Moss Landing, we conducted a preliminary incubation trial at UC Davis in November 2000 using (1) Abbott Mine sieved tailings (94% solids, 336 ppm totHg) and (2) Sulphur Creek floc precipitate (36% solids, 9.65 ppm totHg) as SOURCE materials and Venice Cut peat sediment (13% solids, 0.14 ppm totHg) from the Delta as the RECEIVING material. SOURCE materials were collected on 11/8/00 and RECEIVING sediment was collected on 11/13/00, with the incubation trial running from 11/14/00-11/22/00. By mixing SOURCE spike material with site water (to ensure proper and consistent mixing), the various SOURCE materials were mixed and diluted with RECEIVING materials to produce a final total Hg concentration in the combined slurry mixture of: 0.02 ppm, 0.2 ppm and 2.0 ppm. Two parts water were then mixed to one part sediment mixture to produce the final slurry. During the mixing process, the entire mixture was sparged with N₂. Slurry mixtures were incubated in stoppered and taped 4 oz jars (anoxic conditions) under agitation, at room temperature (20-22°C) for 8 days. Methyl Hg concentrations at times 0, 4 and 8 days were analyzed (using extraction method) at Battelle Northwest Laboratories, and are reported in Figure 23 below.

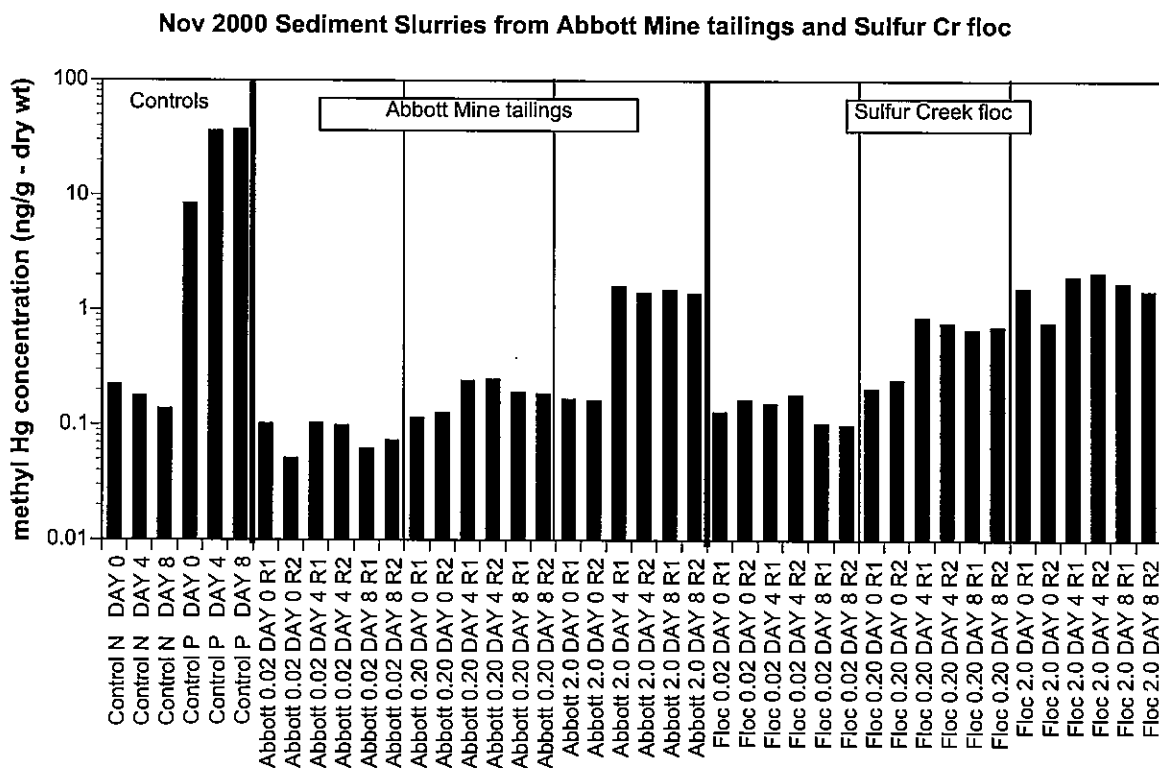


Figure 23. Analytical results from the preliminary incubation trial in Nov 2000. Control N represents Venice Cut peat RECEIVING material with no SOURCE materials added. Control P represents Venice Cut peat RECEIVING material with 1 ppm mercuric chloride added.

In these trials, methyl Hg production was relatively consistent for each treatment. Source material from both Abbott Mine and from Jones Fountain of Life floc yielded approximately a 3-5 factor increase in the concentration of methyl Hg over the 8-day trial. In addition, except at the lowest Hg concentrations, there appeared to be a significant increase in methyl Hg over the 8-day trial period, especially for days 4 and 8. These preliminary results were encouraging and suggested that there are potentially significant differences (in some cases ca. an order of magnitude) between highly bioavailable mercuric chloride (Control P) and the slurry mixtures produced from the Abbott Mine tailings and the Sulphur Creek floc. We were hopeful that the experimental design we had outlined above and below would provide meaningful insights into the relative bioavailability of various source materials from the upper Cache Creek mining regions when they were mixed with downstream receiving sediments.

QA/QC data, including results from laboratory spikes, splits, equipment blanks, etc. for Hg analyzed in the preliminary incubation trials are provided in Appendix 10.

Because of funding and logistical limitations, we were forced to limit the number of SOURCE and RECEIVING materials. The sediments ultimately chosen for these methylation trials and collected by the U.C. Davis group were as follows.

Four SOURCE MATERIALS:

- 1) Abbott Mine tailings pile: fine grained sieved particulate material from the main waste pile.
- 2) Turkey Run Mine waste material that appeared to have the potential to become mobilized during precipitation events
- 3) Manzanita Mine (Sulphur Creek region) tailings pile: fine grained sieved particulate material
- 4) Floc precipitate material from below geothermal spring on Sulphur Creek

One RECEIVING material:

- 1) Accumulated sediments from the depositional environment of Cache Creek immediately upstream of the Capay Dam

These SOURCE materials and RECEIVING material were transported (on ice) to Frontier Geosciences where the trials took place. See report by N. Bloom for results of these trials.

Data from the follow-on 7-day incubation experiments (conducted in December 2000) reported by Bloom and Preus (using the same source materials provided by U.C. Davis used in the incubation trials above) suggest a much more significant difference in methyl Hg production between mine sediments from the Abbott Mine and the floc collected immediately below the Jones Fountain of Life in Sulphur Creek. Our 8-day trial yielded about a 3-5 fold increase in methyl Hg concentrations for the two types of source materials and the HgCl₂. Bloom and Preus reported a similar increase for the Jones Fountain of Life floc (2.8 X), but the Abbott Mine tailings yielded a much higher (74 fold) increase. Because there were significant differences in the relative reported bioavailability of Hg from Harley Gulch sediments (Abbott Mine source material) versus Sulphur Creek floc (derived from the Jones Fountain of Life), and because there were some adjusted methods used for the latter trials, it is unclear why there was such a discrepancy between our preliminary results and those later results reported by Bloom and Preus.

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ACKNOWLEDGEMENTS

The U.S. Geological Survey (USGS) contributed significantly to the development and production of this report. USGS personnel, specifically Charles Alpers and Joseph Domagalski, cooperated and collaborated with us to produce independent estimates of Hg loading. USGS also ran the elemental suite analyses on stream and geothermal spring waters provided in Appendix 2 and Appendix 3.

APPENDIX 1. Water quality data from Hydrolab™ multi-probe unit on mine site waters from February 2001.

Site ID	Time	Temp	DO (ppm)	DO%	Cnd (uS)	SpC(uS)	pH	orp (mV)
HARLEY GULCH								
HAR-530	1036	8.14	5.88	50.2	0.763	1.12	8.29	232.8
ATM-701	1050	7.88	6.47	54.6	0.363	0.54	8.12	243.8
ATM-702	1107	8.79	5.72	49.9	2.151	3.11	8.02	242.8
ATM-703	1135	10.01	5.13	45.9	1.072	1.48	8.1	241.9
ATM-704	1200	na	na	na	na	na	na	na
ATM-705	1215	17.43	3.48	37.3	5.75	6.72	8.06	231
ATM-709	1248	27.5	1.04	13.1	7.275	6.92	6.55	-169.2
ATM-706	1340	10.37	1.62	14.5	0.922	1.27	8.7	47.2
ATM-707	1405	9.22	1.53	13.3	0.488	0.7	8.37	75.3
ATM-708	1500	8.52	1.41	12.1	0.286	0.41	8.08	104.1
SULPHUR CREEK								
SUL-540	1010	6.96	0.56	4.7	1.41	2.15	8.14	111.6
SCM-600	1040	7.15	0.51	4.3	1.377	2.09	8.09	-37.4
SCM-601.1	1145	51.45	7.74	135.1	45.096	30	6.71	-413
SCM-601.2	1155	na	na	na	na	na	na	na
SCM-601.3	1215	na	na	na	na	na	na	na
SCM-601	1310	9.52	0.6	5.3	0.933	1.32	7.98	-34.8
SCM-602	1355	8.23	0.41	3.7	0.299	0.44	8.72	-183.8
SCM-603	1334	53.18	-1.14	-24.5	44.93	26.42	7.28	-410.8
SCM-604	1415	9.77	0.5	4.5	0.864	1.21	8.4	-185.1
SCM-606	1500	15.96	0.19	2	7.179	8.67	7.97	-306.6
SCM-605	1515	9.95	0.44	na	1.388	1.94	8.46	-160.1
SCM-607	1540	9.5	0.59	5.2	0.796	1.12	8.39	-143.5
SCM-608	1610	8.7	0.65	5.6	0.675	0.97	8.38	-86.4

Mercury Loading and Source Bioavailability from the Upper Cache Creek Mining Districts

APPENDIX 2A. Total elemental suite data from the Harley Gulch sites on February 21, 2001. Samples analyzed by USGS.

Elemental Suite - USGS analyses - ABBOTT/TURKEY RUN MINING REGION (Feb-2001)													
Site	Sample Date	ATM-701		ATM-702		ATM-706		ATM-708		ATM-709		HARS530	
		2/22/05	2/22/05	2/22/05	2/22/05	2/22/05	2/22/05	2/22/05	2/22/05	2/22/05	2/22/05	2/22/05	2/22/05
Sample No	Sample Time	1 of 2	2 of 2	1 of 2	2 of 2	1 of 2	2 of 2	1 of 2	2 of 2	1 of 2	2 of 2	1 of 2	2 of 2
Al	µg/L	1500	1600	200	200	340	340	1600	1600	160	130	1200	1100
	SD	100	100	10	20	30	100	100	200	10	10	0	100
As	µg/L	<20	<20	<20	<20	<20	<20	<20	<20	<50	<50	<20	<20
	SD	10	20	10	10	10	10	20	10	70	90	20	10
B	µg/L	440	510	16,000	16,000	2,300	2,100	650	750	37,000	37,000	3,500	3,500
	SD	50	0	0	4,000	400	300	50	220	4,000	2,000	400	300
Ba	µg/L	46	44	31	34	38	38	55	54	38	39	41	43
	SD	2	2	4	3	4	5	3	3	4	4	2	1
Be	µg/L	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
	SD	0.1	0.0	0.0	0.0	0.1	0.2	0.3	0.2	0.03	0.01	0.0	0.0
Bi	µg/L	0.099	0.046	0.010	0.015	0.007	<0.006	0.011	0.011	0.013	0.013	0.008	0.006
	SD	0.117	0.011	0.005	0.006	0.004	0.002	0.003	0.002	0.005	0.005	0.002	0.003
Ca	mg/L	21	22	42	42	46	45	26	25	51	53	27	26
	SD	0	2	1	9	4	2	0	2	5	6	1	1
Cd	µg/L	<0.03	<0.03	<0.03	<0.03	<0.03	0.05	0.17	0.05	0.10	0.10	<0.03	<0.03
	SD	0.00	0.01	0.02	0.03	0.02	0.12	0.30	0.10	0.01	0.02	0.03	0.03
Ce	µg/L	0.62	0.62	0.090	0.085	0.15	0.16	0.71	0.70	0.26	0.25	0.48	0.50
	SD	0.03	0.02	0.016	0.006	0.02	0.02	0.04	0.04	0.02	0.02	0.00	0.01
Co	µg/L	0.42	0.41	0.03	0.04	0.03	0.02	0.86	0.77	0.18	0.13	0.31	0.31
	SD	0.01	0.03	0.03	0.04	0.04	0.02	0.29	0.04	0.03	0.04	0.02	0.04
Cr	µg/L	7	8	8	8	7	6	9	9	7	6	7	7
	SD	0	0	2	2	1	2	1	1	1	1	0	0
Cs	µg/L	0.6	<0.6	2.1	2.2	<0.6	0.7	0.6	<0.6	77	79	1.8	0.8
	SD	0.8	0.1	0.3	0.2	0.3	0.2	0.3	0.2	5	6	0.0	0.0
Cu	µg/L	5.9	5.8	2.3	1.8	2.9	3.1	5.2	5.0	1.9	1.5	4.5	4.5
	SD	0.1	0.0	0.2	0.2	0.1	0.2	0.6	0.2	0.2	0.3	0.3	0.2
Dy	µg/L	0.089	0.084	0.017	0.017	0.024	0.022	0.091	0.084	0.049	0.040	0.072	0.079
	SD	0.005	0.001	0.001	0.001	0.002	0.004	0.010	0.008	0.008	0.006	0.009	0.008
Er	µg/L	0.047	0.027	0.012	0.016	0.009	0.013	0.041	0.038	0.039	0.039	0.025	0.034
	SD	0.000	0.006	0.000	0.004	0.003	0.001	0.005	0.008	0.004	0.007	0.002	0.005
Eu	µg/L	0.076	0.022	0.003	0.003	0.007	0.008	0.023	0.023	0.008	0.011	0.020	0.024
	SD	0.003	0.001	0.001	0.001	0.002	0.001	0.005	0.001	0.002	0.004	0.001	0.001
Fe	µg/L	1600	1600	190	170	410	340	1,900	1,800	630	600	1,300	1,300
	SD	100	0	20	50	30	100	30	100	0	60	100	100
Gd	µg/L	0.09	0.10	0.02	0.02	0.02	0.03	0.10	0.10	0.044	0.046	0.08	0.07
	SD	0.01	0.01	0.00	0.00	0.00	0.00	0.01	0.01	0.010	0.005	0.01	0.01
Ho	µg/L	0.015	0.014	0.0047	0.0042	0.0048	0.0039	0.015	0.015	0.018	0.017	0.014	0.013
	SD	0.000	0.002	0.0002	0.0004	0.0011	0.0006	0.002	0.002	0.001	0.004	0.000	0.001
K	mg/L	1.3	1.2	9.3	10	3.3	2.8	1.8	1.7	38	38	2.7	2.7
	SD	0.3	0.0	1.2	4	0.6	0.3	0.2	0.1	4	5	0.5	0.5
La	µg/L	0.25	0.23	0.025	0.026	0.056	0.055	0.26	0.25	0.098	0.091	0.19	0.18
	SD	0.02	0.02	0.004	0.000	0.005	0.010	0.03	0.02	0.006	0.005	0.00	0.00
Li	µg/L	25	25	510	570	110	110	26	26	2,100	2,100	130	130
	SD	0	0	40	50	10	10	3	2	100	0	10	10
Lu	µg/L	0.0016	0.0042	0.0011	<0.0007	0.0016	0.0017	0.0048	0.0039	0.004	0.005	0.0048	0.0042
	SD	0.0007	0.0006	0.0006	0.0002	0.0007	0.0003	0.0006	0.0003	0.0003	0.0002	0.0004	0.0001
Mg	mg/L	46	50	300	300	140	130	35	33	630	630	100	100
	SD	0	6	10	70	30	20	0	4	20	30	0	5
Mn	µg/L	<7	<7	<7	<7	<7	<7	19	19	140	140	<7	<7
	SD	3	2	2	0	1	1	4	3	0	0	0	0
Mo	µg/L	1.0	0.9	1.4	1.6	1.0	1.4	2.3	1.0	<0.1	<0.1	1.0	1.1
	SD	0.4	0.3	0.1	0.1	0.1	0.7	3.1	0.8	0.1	0.0	0.1	0.2
Nb	µg/L	30	29	400	450	97	85	36	36	1,000	1,000	100	99
	SD	3	3	10	40	9	17	3	3	100	0	0	5
Nd	µg/L	0.42	0.39	0.050	0.045	0.097	0.091	0.45	0.47	0.17	0.16	0.31	0.31
	SD	0.031	0.02	0.006	0.002	0.006	0.002	0.03	0.04	0.01	0.02	0.01	0.01
Ni	µg/L	9.0	8.9	9.2	9.7	10.0	10.0	18	18	5.3	4.7	8.7	8.6
	SD	0.4	0.3	0.3	1.2	0.8	1.1	2	1	0.3	0.1	0.0	0.1
Pb	µg/L	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.07	0.08	<0.5	<0.5
	SD	0.2	0.2	0.2	0.2	0.3	0.2	0.6	0.1	0.09	0.07	0.1	0.1
Pr	µg/L	0.091	0.097	0.011	0.011	0.021	0.023	0.10	0.095	0.027	0.026	0.069	0.073
	SD	0.006	0.001	0.003	0.002	0.003	0.002	0.01	0.007	0.003	0.003	0.002	0.005
Rb	µg/L	1.6	1.6	6.3	7.0	1.5	1.6	1.5	1.5	97	95	2.5	2.5
	SD	0.1	0.1	0.6	0.5	0.2	0.2	0.1	0.1	2	8	0.1	0.1
Re	µg/L	0.008	0.010	0.014	0.011	0.016	0.016	0.003	0.004	<0.002	<0.002	0.009	0.008
	SD	0.002	0.000	0.001	0.002	0.005	0.002	0.002	0.003	0.001	0.001	0.005	0.005
S	mg/L	35	36	290	290	170	180	33	32	500	500	89	88
	SD	0	4	10	60	0	10	1	3	0	20	2	3
Sb	µg/L	0.23	0.17	0.87	1.0	0.86	0.93	0.56	0.37	<0.05	0.15	0.29	0.31
	SD	0.10	0.01	0.04	0.1	0.06	0.15	0.57	0.22	0.03	0.11	0.03	0.00
Se	µg/L	3	4	12	13	4	4	3	3	6	5	5	5
	SD	1	0	0	1	1	0	0	0	1	1	1	1
SiO2	mg/L	16	16	19	20	18	16	24	23	74	74	17	16
	SD	0	2	0	4	2	3	0	2	5	4	1	1
Sm	µg/L	0.10	0.091	0.006	0.017	0.028	0.022	0.11	0.11	0.040	0.041	0.071	0.074
	SD	0.01	0.008	0.002	0.006	0.005	0.002	0.02	0.02	0.008	0.008	0.003	0.008
Sr	µg/L	370	370	840	940	610	630	280	290	3,000	3,100	480	480
	SD	20	20	80	80	50	80	20	30	200	200	20	20
Tb	µg/L	0.017	0.014	0.002	<0.002	0.004	0.003	0.014	0.014	0.0087	0.0077	0.012	0.011
	SD	0.000	0.002	0.001	0.000	0.002	0.001	0.001	0.001	0.0015	0.0003	0.001	0.001
Te	µg/L	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	0.8	0.7	<0.1	<0.1
	SD	0.1	0.0	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.0	0.0
Th	µg/L	0.024	0.023	0.012	0.013	0.010	0.013	0.030	0.021	0.004	0.010	0.027	0.021
	SD	0.006	0.002	0.007	0.006	0.002	0.004	0.014	0.001	0.003	0.001	0.001	0.000
Tl	µg/L	0.08	<0.01	0.04	0.13	0.03	0.18	0.03	<0.01	<0.02	<0.02	<0.01	<0.01
	SD	0.17	0.01	0.03	0.13	0.01	0.27	0.08	0.02	0.02	0.00	0.03	0.01
Tm	µg/L	0.0045	0.0056	0.0016	0.0012	0.0022	0.0019	0.0046	0.0045	0.003	0.003	0.0048	0.0038

APPENDIX 4A. Data and QA/QC Report for RAW (unfiltered) water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/14/00 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 1 of 4.

U.C. Davis
 CALFED Cache Creek
 February 2000
 Results Summary

Analysis: Total Mercury, Methyl Mercury
 Method: SOP MSL-J-013-02 (Total), SOP MSL-J-014-01 (Methyl)
 Matrix: Raw Water
 Laboratory: Battelle/MSL

Sample Received	Sample Description	Sample ID	MSL Lab ID	Field QC	Test	Batch	Value	Flag	Units	Test	Batch	Value	Flag	Units
021500	HAR-560-RAW-021400	1459*20			Total Hg	022400HGA	432		ng/L	MeHg	021600MEB	0.354		ng/L
021500	SUL-550-RAW-021400	1459*21			Total Hg	022400HGA	974		ng/L	MeHg	021600MEB	0.456		ng/L
021500	ATM-701-RAW-021400	1459*22			Total Hg	030300HGA	135		ng/L					
021500	ATM-702-RAW-021400	1459*23			Total Hg	030200HGA	2070		ng/L					
021500	ATM-703-RAW-021400	1459*24			Total Hg	030200HGA	1930		ng/L					
021500	ATM-704-RAW-021400	1459*25			Total Hg	030600HGA	7070		ng/L					
021500	ATM-705-RAW-021400	1459*26			Total Hg	030200HGA	404		ng/L					
021500	ATM-706-RAW-021400	1459*27			Total Hg	030200HGA	1650		ng/L					
021500	ATM-707-RAW-021400	1459*28			Total Hg	030200HGA	1910		ng/L					
021500	ATM-DUP-RAW-021400	1459*29		DUP	Total Hg	030200HGA	1530		ng/L					
021500	ATM-708-RAW-021400	1459*30			Total Hg	030200HGA	181		ng/L					
021500	ATM-709-RAW-021400	1459*31			Total Hg	030200HGA	4.32		ng/L					
021500	SCM-601-RAW-021400	1459*32			Total Hg	030200HGA	620		ng/L					
021500	SCM-602-RAW-021400	1459*33			Total Hg	030200HGA	673		ng/L					
021500	SCM-DUP-RAW-021400	1459*34		DUP	Total Hg	030200HGA	229		ng/L					
021500	SCM-603-RAW-021400	1459*35			Total Hg	030200HGA	24300		ng/L					
021500	SCM-604-RAW-021400	1459*36			Total Hg	030200HGA	386		ng/L					
021500	SCM-605-RAW-021400	1459*37			Total Hg	030200HGA	2450		ng/L					
021500	SCM-606-RAW-021400	1459*38			Total Hg	030200HGA	1110		ng/L					
021500	SCM-607-RAW-021400	1459*39			Total Hg	030200HGA	230		ng/L					
021500	SCM-608-RAW-021400	1459*40			Total Hg	030200HGA	340		ng/L					

Approvals: _____

Project Manager: _____ Date: _____

QA/QC Reviewer: _____ Date: _____

APPENDIX 4B. Data and QA/QC Report for RAW (unfiltered) water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/14/00 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 2 of 4.

QA/QC Results:

METHOD BLANKS

BLANK 1	RB022400	Total Hg	022400HGA	0.0910	ng/L
BLANK 1	RB030200	Total Hg	030200HGA	0.159	ng/L
BLANK 1	RB030600	Total Hg	030600HGA	0.0357	ng/L
Blank-1	BLK021600			MeHg	021600MEB 0.0509 ng/L

STANDARD REFERENCE MATERIAL

Standard Reference Material	1641c	Total Hg	022400HGA	1470000	ng/L
Certified Value	1641c	Total Hg	030200HGA	1630000	ng/L
Percent Recovery	1641c	Total Hg	030600HGA	1620000	ng/L
		Total Hg		1470000	ng/L
		Percent Recovery		100	%
				111	%
				110	%

Standard Reference Material

Certified Value	DORM-2	MeHg	021600MEB	3.70	µg/g
Percent Recovery				4.47	%
				83	%

TAP WATER SPIKE RESULTS

Amount Spiked		Total Hg		4.84	ng/L
Tap Water		Total Hg	022400HGA	0.226	ng/L
Tap Water + Spike		Total Hg	022400HGA	5.20	ng/L
Amount Recovered		Total Hg		4.98	ng/L
Percent Recovery		Total Hg		103	%

Amount Spiked

Tap Water		Total Hg		4.84	ng/L
Tap Water + Spike	run 1	Total Hg	030300HGA	0.211	ng/L
Amount Recovered		Total Hg	030300HGA	5.44	ng/L
Percent Recovery		Total Hg		5.23	ng/L
		Total Hg		108	%

TAP WATER SPIKE RESULTS

Amount Spiked		Total Hg		4.84	ng/L
Tap Water		Total Hg	030200HGA	0.211	ng/L
Tap Water + Spike	run 2	Total Hg	030200HGA	5.51	ng/L
Amount Recovered		Total Hg		5.30	ng/L
Percent Recovery		Total Hg		109	%

APPENDIX 5A. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/14/00 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 1 of 3.

U.C. Davis
 CALFED Cache Creek
 February 2000
 Results Summary

Analysis: Total Mercury, Methyl Mercury
 Method: SOP MSL-J-013-02 (Total Hg), SOP MSL-I-014-01 (Methyl Hg)
 Matrix: Filtered Water
 Laboratory: Battelle/MSL

Sample Received	Sample Description	Sample ID	MSL Lab ID	Field QC	Test	Batch	Value	Flag	Units	Test	Batch	Value	Flag	Units
021500	HAR-560-RAW-021400		1459*41		Total Hg	030200HGA	42.2		ng/L	MeHg	021600MEB	0.298		ng/L
021500	SUL-550-RAW-021400		1459*42		Total Hg	030100HGA	100		ng/L	MeHg	021600MEB	0.453		ng/L
021500	ATM-701-RAW-021400		1459*43		Total Hg	030100HGA	20.5		ng/L					
021500	ATM-702-RAW-021400		1459*44		Total Hg	030100HGA	128		ng/L					
021500	ATM-703-RAW-021400		1459*45		Total Hg	030100HGA	85.7		ng/L					
021500	ATM-704-RAW-021400		1459*46		Total Hg	030100HGA	74.1		ng/L					
021500	ATM-705-RAW-021400		1459*47		Total Hg	030100HGA	43.6		ng/L					
021500	ATM-706-RAW-021400		1459*48		Total Hg	030100HGA	89.2		ng/L					
021500	ATM-707-RAW-021400		1459*49		Total Hg	030100HGA	78.8		ng/L					
021500	ATM-DUP-RAW-021400		1459*50	DUP	Total Hg	030100HGA	84.5		ng/L					
021500	ATM-708-RAW-021400		1459*51		Total Hg	030100HGA	29.8		ng/L					
021500	ATM-709-RAW-021400		1459*52		Total Hg	030100HGA	2.64		ng/L					
021500	SCM-601-RAW-021400		1459*53		Total Hg	030100HGA	83.2		ng/L					
021500	SCM-602-RAW-021400		1459*54		Total Hg	030100HGA	87.6		ng/L					
021500	SCM-DUP-RAW-021400		1459*55	DUP	Total Hg	030100HGA	35.8		ng/L					
021500	SCM-603-RAW-021400		1459*56		Total Hg	030100HGA	7690		ng/L					
021500	SCM-604-RAW-021400		1459*57		Total Hg	030100HGA	80.7		ng/L					
021500	SCM-605-RAW-021400		1459*58		Total Hg	030200HGA	1420		ng/L					
021500	SCM-606-RAW-021400		1459*59		Total Hg	030100HGA	224		ng/L					
021500	SCM-607-RAW-021400		1459*60		Total Hg	030100HGA	64.2		ng/L					
021500	SCM-608-RAW-021400		1459*61		Total Hg	030200HGA	226		ng/L					

Approvals: _____ Date _____

Project Manager _____ Date _____

QA/QC Reviewer _____ Date _____

APPENDIX 5B. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/14/00 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 2 of 3.

QA/QC Results:

Method	Sample ID	Matrix	Concentration	Units	Notes
METHOD BLANKS					
BLANK 1	RB030100	Total Hg	0.260	ng/L	
Blank-1	RB030200	Total Hg	0.159	ng/L	
	BLK021600	MeHg	0.0509	ng/L	
STANDARD REFERENCE MATERIAL					
Certified Value	1641c	Total Hg	1530000	ng/L	
Percent Recovery	1641c	Total Hg	1630000	ng/L	
		Total Hg	1470000	ng/L	
		Total Hg	104	%	
		Total Hg	111	%	
REPLICATE ANALYSES					
ATM-704-RAW-021400	Rep 1	Total Hg	74.1	ng/L	
ATM-704-RAW-021400	Rep 2	Total Hg	73.2	ng/L	
RPD		Total Hg	1	%	
SCM-603-RAW-021400	Rep 1	Total Hg	7690	ng/L	
SCM-603-RAW-021400	Rep 2	Total Hg	8550	ng/L	
RPD		Total Hg	11	%	
TAP WATER SPIKE RESULTS					
Amount Spiked		Total Hg	4.93	ng/L	
Tap Water		Total Hg	0.388	ng/L	
Tap Water + Spike	run 1	Total Hg	5.07	ng/L	
Amount Recovered		Total Hg	4.68	ng/L	
Percent Recovery		Total Hg	95	%	
MeHg Results					
	DORM-2	MeHg	3.70	ug/g	
		MeHg	4.47	ug/g	
		MeHg	83	%	

APPENDIX 5C. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/14/00 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 3 of 3.

TAP WATER SPIKE RESULTS					
Amount Spiked				4.93	ng/L
Tap Water	run 2		030100HGA	0.388	ng/L
Tap Water + Spike			030100HGA	5.28	ng/L
Amount Recovered				4.89	ng/L
Percent Recovery				99	%
Amount Spiked				4.84	ng/L
Tap Water			030200HGA	0.211	ng/L
Tap Water + Spike	run 2		030200HGA	5.51	ng/L
Amount Recovered				5.30	ng/L
Percent Recovery				109	%
MATRIX SPIKE RESULTS					
Amount Spiked				12.7	ng/L
SCM-602-RAW-021400		1459*54	030100HGA	87.6	ng/L
SCM-602-RAW-021400 + Spike			030100HGA	99.0	ng/L
Amount Recovered				11.4	ng/L
Percent Recovery				90	%
Amount Spiked				11.7	ng/L
SCM-602-RAW-021400		1459*54	030100HGA	87.6	ng/L
SCM-602-RAW-021400 + Spike			030100HGA	101	ng/L
Amount Recovered				13.4	ng/L
Percent Recovery				115	%

Source Bioavailability and Mine Remediation Feasibility in the Cache Creek Watershed

APPENDIX 6A. Data and QA/QC Report for RAW (unfiltered) water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 1 of 7.

U.C. Davis
 CALFED Cache Creek
 Minesite Samples February 2001
 Results Summary

Analysis: Total Mercury, Methyl Mercury
 Method: SOP MSL-I-013-02 (Total Hg), SOP MSL-I-014-01 (Methyl Hg)
 Matrix: Raw Water
 Laboratory: Battelle/MSL

Sample Received	Sample Description	Sample ID	MSL Lab ID	Field QC	Test	Batch	Value	Flag	Units	Test	Batch	Value	Flag	Units
022201	HAR-530-WTRS-THg-MeHg-NA	1459-505		Total Hg	030501HGA	91.8		ng/L	MeHg	022701MEB	0.344		ng/L	
022201	ATM-701-WTRS-THg-NA	1459-506		Total Hg	030501HGA	21.5		ng/L	MeHg					ng/L
022201	ATM-702-WTRS-THg-MeHg-NA	1459-507		Total Hg	030501HGA	385		ng/L	MeHg	030201MEB	0.149		ng/L	
022201	ATM-703-WTRS-THg-MeHg-NA	1459-508		Total Hg	030501HGA	933		ng/L	MeHg	030201MEB	0.253		ng/L	
022201	ATM-707-WTRS-THg-DU	1459-509		DUP	030501HGA	141		ng/L	MeHg					ng/L
022201	ATM-705-WTRS-THg-NA	1459-510		Total Hg	030501HGA	87.4		ng/L	MeHg					ng/L
022201	ATM-709-WTRS-THg-NA	1459-511		Total Hg	030601HGA	5.87		ng/L	MeHg					ng/L
022201	ATM-706-WTRS-THg-MeHg-NA	1459-512		Total Hg	030601HGA	283		ng/L	MeHg	030201MEB	0.297		ng/L	
022201	ATM-707-WTRS-THg-NA	1459-513		Total Hg	030601HGA	180		ng/L	MeHg					ng/L
022201	ATM-708-WTRS-THg-NA	1459-514		Total Hg	030801HGA	62.0		ng/L	MeHg					ng/L
022301	EB-WTZP-THg-MeHg-NA	1459-515		Total Hg	030801HGA	0.0806		ng/L	MeHg	022701MEB	0.137	U	ng/L	
022301	SUL-540-WTRS-THg-MeHg-NA	1459-527		Total Hg	030701HGA	1340		ng/L	MeHg	022701MEB	0.489		ng/L	
022301	SCM-600-WTRS-THg-NA	1459-528		Total Hg	030701HGA	1110		ng/L	MeHg					ng/L
022301	SCM-601-WTRS-THg-NA	1459-529		Total Hg	030801HGA	465		ng/L	MeHg					ng/L
022301	SCM-602-WTRS-THg-NA	1459-530		Total Hg	030701HGA	137		ng/L	MeHg					ng/L
022301	SCM-603-WTRS-THg-MeHg-NA	1459-531		Total Hg	030801HGA	33600		ng/L	MeHg					ng/L
022301	SCM-603-WTRS-THg-DU	1459-532		Total Hg	030801HGA	39700		ng/L	MeHg	030201MEB	20.4		ng/L	
022301	SCM-604-WTRS-THg-NA	1459-533		Total Hg	030701HGA	374		ng/L	MeHg					ng/L
022301	SCM-605-WTRS-THg-NA	1459-534		Total Hg	030801HGA	4300		ng/L	MeHg					ng/L
022301	SCM-606-WTRS-THg-NA	1459-535		Total Hg	030801HGA	2110		ng/L	MeHg					ng/L
022301	SCM-607-WTRS-THg-MeHg-NA	1459-536		Total Hg	030801HGA	289		ng/L	MeHg	022701MEB	0.503		ng/L	
022301	SCM-608-WTRS-THg-NA	1459-537		Total Hg	030801HGA	330		ng/L	MeHg					ng/L
022301	SCM-601.1-WTRS-THg-MeHg-NA	1459-538		Total Hg	030801HGA	3460		ng/L	MeHg	022701MEB	3.73		ng/L	
022301	SCM-601.2-WTRS-THg-MeHg-NA	1459-539		Total Hg	030801HGA	7250		ng/L	MeHg	022701MEB	2.01		ng/L	
022301	SCM-601.3-WTRS-THg-MeHg-NA	1459-540		Total Hg	030801HGA	3970		ng/L	MeHg	030201MEB	1.28		ng/L	
022301	EB-WTZP-THg-MEhg-NA	1459-541		Total Hg	030801HGA	0.219		ng/L	MeHg	022701MEB	0.137	U	ng/L	

U Not detected at or above the given concentration.
 # Exceeds Data Quality Objective

Approvals: _____

Project Manager _____ QA/QC Reviewer _____ Date _____

APPENDIX 6B. Data and QA/QC Report for RAW (unfiltered) water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 2 of 7.

QA/QC Results:

METHOD BLANKS

BLANK 1	Total Hg	030501HGA	0.0298	ng/L	
BLANK 2	Total Hg	030501HGA	0.0999	ng/L	
BLANK 3	Total Hg	030501HGA	0.0829	ng/L	
BLANK 1	Total Hg	030601HGA	0.0182	U	
BLANK 1	Total Hg	030701HGA	0.124	ng/L	
BLANK 2	Total Hg	030701HGA	0.422	ng/L	
BLANK 3	Total Hg	030701HGA	0.0382	ng/L	
BLANK 1	Total Hg	030801HGA	0.0180	U	
BLANK 2	Total Hg	030801HGA	0.162	ng/L	
Blank-1					MeHg 022701MEB 0.0251
Blank-2					MeHg 022701MEB 0.0135 U
Blank-3					MeHg 022701MEB 0.0137 U
Blank-1					MeHg 030201MEB 0.0160 U
Blank-2					MeHg 030201MEB 0.0162 U
Blank-3					MeHg 030201MEB 0.0162 U

STANDARD REFERENCE MATERIAL

Standard Reference Material	1641d				
	Total Hg	030501HGA	1630000	ng/L	
	Total Hg	030601HGA	1590000	ng/L	
	Total Hg	030701HGA	1640000	ng/L	
	Total Hg	030801HGA	1630000	ng/L	
Certified Value	Total Hg		1590000	ng/L	
Percent Recovery	Total Hg		103	%	
	Total Hg		100	%	
	Total Hg		103	%	
Total Hg		103	%		

APPENDIX 6D. Data and QA/QC Report for RAW (unfiltered) water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 4 of 7.

IAP WATER SPIKE RESULTS (OPR)

Amount Spiked				4.82	ng/L
BLANK			030501HGA	0.232	ng/L
BLANK + Spike	run 2		030501HGA	5.48	ng/L
Amount Recovered				5.25	ng/L
Percent Recovery				109	%
Amount Spiked				4.94	ng/L
BLANK			030601HGA	0.264	ng/L
BLANK + Spike	run 1		030601HGA	5.31	ng/L
Amount Recovered				5.05	ng/L
Percent Recovery				102	%
Amount Spiked				4.94	ng/L
BLANK			030601HGA	0.264	ng/L
BLANK + Spike	run 2		030601HGA	3.56	ng/L
Amount Recovered				3.30	ng/L
Percent Recovery				67	#
Amount Spiked				4.95	ng/L
BLANK			030701HGA	0.0330	U
BLANK + Spike	run 1		030701HGA	5.32	ng/L
Amount Recovered				5.32	ng/L
Percent Recovery				107	%
Amount Spiked				4.95	ng/L
BLANK			030701HGA	0.0330	U
BLANK + Spike	run 2		030701HGA	5.21	ng/L
Amount Recovered				5.21	ng/L
Percent Recovery				105	%

APPENDIX 6E. Data and QA/QC Report for RAW (unfiltered) water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 5 of 7.

IAP WATER SPIKE RESULTS (OPR)

Amount Spiked				4.96	ng/L
BLANK			030801HGA	0.201	ng/L
BLANK + Spike	run 1		030801HGA	5.20	ng/L
Amount Recovered				5.00	ng/L
Percent Recovery				101	%
Amount Spiked				4.96	ng/L
BLANK			030801HGA	0.201	ng/L
BLANK + Spike	run 2		030801HGA	4.71	ng/L
Amount Recovered				4.51	ng/L
Percent Recovery				91	%

MATRIX SPIKE RESULTS

Amount Spiked									
HAR-530-WTRS-THg-MeHg-NA									ng/L
HAR-530-WTRS-THg-MeHg-NA + Spike	1459-505					022701MEB		9.95	ng/L
Amount Recovered								0.344	ng/L
Percent Recovery								10.19	ng/L
Amount Spiked								9.85	ng/L
HAR-530-WTRS-THg-MeHg-NA								99	%
HAR-530-WTRS-THg-MeHg-NA + Spike Duplicate	1459-505					022701MEB		9.95	ng/L
Amount Recovered								0.344	ng/L
Percent Recovery								9.15	ng/L
Amount Spiked								8.61	ng/L
ATM-702-WTRS-THg-MeHg-NA								89	%
ATM-702-WTRS-THg-MeHg-NA + Spike	1459-507					030201MEB		0.801	ng/L
Amount Recovered								0.149	ng/L
Percent Recovery								1.08	ng/L
Amount Spiked								0.931	ng/L
ATM-702-WTRS-THg-MeHg-NA								116	%
ATM-702-WTRS-THg-MeHg-NA + Spike									
Amount Recovered									
Percent Recovery									

APPENDIX 6G. Data and QA/QC Report for RAW (unfiltered) water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 7 of 7.

MATRIX SPIKE RESULTS

Amount Spiked									
SCM-602-WTRS-THg-NA	1459-530		030701HGA			23.3	ng/L		
SCM-602-WTRS-THg-NA + Spike						137	ng/L		
Amount Recovered						162	ng/L		
Percent Recovery						25.0	ng/L		
						107	%		
Amount Spiked						29.1	ng/L		
SCM-602-WTRS-THg-NA	1459-530		030701HGA			137	ng/L		
SCM-602-WTRS-THg-NA + Spike Duplicate						179	ng/L		
Amount Recovered						42.0	ng/L		
Percent Recovery						144	%		
Amount Spiked						227	ng/L		
SCM-608-WTRS-THg-NA	1459-537		030801HGA			330	ng/L		
SCM-608-WTRS-THg-NA + Spike						555	ng/L		
Amount Recovered						225.0	ng/L		
Percent Recovery						99	%		
Amount Spiked						226	ng/L		
SCM-608-WTRS-THg-NA	1459-537		030801HGA			330	ng/L		
SCM-608-WTRS-THg-NA + Spike Duplicate						561	ng/L		
Amount Recovered						231.0	ng/L		
Percent Recovery						102	%		

APPENDIX 7A. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 1 of 6.

U.C. Davis
 CALFED Cache Creek
 Minesite Samples February 2001
 Results Summary

Analysis: Total Mercury, Methyl Mercury
 Method: SOP MSL-I-013-02 (Total Hg), SOP MSL-I-014-01 (Methyl Hg)
 Matrix: Filtered Water
 Laboratory: Battelle/MSL

Sample Received	Sample Description	MSL Lab ID	Field QC	Test	Batch	Value	Flag	Units	Test	Batch	Value	Flag	Units
022201	HAR-530-WTRS-Thg-MeHg-NA	1459-516		Total Hg	030801HGA	48.4		ng/L	MeHg	022801MEB	0.224		ng/L
022201	ATM-701-WTRS-Thg-NA	1459-517		Total Hg	030501HGA	10.3		ng/L	MeHg				ng/L
022201	ATM-702-WTRS-Thg-MeHg-NA	1459-518		Total Hg	030501HGA	256		ng/L	MeHg	030201MEB	0.0776		ng/L
022201	ATM-703-WTRS-Thg-MeHg-NA	1459-519		Total Hg	030501HGA	484		ng/L	MeHg	030201MEB	0.122		ng/L
022201	ATM-707-WTRS-Thg-DU	1459-520	DUP	Total Hg	030501HGA	63.3		ng/L	MeHg				ng/L
022201	ATM-705-WTRS-Thg-NA	1459-521		Total Hg	030501HGA	40.4		ng/L	MeHg				ng/L
022201	ATM-709-WTRS-Thg-NA	1459-522		Total Hg	030501HGA	2.13		ng/L	MeHg				ng/L
022201	ATM-706-WTRS-Thg-MeHg-NA	1459-523		Total Hg	030501HGA	124		ng/L	MeHg	030201MEB	0.278		ng/L
022201	ATM-707-WTRS-Thg-NA	1459-524		Total Hg	030501HGA	66.1		ng/L	MeHg				ng/L
022201	ATM-708-WTRS-Thg-NA	1459-525		Total Hg	030501HGA	25.9		ng/L	MeHg				ng/L
022201	EB-WTZP-Thg-MeHg-NA	1459-526		Total Hg	030501HGA	0.447		ng/L	MeHg	022801MEB	0.0138	U	ng/L
022301	SUL-540-WTRS-Thg-MeHg-NA	1459-542		Total Hg	030601HGA	160		ng/L	MeHg	030201MEB	0.0840		ng/L
022301	SCM-600-WTRS-Thg-NA	1459-543		Total Hg	030601HGA	177		ng/L	MeHg				ng/L
022301	SCM-601-WTRS-Thg-NA	1459-544		Total Hg	030601HGA	117		ng/L	MeHg				ng/L
022301	SCM-602-WTRS-Thg-NA	1459-545		Total Hg	030601HGA	33.1		ng/L	MeHg				ng/L
022301	SCM-603-WTRS-Thg-MeHg-NA	1459-546		Total Hg	030801HGA	9880		ng/L	MeHg	030201MEB	14.4		ng/L
022301	SCM-603-WTRS-Thg-DU	1459-547	DUP	Total Hg	030801HGA	5470		ng/L	MeHg				ng/L
022301	SCM-604-WTRS-Thg-NA	1459-548		Total Hg	030701HGA	103		ng/L	MeHg				ng/L
022301	SCM-605-WTRS-Thg-NA	1459-549		Total Hg	030701HGA	2219		ng/L	MeHg				ng/L
022301	SCM-606-WTRS-Thg-NA	1459-550		Total Hg	030701HGA	959		ng/L	MeHg				ng/L
022301	SCM-607-WTRS-Thg-MeHg-NA	1459-551		Total Hg	030601HGA	102		ng/L	MeHg	030201MEB	0.206		ng/L
022301	SCM-608-WTRS-Thg-NA	1459-552		Total Hg	030601HGA	87.4		ng/L	MeHg				ng/L
022301	SCM-601.1-WTRS-Thg-MeHg-NA	1459-553		Total Hg	030601HGA	2300		ng/L	MeHg	022801MEB	3.24		ng/L
022301	SCM-601.2-WTRS-Thg-MeHg-NA	1459-554		Total Hg	030801HGA	1900		ng/L	MeHg	022801MEB	2.27		ng/L
022301	SCM-601.3-WTRS-Thg-MeHg-NA	1459-555		Total Hg	030801HGA	2750		ng/L	MeHg	030201MEB	0.592		ng/L
022301	EB-WTZP-Thg-MEhg-NA	1459-556		Total Hg	030601HGA	0.310		ng/L	MeHg	022801MEB	0.0139	U	ng/L

U Not detected at or above the given concentration.
 # Exceeds Data Quality Objective

Approvals:

Project Manager _____ Date _____	QA/QC Reviewer _____ Date _____
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APPENDIX 7B. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 2 of 6.

QA/QC Results:

METHOD BLANKS

BLANK 1	Total Hg	030501HGA	0.0298	ng/L			
BLANK 2	Total Hg	030501HGA	0.0999	ng/L			
BLANK 3	Total Hg	030501HGA	0.0829	ng/L			
BLANK 1	Total Hg	030601HGA	0.0182 U	ng/L			
BLANK 2	Total Hg	030701HGA	0.124	ng/L			
BLANK 3	Total Hg	030701HGA	0.422	ng/L			
BLANK 1	Total Hg	030701HGA	0.0382	ng/L			
BLANK 2	Total Hg	030801HGA	0.0180 U	ng/L			
BLANK 3	Total Hg	030801HGA	0.162	ng/L			
Blank-1					MeHg	022801MEB	0.0141 U ng/L
Blank-2					MeHg	022801MEB	0.0137 U ng/L
Blank-3					MeHg	022801MEB	0.0139 U ng/L
Blank-1					MeHg	030201MEB	0.0160 U ng/L
Blank-2					MeHg	030201MEB	0.0162 U ng/L
Blank-3					MeHg	030201MEB	0.0162 U ng/L

STANDARD REFERENCE MATERIAL

Standard Reference Material	1641d						
	Total Hg	030501HGA	1630000	ng/L			
	Total Hg	030601HGA	1590000	ng/L			
	Total Hg	030701HGA	1640000	ng/L			
	Total Hg	030801HGA	1630000	ng/L			
Certified Value	Total Hg		1590000	%			
Percent Recovery	Total Hg		103	%			
	Total Hg		100	%			
	Total Hg		103	%			
	Total Hg		103	%			

APPENDIX 7C. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 3 of 6.

<u>STANDARD REFERENCE MATERIAL</u>							
Standard Reference Material		DORM-2					
Certified Value							µg/g
Percent Recovery							µg/g
							%
							%
REPLICATE ANALYSES							
SCM-603-WTRS-THg-MeHg-NA		1459-546					14.4 ng/L
SCM-603-WTRS-THg-MeHg-NA		1459-546					14.2 ng/L
RPD							1 %
SCM-601.3-WTRS-THg-MeHg-NA		1459-555					0.592 ng/L
SCM-601.3-WTRS-THg-MeHg-NA		1459-555					0.657 ng/L
RPD							10 %
ATM-702-WTRS-THg-MeHg-NA		1459-518	Total Hg	030501HGA		256	ng/L
ATM-702-WTRS-THg-MeHg-NA		1459-518	Total Hg	030501HGA		247	ng/L
RPD						4	%
SCM-601-WTRS-THg-NA		1459-544	Total Hg	030601HGA		117	ng/L
SCM-601-WTRS-THg-NA		1459-544	Total Hg	030601HGA		101	ng/L
RPD						15	%
TAP WATER SPIKE RESULTS (OPR)							
Amount Spiked			Total Hg			4.82	ng/L
BLANK			Total Hg	030501HGA		0.232	ng/L
BLANK + Spike		run 1	Total Hg	030501HGA		5.39	ng/L
Amount Recovered			Total Hg			5.16	ng/L
Percent Recovery			Total Hg			107	%

APPENDIX 7D. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 4 of 6.

TAP WATER SPIKE RESULTS (OPR)

Amount Spiked				4.82	ng/L
BLANK			030501HGA	0.232	ng/L
BLANK + Spike	run 2		030501HGA	5.48	ng/L
Amount Recovered				5.25	ng/L
Percent Recovery				109	%
Amount Spiked				4.94	ng/L
BLANK			030601HGA	0.2640	ng/L
BLANK + Spike	run 1		030601HGA	5.31	ng/L
Amount Recovered				5.05	ng/L
Percent Recovery				102	%
Amount Spiked				4.94	ng/L
BLANK			030601HGA	0.2640	ng/L
BLANK + Spike	run 2		030601HGA	3.56	ng/L
Amount Recovered				3.30	ng/L
Percent Recovery				67 #	%
Amount Spiked				4.95	ng/L
BLANK			030701HGA	0.0330 U	ng/L
BLANK + Spike	run 1		030701HGA	5.32	ng/L
Amount Recovered				5.29	ng/L
Percent Recovery				107	%
Amount Spiked				4.95	ng/L
BLANK			030701HGA	0.0330 U	ng/L
BLANK + Spike	run 2		030701HGA	5.21	ng/L
Amount Recovered				5.18	ng/L
Percent Recovery				105	%

APPENDIX 7E. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 5 of 6.

TAP WATER SPIKE RESULTS (OPR)

Amount Spiked				4.96	ng/L
BLANK		030801HGA		0.201	ng/L
BLANK + Spike	run 1	030801HGA		5.20	ng/L
Amount Recovered				5.00	ng/L
Percent Recovery				101	%
Amount Spiked				4.96	ng/L
BLANK		030801HGA		0.201	ng/L
BLANK + Spike	run 2	030801HGA		4.71	ng/L
Amount Recovered				4.51	ng/L
Percent Recovery				91	%

MATRIX SPIKE RESULTS

Amount Spiked									
HAR-530-WTRS-THg-MeHg-NA			1459-516			MeHg	022801MEB	0.990	ng/L
HAR-530-WTRS-THg-MeHg-NA + Spike						MeHg	022801MEB	0.224	ng/L
Amount Recovered						MeHg		1.25	ng/L
Percent Recovery						MeHg		1.03	ng/L
						MeHg		104	%
Amount Spiked						MeHg		1.00	ng/L
HAR-530-WTRS-THg-MeHg-NA			1459-516			MeHg	022801MEB	0.224	ng/L
HAR-530-WTRS-THg-MeHg-NA + Spike Duplicate						MeHg	022801MEB	1.21	ng/L
Amount Recovered						MeHg		0.983	ng/L
Percent Recovery						MeHg		98	%
Amount Spiked						MeHg		1.58	ng/L
SCM-601.3-WTRS-THg-MeHg-NA			1459-555			MeHg	030201MEB	0.592	ng/L
SCM-601.3-WTRS-THg-MeHg-NA + Spike Duplicate						MeHg	030201MEB	1.72	ng/L
Amount Recovered						MeHg		1.13	ng/L
Percent Recovery						MeHg		71	#

MATRIX SPIKE RESULTS

Amount Spiked				14.0	ng/L
ATM-706-WTRS-THg-MeHg-NA		030501HGA		124	ng/L
ATM-706-WTRS-THg-MeHg-NA + Spike				134	ng/L
Amount Recovered				10.0	ng/L
Percent Recovery				71	#

APPENDIX 7F. Data and QA/QC Report for FILTERED water samples analyzed by Battelle MSL for total Hg and methyl Hg from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 6 of 6.

Amount Spiked					15.1	ng/L
ATM-706-WTRS-THg-MeHg-NA	1459-523		030501HGA	Total Hg	124	ng/L
ATM-706-WTRS-THg-MeHg-NA + Spike Duplicate				Total Hg	139	ng/L
Amount Recovered				Total Hg	15.0	ng/L
Percent Recovery				Total Hg	99	%
Amount Spiked				Total Hg	225	ng/L
SUL-540-WTRS-THg-MeHg-NA	1459-542		030601HGA	Total Hg	160	ng/L
SUL-540-WTRS-THg-MeHg-NA + Spike				Total Hg	367	ng/L
Amount Recovered				Total Hg	207	ng/L
Percent Recovery				Total Hg	92	%
Amount Spiked				Total Hg	227	ng/L
SUL-540-WTRS-THg-MeHg-NA	1459-542		030601HGA	Total Hg	160	ng/L
SUL-540-WTRS-THg-MeHg-NA + Spike Duplicate				Total Hg	362	ng/L
Amount Recovered				Total Hg	202	ng/L
Percent Recovery				Total Hg	89	%

APPENDIX 8A. Data and QA/QC Report for water samples analyzed by Columbia Analytical Laboratories for total suspended solids (TSS) and sulfate (SO₄) from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 1 of 2.

U.C. Davis
CALFED Cache Creek
Minesite Samples February 2001
Results Summary

Analysis: Sulfate and TSS
Method: 160.2 (TSS) and 300.0 (Sulfate)
Matrix: Raw Water
Laboratory: Columbia Analytical

Sample Received	Sample Description	Sample ID	CAS Lab ID	Field QC	Test	Batch	Value	Flag	Units	Test	Batch	Value	Flag	Units
022201	HAR-530-WTRS-Thg-MeHg-NA		K2101316-001		TSS	022701TSS	13		mg/L	Sulfate	022301SUL	288		mg/L
022201	ATM-701-WTRS-Thg-NA		K2101316-002		TSS	022701TSS	17		mg/L	Sulfate	022301SUL	107		mg/L
022201	ATM-702-WTRS-Thg-MeHg-NA		K2101316-003		TSS	022701TSS	1	U	mg/L	Sulfate	022301SUL	773		mg/L
022201	ATM-703-WTRS-Thg-MeHg-NA		K2101316-004		TSS	022701TSS	4		mg/L	Sulfate	022301SUL	675		mg/L
022201	ATM-707-WTRS-Thg-DU		K2101316-005	DUP	TSS	022701TSS	4		mg/L	Sulfate	022301SUL	213		mg/L
022201	ATM-705-WTRS-Thg-NA		K2101316-006		TSS	022701TSS	1	U	mg/L	Sulfate	022301SUL	1140		mg/L
022201	ATM-709-WTRS-Thg-NA		K2101316-007		TSS	022701TSS	1	U	mg/L	Sulfate	022301SUL	1350		mg/L
022201	ATM-706-WTRS-Thg-MeHg-NA		K2101316-008		TSS	022701TSS	5		mg/L	Sulfate	022301SUL	515		mg/L
022201	ATM-707-WTRS-Thg-NA		K2101316-009		TSS	022701TSS	5		mg/L	Sulfate	022301SUL	207		mg/L
022201	ATM-708-WTRS-Thg-NA		K2101316-010		TSS	022701TSS	7		mg/L	Sulfate	022301SUL	87.4		mg/L
022301	SUL-540-WTRS-Thg-MeHg-NA		K2101355-001		TSS	022801TSS	56		mg/L	Sulfate	022701SUL	50.8		mg/L
022301	SCM-600-WTRS-Thg-NA		K2101355-002		TSS	022801TSS	43		mg/L	Sulfate	022701SUL	49.9		mg/L
022301	SCM-601-WTRS-Thg-NA		K2101355-003		TSS	022801TSS	22		mg/L	Sulfate	022701SUL	32.8		mg/L
022301	SCM-602-WTRS-Thg-NA		K2101355-004		TSS	022801TSS	25		mg/L	Sulfate	022701SUL	34.9		mg/L
022301	SCM-603-WTRS-Thg-MeHg-NA		K2101355-005		TSS	022801TSS	46		mg/L	Sulfate	022701SUL	57.2		mg/L
022301	SCM-603-WTRS-Thg-DU		K2101355-006		TSS	022801TSS	13		mg/L	Sulfate	022701SUL	41.6		mg/L
022301	SCM-604-WTRS-Thg-NA		K2101355-007		TSS	022801TSS	22		mg/L	Sulfate	022701SUL	31.8		mg/L
022301	SCM-605-WTRS-Thg-NA		K2101355-008		TSS	022801TSS	26		mg/L	Sulfate	022701SUL	58.7		mg/L
022301	SCM-606-WTRS-Thg-NA		K2101355-009		TSS	022801TSS	135		mg/L	Sulfate	022701SUL	88.2		mg/L
022301	SCM-607-WTRS-Thg-MeHg-NA		K2101355-010		TSS	022801TSS	15		mg/L	Sulfate	022701SUL	31.0		mg/L
022301	SCM-608-WTRS-Thg-NA		K2101355-014		TSS	022801TSS	15		mg/L	Sulfate	022701SUL	29.3		mg/L
022301	SCM-601.1-WTRS-Thg-MeHg-NA		K2101355-011		TSS	022801TSS	5		mg/L	Sulfate	022701SUL	81.4		mg/L
022301	SCM-601.2-WTRS-Thg-MeHg-NA		K2101355-012		TSS	022801TSS	6		mg/L	Sulfate	022701SUL	54.0		mg/L
022301	SCM-601.3-WTRS-Thg-MeHg-NA		K2101355-013		TSS	022801TSS	12		mg/L	Sulfate	022701SUL	58.6		mg/L

U Not detected at or above the given concentration.

Approvals:

Project Manager	QA/QC Reviewer
Date	Date

APPENDIX 8B. Data and QA/QC Report for water samples analyzed by Columbia Analytical Laboratories for total suspended solids (TSS) and sulfate (SO₄) from 2/21/01 and 2/22/01 collections from the Harley Gulch and Sulphur Creek Mining Regions: Page 2 of 2.

QA/QC Results:									
METHOD BLANKS									
BLANK 1	K2101316-MB	TSS	022701TSS	1 U	mg/L	0.2 U	mg/L		
	K2101355-MB	TSS	022801TSS	1 U	mg/L	0.2 U	mg/L		
STANDARD REFERENCE MATERIAL									
Laboratory Control Sample									
Known Value									
Percent Recovery									
Laboratory Control Sample									
Known Value									
Percent Recovery									
REPLICATE ANALYSES									
HAR-530-WTRS-THg-MeHg-NA	K2101316-001								
HAR-530-WTRS-THg-MeHg-NA	K2101316-001								
RPD									
SUL-540-WTRS-THg-MeHg-NA									
SUL-540-WTRS-THg-MeHg-NA									
RPD									
MATRIX SPIKE RESULTS									
Amount Spiked									
HAR-530-WTRS-THg-MeHg-NA									
HAR-530-WTRS-THg-MeHg-NA + Spike									
Amount Recovered									
Percent Recovery									
Amount Spiked									
SUL-540-WTRS-THg-MeHg-NA									
SUL-540-WTRS-THg-MeHg-NA + Spike									
Amount Recovered									
Percent Recovery									

APPENDIX 9A. Data and QA/QC Report for Sulphur Creek microcosm experiment water samples analyzed by Battelle MSL for total Hg and methyl Hg. Page 1 of 2.

U.C. Davis
Sulfur Creek Samples
November 2000
Results Summary

Analysis: Total Mercury, Methyl Mercury
Method: SOP MSL-I-013-02 (Total Hg), SOP MSL-I-014-01 (Methyl Hg)
Matrix: Filtered Water
Laboratory: Battelle/MSL

Sample Received	Sample Description	Sample ID	MSL Lab ID	Field QC	Test	Batch	Value	Flag	Units	Test	Batch	Value	Flag	Units
111600	FL-na-WTR-NE-MeTHg-CBC-na-DAY0-001110	00-11-260	1591-25		Total Hg	120100HGA	0.822		ng/L	MeHg	120600MEB	0.0214	U	ng/L
111600	SuC-WTR-NE-Ox-na-DAY2.5-001113	00-11-261	1591-26							MeHg	120600MEB	0.0365	U	ng/L
111600	SuC-WTR-Dup--Ox-na-DAY2.5-001113	00-11-262	1591-27	DUP						MeHg	120600MEB	0.0351	U	ng/L
111600	CWB-WTR-NE-Ox-na-DAY2.5-001113	00-11-263	1591-28							MeHg	120600MEB	0.0214	U	ng/L
111600	SuC-WTR-NE-Aox-na-DAY2.5-001113	00-11-264	1591-29							MeHg	120600MEB	0.0338	U	ng/L
111600	SuC-WTR-Dup--Aox-na-DAY2.5-001113	00-11-265	1591-30	DUP						MeHg	120600MEB	0.0317	U	ng/L
111600	CWB-WTR--Aox-na-DAY2.5-001113	00-11-266	1591-31							MeHg	120600MEB	0.0217	U	ng/L
111600	FL-na-WTR-NE-MeTHg-CBC-na-DAY2.5-001113	00-11-273	1591-32		Total Hg	120100HGA	0.612		ng/L	MeHg	120600MEB	0.0213	U	ng/L
111700	SuC-WTR-NE-Ox-na-DAYS-001115	00-11-267	1591-33							MeHg	120600MEB	0.0217	U	ng/L
111700	SuC-WTR-Dup-Ox-na-DAY5-001115	00-11-268	1591-34	DUP						MeHg	120600MEB	0.0214	U	ng/L
111700	CWB-WTR-Ox-na-DAYS-001115	00-11-269	1591-35							MeHg	120700MEB	0.0214	U	ng/L
111700	SuC-WTR-NE-Aox-na-DAY5-001115	00-11-270	1591-36							MeHg	120700MEB	0.0209	U	ng/L
111700	SuC-WTR-DUP-Aox-na-DAY5-001115	00-11-271	1591-37	DUP						MeHg	120700MEB	0.0501	U	ng/L
111700	CWB-WTR-Aox-na-DAYS-001115	00-11-272	1591-38							MeHg	120700MEB	0.0211	U	ng/L

U Not detected at or above the given concentration.

Approvals:

Project Manager	Date	QA/QC Reviewer	Date

Source Bioavailability and Mine Remediation Feasibility in the Cache Creek Watershed

APPENDIX 9B. Data and QA/QC Report for Sulphur Creek microcosm experiment water samples analyzed by Battelle MSL for total Hg and methyl Hg. Page 2 of 2.

QA/QC Results:		Total Hg	120100HGA	0.0380 U	ng/L	Methg	120600MEB	0.0214 U	ng/L
METHOD: BLANKS									
BLANK 1									
Blank-1									
STANDARD REFERENCE MATERIAL									
Standard Reference Material	1641d	Total Hg	120100HGA	1510000	ng/L				
Certified Value		Total Hg		1550000	ng/L				
Percent Recovery		Total Hg	120100HGA	101	%				
Standard Reference Material									
Certified Value		Methg	120600MEB	4.71	ng/g				
Percent Recovery		Methg	120700MEB	5.23	ng/g				
		Methg	120700MEB	4.74	ng/g				
		Methg	120600MEB	4.47	ng/g				
		Methg	120600MEB	105	%				
		Methg	120700MEB	117	%				
		Methg	120700MEB	106	%				
REPLICATE ANALYSES									
LS-01-WTRD-NE-Ax-na-DAYS-001109	00-11-207	1591-18				Methg	120600MEB	0.0312 U	ng/L
LS-01-WTRD-HG-BU-001109	00-11-207	1591-18				Methg	120600MEB	0.0216 U	ng/L
RPD								NA	%
SUC-WTR-NE-Ax-na-DAYS-001115	00-11-270	1591-36				Methg	120700MEB	0.0209 U	ng/L
SUC-WTR-NE-Ax-na-DAYS-001115	00-11-270	1591-36				Methg	120700MEB	0.0209 U	ng/L
RPD								NA	%
TAP WATER SPIKE RESULTS									
Amount Spiked		Total Hg		5.10	ng/L				
Tap Water		Total Hg	120100HGA	0.402	ng/L				
Tap Water + Spike	run 1	Total Hg	120100HGA	5.51	ng/L				
Amount Recovered		Total Hg		5.11	ng/L				
Percent Recovery		Total Hg		100	%				
Amount Spiked		Total Hg		5.10	ng/L				
Tap Water	run 2	Total Hg	120100HGA	0.402	ng/L				
Tap Water + Spike		Total Hg	120100HGA	5.68	ng/L				
Amount Recovered		Total Hg		5.28	ng/L				
Percent Recovery		Total Hg		103	%				
MATRIX SPIKE RESULTS									
Amount Spiked		Methg	120600MEB	5.79	ng/L				
SUC-WTR-NE-Ox-na-DAYS-001113	00-11-261	Methg	120600MEB	0.0365 U	ng/L				
SUC-WTR-NE-Ox-na-DAYS-001113 + Spike		Methg	120600MEB	5.85	ng/L				
Amount Recovered		Methg		5.61	ng/L				
Percent Recovery		Methg		100	%				
Amount Spiked		Methg	120600MEB	6.01	ng/L				
SUC-WTR-NE-Ox-na-DAYS-001113	00-11-261	Methg	120600MEB	0.0365 U	ng/L				
SUC-WTR-NE-Ox-na-DAYS-001113 + Spike Duplicate		Methg	120600MEB	5.97	ng/L				
Amount Recovered		Methg		5.95	ng/L				
Percent Recovery		Methg		99	%				
MATRIX SPIKE RESULTS									
Amount Spiked		Methg	120700MEB	3.51	ng/L				
SUC-WTR-DUP-Ax-na-DAYS-001115	00-11-271	Methg	120700MEB	0.0501	ng/L				
SUC-WTR-DUP-Ax-na-DAYS-001115 + Spike		Methg	120700MEB	3.87	ng/L				
Amount Recovered		Methg		3.62	ng/L				
Percent Recovery		Methg		109	%				
Amount Spiked		Methg	120700MEB	3.47	ng/L				
SUC-WTR-DUP-Ax-na-DAYS-001115	00-11-271	Methg	120700MEB	0.0501	ng/L				
SUC-WTR-DUP-Ax-na-DAYS-001115 + Spike Duplicate		Methg	120700MEB	3.55	ng/L				
Amount Recovered		Methg		3.50	ng/L				
Percent Recovery		Methg		101	%				

APPENDIX 10A. Data and QA/QC Report for preliminary slurry experiment water samples analyzed by Battelle MSL for total Hg and methyl Hg. Page 1 of 2.

U.C. Davis
CALFED
January 2001
Results Summary

Analysis: Methyl Mercury
Method: SOP MSL-M-029 (Methyl) - by extraction
Matrix: Sediment/Slurries
Laboratory: Battelle/MSL

Sample Received	Sample ID	Sample Description	MSL Lab ID	Field QC	Test	Analytical Batch	Value	Flag	Units	Blk. Cor. Value	Analytical Batch	Test	Units	Flag	Percent Dry Wt.
1/11/01	1459-422	Abbott 0.02 DAY 0 R1	1459-422		Total Hg	011701MEB	NA	NA	µg/g	0.102	011701MEB	MeHg	ng/g		NA
1/11/01	1459-423	Abbott 0.02 DAY 0 R2	1459-423		Total Hg	011701MEB	NA	NA	µg/g	0.0514	011701MEB	MeHg	ng/g		4.4
1/11/01	1459-424	Abbott 0.02 DAY 4 R1	1459-424		Total Hg	011701MEB	NA	NA	µg/g	0.103	011701MEB	MeHg	ng/g		NA
1/11/01	1459-425	Abbott 0.02 DAY 4 R2	1459-425		Total Hg	011701MEB	NA	NA	µg/g	0.0391	011701MEB	MeHg	ng/g		NA
1/11/01	1459-426	Abbott 0.02 DAY 8 R1	1459-426		Total Hg	011701MEB	NA	NA	µg/g	0.0622	011701MEB	MeHg	ng/g		NA
1/11/01	1459-427	Abbott 0.02 DAY 8 R2	1459-427		Total Hg	011701MEB	NA	NA	µg/g	0.0728	011701MEB	MeHg	ng/g		NA
1/11/01	1459-428	Abbott 0.20 DAY 0 R1	1459-428		Total Hg	011701MEB	NA	NA	µg/g	0.114	011701MEB	MeHg	ng/g		NA
1/11/01	1459-429	Abbott 0.20 DAY 0 R2	1459-429		Total Hg	011701MEB	NA	NA	µg/g	0.128	011701MEB	MeHg	ng/g		NA
1/11/01	1459-430	Abbott 0.20 DAY 4 R1	1459-430		Total Hg	011701MEB	NA	NA	µg/g	0.242	011701MEB	MeHg	ng/g		NA
1/11/01	1459-431	Abbott 0.20 DAY 4 R2	1459-431		Total Hg	011701MEB	NA	NA	µg/g	0.248	011701MEB	MeHg	ng/g		NA
1/11/01	1459-432	Abbott 0.20 DAY 8 R1	1459-432		Total Hg	011701MEB	NA	NA	µg/g	0.191	011701MEB	MeHg	ng/g		NA
1/11/01	1459-433	Abbott 0.20 DAY 8 R2	1459-433		Total Hg	011701MEB	NA	NA	µg/g	0.186	011701MEB	MeHg	ng/g		NA
1/11/01	1459-434	Abbott 2.0 DAY 0 R1	1459-434		Total Hg	011701MEB	NA	NA	µg/g	0.167	011701MEB	MeHg	ng/g		NA
1/11/01	1459-435	Abbott 2.0 DAY 0 R2	1459-435		Total Hg	011701MEB	NA	NA	µg/g	0.161	011701MEB	MeHg	ng/g		NA
1/11/01	1459-436	Abbott 2.0 DAY 4 R1	1459-436		Total Hg	011701MEB	NA	NA	µg/g	1.61	011701MEB	MeHg	ng/g		NA
1/11/01	1459-437	Abbott 2.0 DAY 4 R2	1459-437		Total Hg	011701MEB	NA	NA	µg/g	1.42	011701MEB	MeHg	ng/g		NA
1/11/01	1459-438	Abbott 2.0 DAY 8 R1	1459-438		Total Hg	011901MEB	NA	NA	µg/g	1.49	011901MEB	MeHg	ng/g		NA
1/11/01	1459-439	Abbott 2.0 DAY 8 R2	1459-439		Total Hg	011901MEB	NA	NA	µg/g	1.39	011901MEB	MeHg	ng/g		NA
1/11/01	1459-440	Floc 0.02 DAY 0 R1	1459-440		Total Hg	011901MEB	NA	NA	µg/g	0.129	011901MEB	MeHg	ng/g		2.5
1/11/01	1459-441	Floc 0.02 DAY 0 R2	1459-441		Total Hg	011901MEB	NA	NA	µg/g	0.165	011901MEB	MeHg	ng/g		NA
1/11/01	1459-442	Floc 0.02 DAY 4 R1	1459-442		Total Hg	011901MEB	NA	NA	µg/g	0.153	011901MEB	MeHg	ng/g		NA
1/11/01	1459-443	Floc 0.02 DAY 4 R2	1459-443		Total Hg	011901MEB	NA	NA	µg/g	0.181	011901MEB	MeHg	ng/g		NA
1/11/01	1459-444	Floc 0.02 DAY 8 R1	1459-444		Total Hg	012601MEB	NA	NA	µg/g	0.103	012601MEB	MeHg	ng/g		NA
1/11/01	1459-445	Floc 0.02 DAY 8 R2	1459-445		Total Hg	012601MEB	NA	NA	µg/g	0.059	012601MEB	MeHg	ng/g		NA
1/11/01	1459-446	Floc 0.20 DAY 0 R1	1459-446		Total Hg	011901MEB	NA	NA	µg/g	0.208	011901MEB	MeHg	ng/g		NA
1/11/01	1459-447	Floc 0.20 DAY 0 R2	1459-447		Total Hg	011901MEB	NA	NA	µg/g	0.246	011901MEB	MeHg	ng/g		NA
1/11/01	1459-448	Floc 0.20 DAY 4 R1	1459-448		Total Hg	011901MEB	NA	NA	µg/g	0.657	011901MEB	MeHg	ng/g		NA
1/11/01	1459-449	Floc 0.20 DAY 4 R2	1459-449		Total Hg	011901MEB	NA	NA	µg/g	0.773	011901MEB	MeHg	ng/g		NA
1/11/01	1459-450	Floc 0.20 DAY 8 R1	1459-450		Total Hg	011901MEB	NA	NA	µg/g	0.679	011901MEB	MeHg	ng/g		NA
1/11/01	1459-451	Floc 0.20 DAY 8 R2	1459-451		Total Hg	011901MEB	NA	NA	µg/g	0.711	011901MEB	MeHg	ng/g		NA
1/11/01	1459-452	Floc 2.0 DAY 0 R1	1459-452		Total Hg	011901MEB	NA	NA	µg/g	1.55	011901MEB	MeHg	ng/g		23.4
1/11/01	1459-453	Floc 2.0 DAY 0 R2	1459-453		Total Hg	011901MEB	NA	NA	µg/g	0.776	011901MEB	MeHg	ng/g		11.2
1/11/01	1459-454	Floc 2.0 DAY 4 R1	1459-454		Total Hg	012401MEB	NA	NA	µg/g	1.97	012401MEB	MeHg	ng/g		NA
1/11/01	1459-455	Floc 2.0 DAY 4 R2	1459-455		Total Hg	012401MEB	NA	NA	µg/g	2.12	012401MEB	MeHg	ng/g		NA
1/11/01	1459-456	Floc 2.0 DAY 8 R1	1459-456		Total Hg	012401MEB	NA	NA	µg/g	1.72	012401MEB	MeHg	ng/g		NA
1/11/01	1459-457	Floc 2.0 DAY 8 R2	1459-457		Total Hg	012401MEB	NA	NA	µg/g	1.46	012401MEB	MeHg	ng/g		NA
1/11/01	1459-458	Control N DAY 0	1459-458		Total Hg	012401MEB	NA	NA	µg/g	0.223	012401MEB	MeHg	ng/g		6.5
1/11/01	1459-459	Control N DAY 4	1459-459		Total Hg	012401MEB	NA	NA	µg/g	0.177	012401MEB	MeHg	ng/g		NA
1/11/01	1459-460	Control N DAY 8	1459-460		Total Hg	012401MEB	NA	NA	µg/g	0.137	012401MEB	MeHg	ng/g		NA
1/11/01	1459-461	Control P DAY 0	1459-461		Total Hg	012601MEB	NA	NA	µg/g	36.0	012601MEB	MeHg	ng/g		NA
1/11/01	1459-462	Control P DAY 4	1459-462		Total Hg	012601MEB	NA	NA	µg/g	37.2	012601MEB	MeHg	ng/g		NA
1/11/01	1459-463	Control P DAY 8	1459-463		Total Hg	012601MEB	NA	NA	µg/g						

Source Bioavailability and Mine Remediation Feasibility in the Cache Creek Watershed

APPENDIX 10B. Data and QA/QC Report for preliminary slurry experiment water samples analyzed by Battelle MSL for total Hg and methyl Hg. Page 2 of 2.

REPLICATE ANALYSES	1459-422	01701MEB	0.102	ng/g
Abbott 0.02 DAY 0 R1	1459-422	01701MEB	0.0998	ng/g
Abbott 0.02 DAY 0 R1			3	%
RPD				
Abbott 2.0 DAY 8 R2	1459-439	01901MEB	1.39	ng/g
Abbott 2.0 DAY 8 R2	1459-439	01901MEB	1.80	ng/g
RPD			26 #	%
Floc 2.0 DAY 4 R1	1459-454	012401MEB	1.97	ng/g
Floc 2.0 DAY 4 R1	1459-454	012401MEB	2.40	ng/g
RPD			20	%
REPLICATE ANALYSES				
Control N DAY 0	1459-458	012401MEB	0.233	ng/g
Control N DAY 0	1459-458	012401MEB	0.272	ng/g
RPD			20	%
Floc 2.0 DAY 0 R1	1459-462	01901MEB	1.55	ng/g
Floc 2.0 DAY 0 R1	1459-462	012601MEB	1.53	ng/g
			1	%
Floc 2.0 DAY 0 R1	1459-462	011001MEB	1.55	ng/g
Floc 2.0 DAY 0 R1	1459-462	012601MEB	1.53	ng/g
			1	%
Floc 2.0 DAY 0 R2	1459-463	01901MEB	0.776	ng/g
Floc 2.0 DAY 0 R2	1459-463	012601MEB	0.767	ng/g
			2	%
MATRIX SPIKE RESULTS				
Abbott 0.02 DAY 0 R2	1459-423	011701MEB	2.43	ng/g
Amount Recovered			0.0514	ng/g
Percent Recovery			2.13	ng/g
Abbott 0.02 DAY 0 R2 - Spike			2.78	ng/g
Amount Recovered			106	%
Percent Recovery				
Amount Spiked			2.37	ng/g
Abbott 0.02 DAY 0 R2	1459-423	011701MEB	0.0514	ng/g
Amount Recovered			2.20	ng/g
Percent Recovery			2.15	ng/g
Abbott 0.02 DAY 0 R2 - Spike Duplicate			91	%
Amount Recovered				
Percent Recovery				
Amount Spiked			0.766	ng/g
Floc 0.02 DAY 0 R1	1459-440	01901MEB	0.128	ng/g
Floc 0.02 DAY 0 R1 + Spike			0.920	ng/g
Amount Recovered			0.791	ng/g
Percent Recovery			100	%
Amount Spiked			0.800	ng/g
Floc 0.02 DAY 0 R1	1459-440	01901MEB	0.179	ng/g
Floc 0.02 DAY 0 R1 + Spike Duplicate			0.954	ng/g
Amount Recovered			0.825	ng/g
Percent Recovery			100	%
Amount Spiked			1.07	ng/g
Control N DAY 0	1459-458	012401MEB	0.248	ng/g
Control N DAY 0 + Spike			1.41	ng/g
Amount Recovered			1.16	ng/g
Percent Recovery			100	%
Amount Spiked			1.09	ng/g
Control N DAY 0	1459-458	012401MEB	1.09	ng/g
Control N DAY 0 + Spike Duplicate			0.248	ng/g
Amount Recovered			1.35	ng/g
Percent Recovery			1.11	ng/g
Amount Spiked			1.02	ng/g

U: Not detected at or above the given concentration.
Exceeds DOQ of 125%

Approval: _____ Date: _____

Project Manager: _____ QA/QC Reviewer: _____ Date: _____

APPENDIX II. Quality Assurance/Quality Control Procedures for U.S.G.S. Elemental Suite Analyses

A variety of measurements and analyses were used to determine the quality of the data associated with this study. Quality assurance and quality control (QA-QC) measures include field and laboratory blank samples, standard reference materials (where available), spike recoveries, and replicate samples. Alpers and other (2000) described the application of these QA-QC measures in a project assessing metals transport in the Sacramento River Basin, in which similar methods of sample collection, preparation, and analysis were used.

Field parameters

The accuracy of field measurements (pH, specific conductance, dissolved oxygen, and temperature) was established by the use of standard methods of analysis with the appropriate calibration standards, as described by Alpers and others (2000).

Major Cations and Trace Elements

Precision and accuracy criteria were evaluated by the analysis of numerous field and laboratory blank samples, standard reference materials (at least 30 % frequency of total samples analyzed), spike addition recovery analysis and replicate sample analysis.

Quantitative analysis was performed, using state-of-the-art analytical chemistry technology, for the determination of both dissolved and total water chemistry constituents. All sample analyses were performed at least in triplicate, (with each analysis consisting of a minimum of 4 replicate instrumental measurements for the plasma spectrometric techniques).

Accuracy

Accuracy is defined in this study as the *measure of the degree of conformance of values generated by a specific method with the true or expected value of that measurement*. The accuracy of laboratory analytical data for trace metals and major anions and cations was assessed by 1) analyzing standard reference materials (SRM) and 2) the recovery of known concentrations of analytes in augmented samples.

The following standard reference materials were used for quality control purposes during these studies: National Institute of Standards and Technology (NIST) 1643b SRM; NIST 1643d (diluted 1:10 to provide elemental concentrations simulating water samples from these studies); *U.S. Geological Survey Standard Reference Water Samples* (T135, T145, T147, T149 and T157); and *U.S. Geological Survey National Research Program, Rare Earth Element Water Standards* (PPREE1 and SCREE1, both at 1:100 dilution) (Verplank and others, 2001).

Correlation coefficients for the statistical regression analysis of these plots are shown in Table I. For elements determined in 3 or more standard reference materials, the regression correlation coefficient (R^2) is 0.9881 or greater (with most of them greater than 0.999), indicating that the overall quality of the data generated for samples determined with the analysis of these standards is of high accuracy.

After inspecting the NIST analysis certificate (NBS, 1984), it is indicated that the value for As is non-certified and reported as "for informational purposes only".

Table 1. Listing of selected trace elements with regression correlation coefficients (R^2) for correlation plots of observed versus reported values of analysis of standard reference materials.

Element	R^2	Element	R^2
Al	0.9995	Mo	0.9998
As	0.9996	Ni	0.9980
B	0.9903	Pb	0.9999
Ba	0.9986	Sb	1.000
Be	1.000	Se	0.9955
Cd	0.9999	Sr	0.9998
Co	0.9996	Tl	0.9989
Cr	0.9974	U	0.9965
Cu	0.9974	V	0.9998
Li	0.9997	Zn	0.9994
Mn	0.9881		

Two types of spike recovery experiments were performed over the duration of the analysis period: 1) spiked blank and 2) spiked samples. "Spiked blanks" were obtained by randomly selecting blanks obtained during a given sampling period and augmenting them in the laboratory with an accurately known quantity of typical selected elements. Similarly, "spiked samples" were obtained by randomly selecting samples obtained during a given sampling period and augmenting them, in the laboratory, with an accurately known quantity of typical selected elements. Both types of samples were analyzed by methods and procedure equivalent to all other samples.

EXHIBIT C

*Mercury Assessment and Monitoring
Protocol for the Bear Creek Watershed,
Colusa, California*, Prepared for the Bureau
of Land Management, Scientific
Investigations Report 2010-5018, U.S.
Department of Interior, U.S. Geological
Survey

Prepared for the Bureau of Land Management

Mercury Assessment and Monitoring Protocol for the Bear Creek Watershed, Colusa County, California



Manzanita Mercury Mine

Scientific Investigations Report 2010-5018

U.S. Department of the Interior
U.S. Geological Survey

Cover: Historical photograph of the 10-pipe retort furnace, Manzanita Mine, Colusa County, which was used to process previously concentrated mercury ore, circa 1900. This photograph is from the 1903 California State Mining Bureau Bulletin 27. Credit to Ron Churchill, California Geological Survey.

Mercury Assessment and Monitoring Protocol for the Bear Creek Watershed, Colusa County, California

By Thomas H. Suchanek, Roger L. Hothem, James J. Rytuba, and Julie L. Yee

Prepared for the Bureau of Land Management

Scientific Investigations Report 2010-5018

U.S. Department of the Interior
U.S. Geological Survey

U.S. Department of the Interior
KEN SALAZAR, Secretary

U.S. Geological Survey
Marcia K. McNutt, Director

U.S. Geological Survey, Reston, Virginia: 2010

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Conversion Factors, Datum, and Acronyms

Conversion Factors

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
acre	4,047	square meter (m ²)
acre	0.4047	hectare (ha)
acre	0.004047	square kilometer (km ²)
Volume		
gallon (gal)	3.785	liter (L)
gallon (gal)	0.003785	cubic meter (m ³)
cubic inch (in ³)	16.39	cubic centimeter (cm ³)
cubic inch (in ³)	0.01639	liter (L)
cubic foot (ft ³)	0.02832	cubic meter (m ³)
Flow rate		
cubic foot per second (ft ³ /s)	0.02832	cubic meter per second (m ³ /s)
gallon per minute (gal/min)	0.06309	liter per second (L/s)
Mass		
gram (g)	0.03527	ounce, avoirdupois (oz)
kilogram (kg)	2.205	pound, avoirdupois (lb)
microgram (µg)	0.0000000353	ounce, avoirdupois (oz)
milligram (mg)	0.0000353	ounce, avoirdupois (oz)
nanogram (ng)	0.000000000353	ounce, avoirdupois (oz)
ounce, avoirdupois (oz)	28.35	gram (g)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
ton, short (2,000 lb)	0.9072	megagram (Mg)
ton, long (2,240 lb)	1.016	megagram (Mg)

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

$$^{\circ}\text{F} = (1.8 \times ^{\circ}\text{C}) + 32.$$

Temperature in degrees Fahrenheit (°F) may be converted to degrees Celsius (°C) as follows:

$$^{\circ}\text{C} = (^{\circ}\text{F} - 32) / 1.8.$$

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (µS/cm at 25 °C).

Concentrations of chemical constituents in water are given in milligrams per liter (mg/L, parts per million), micrograms per liter (µg/L, parts per billion), or nanograms per liter (ng/L, parts per trillion).

Concentrations of chemical constituents in tissues are given in micrograms per gram (µg/g, parts per million).

Concentrations of chemical constituents in sediments are given in micrograms per gram (µg/g, parts per million) or nanograms per gram (ng/g, parts per billion).

Conversion Factors, Datum, and Acronyms—Continued

Datum

Horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

Acronyms

ANOVA	Analysis of variance
ASTM	American Society for Testing and Materials
Au	Gold
B	Boron
BLM	Bureau of Land Management
CDFG	California Department of Fish and Game
Cl-	Chloride
CVRWQCB	Central Valley Regional Water Quality Control Board
DOC	Dissolved organic carbon
Fe	Iron
FLPE	Fluorinated polyethylene
HCl	Hydrochloric acid
Hg	Mercury
K	Potassium
Li	Lithium
MMeHg	Monomethyl mercury
Na	Sodium
NAWQA	National Water-Quality Assessment
ORP	Oxidative-reductive potential
Rb	Rubidium
S	Sulfur
Se	Selenium
Sr	Strontium
TMDL	Total maximum daily load
TotHg	Total mercury
USBM	U.S. Bureau of Mines
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
W	Tungsten
YSI	Yellow Springs Instruments

Mercury Assessment and Monitoring Protocol for the Bear Creek Watershed, Colusa County, California

By Thomas H. Suchanek, Roger L. Hothem, James J. Rytuba, and Julie L. Yee

Abstract

This report summarizes the known information on the occurrence and distribution of mercury (Hg) in physical/chemical and biological matrices within the Bear Creek watershed. Based on these data, a matrix-specific monitoring protocol for the evaluation of the effectiveness of activities designed to remediate Hg contamination in the Bear Creek watershed is presented. The monitoring protocol documents procedures for collecting and processing water, sediment, and biota for estimation of total Hg (TotHg) and monomethyl mercury (MMeHg) in the Bear Creek watershed. The concurrent sampling of TotHg and MMeHg in biota as well as water and sediment from 10 monitoring sites is designed to assess the relative bioavailability of Hg released from Hg sources in the watershed and identify environments conducive to Hg methylation. These protocols are designed to assist landowners, land managers, water quality regulators, and scientists in determining whether specific restoration/mitigation actions lead to significant progress toward achieving water quality goals to reduce Hg in Bear and Sulphur Creeks.

Introduction

Objectives

The objectives of this report are (1) to summarize the known information on the occurrence and distribution of mercury (hereafter Hg) in physical/chemical and biological matrices within the Bear Creek watershed, and (2) using this information as a basis, develop a matrix-specific monitoring protocol for the evaluation of the effectiveness of activities designed to remediate Hg contamination in the Bear Creek watershed.

Study Area

Bear Creek, Cache Creek, and the North Fork of Cache Creek are the major tributaries of the Cache Creek watershed, encompassing 2,978 km² (fig. 1). The Cache Creek watershed

contains soils naturally enriched in mercury (Hg) as well as natural springs (both hot and cold) with varying levels of aqueous Hg. All three tributaries are known to be significant sources of anthropogenically derived Hg from historic mines, both Hg and gold (Au), and associated ore storage/processing sites and facilities (D.G. Slotton, unpub. data, 1995; Foe and Croyle, 1998; Schwarzbach and others, 2001; Tetra Tech EMI, 2003; Domagalski and others, 2004; Slotton, 2004; Suchanek and others, 2004, 2008a, 2009; Gassel and others, 2005).

The Bear Creek watershed is located in the northeastern part of the Clear Lake volcanic field that is composed of Pliocene to Holocene volcanic centers (fig. 2). It is the youngest of the volcanic fields that formed along the margin of the North American plate as the Mendocino triple junction migrated northward along the coast of California. The high heat flow associated with the volcanism resulted in the formation of Hg and gold-silver (Au-Ag) ore deposits. In addition, numerous active hot springs and gas vents are present throughout the volcanic field, including the Bear Creek watershed (figs. 1, 2, 3, 4). The ore deposits are the northernmost and youngest in the Coast Range Hg mineral belt. Mercury and Au-Ag deposits are present on the west side of the Bear Creek watershed and in the drainage area of Sulphur Creek, a major tributary of Bear Creek. Hot springs that are actively depositing Hg and Au are associated with some of these Hg-Au deposits. The geothermal springs reflect the waning stage of the hydrothermal systems that formed the Hg and Au deposits. Cold to weakly thermal carbonate springs also are present in the Bear Creek watershed. These springs are actively depositing travertine, and some of these fluids contain anomalously high concentrations of Hg. The hot springs and cold carbonate springs are characterized by high salinity waters that are derived from evolved connate water (water trapped in pores during deposition of a sediment) present in the sedimentary rocks of the Great Valley sequence.

The Bear Creek watershed is unusual in that meteoric water (groundwater derived from precipitation) does not always dominate the composition of waters in Bear Creek and some of its tributaries. High salinity effluent from the numerous geothermal springs, cold carbonate springs, and high salinity groundwater is a significant source of water to Bear Creek and contributes to its relatively high conductivity.

Bear Creek Watershed Overview

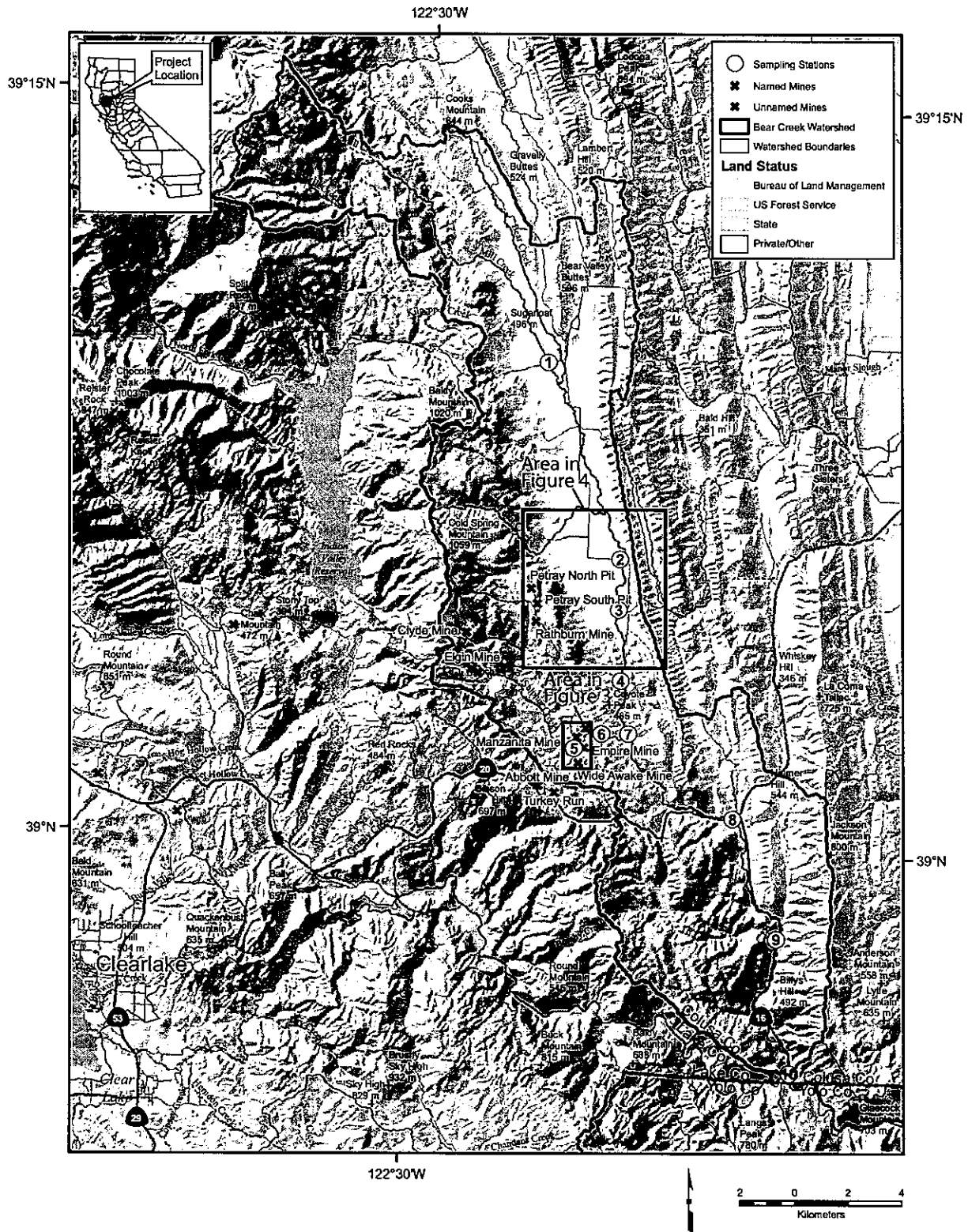


Figure 1. Bear Creek Watershed with locations of mines, springs, and proposed sampling locations for mercury monitoring. Locations of figures 3 and 4 are indicated on this figure.

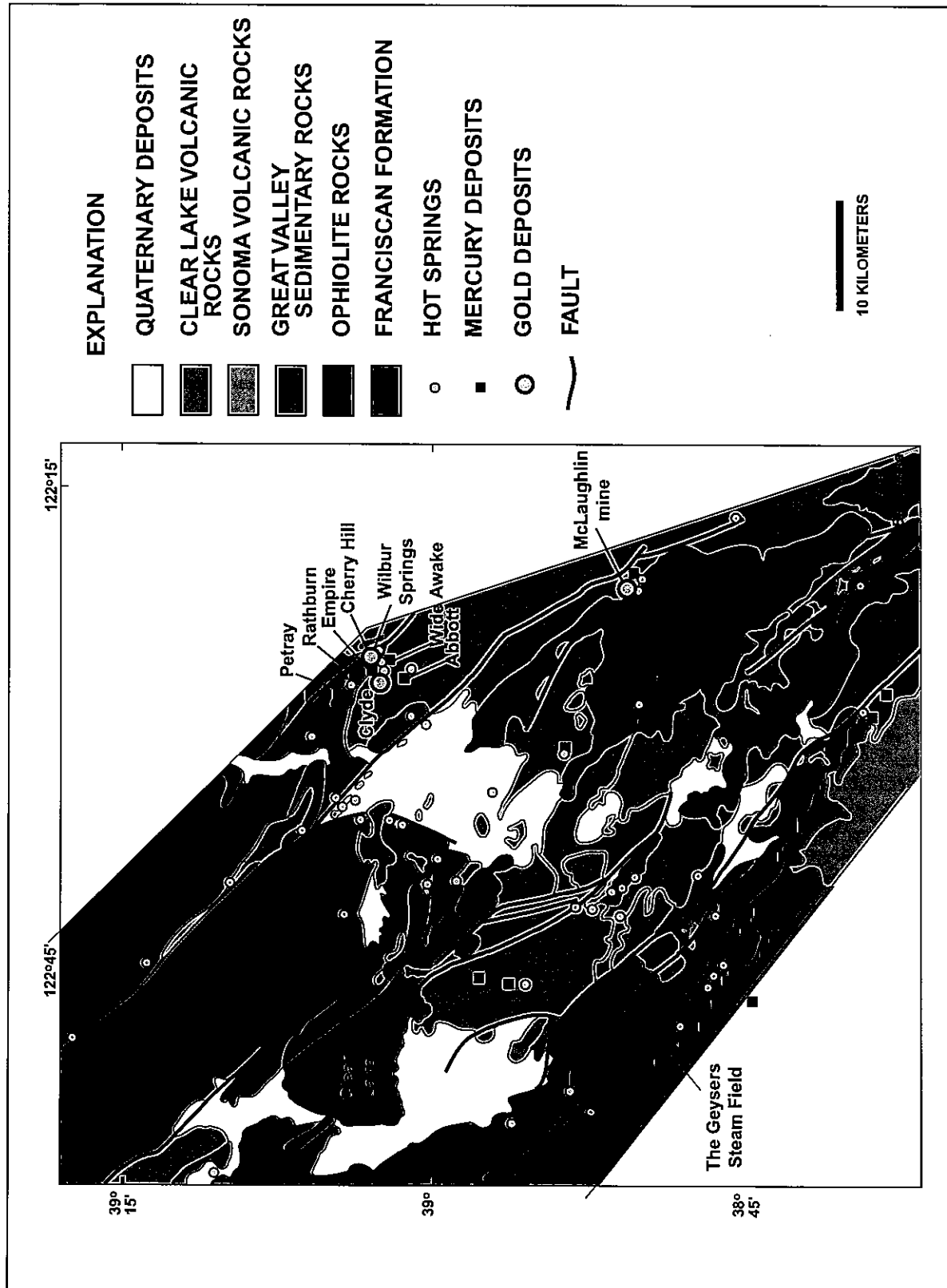


Figure 2. Geological map and ore deposits and geothermal springs located in the Clear Lake volcanic field, including the Bear Creek watershed. Wilbur Springs and adjacent Hg and Au deposits and geothermal springs are significant sources of Hg to Bear Creek.

4 Mercury Assessment and Monitoring Protocol for the Bear Creek Watershed, Colusa County, California

Conductivity under low-flow conditions is 800 $\mu\text{S}/\text{cm}$ in the upper part of the watershed and increases to 1,200 $\mu\text{S}/\text{cm}$ just upstream of the confluence with Sulphur Creek. During the dry season, the effluent from saline springs and groundwater predominate, and Bear Creek water reaches its maximum salinity. During the wet season, runoff reduces the salinity of Bear Creek, and the waters of Bear Creek and its tributaries are predominantly meteoric. The effluent from the high salinity springs also contains elevated concentrations of Hg, sulfate, boron (B), and tungsten (W) that significantly affect water quality, especially under low-flow conditions during the dry season, and during low rainfall years. Important components that contribute to the methylation of Hg include sulfate, salinity, dissolved organic carbon (DOC), and Hg. Thus, seasonal changes in the water chemistry of Bear Creek and some of its tributaries, especially Sulphur Creek, can affect the physical and chemical variables that control Hg methylation. It is, therefore, important that the monitoring protocol specify sampling under similar seasonal and flow conditions so that results may be compared under similar flow conditions.

Geology

The north-south trend of Bear Creek reflects a major geologic boundary in California that is termed the Coast Range fault. The fault separates Cretaceous sedimentary rocks of the Great Valley sequence and the Coast Range ophiolite to the east from rocks of the Franciscan Complex to the west (fig. 2). Initial movement along the Coast Range fault thrust Great Valley sequence rocks above the similar age Franciscan Complex. This initial period of compressional faulting was followed by downward displacement along low-angle detachment faults. The hills that comprise the east side of Bear Valley consist of Great Valley sequence sandstones, siltstones, and shales that have been tilted upward and dip to the east at angles up to 45 degrees. These sedimentary rocks comprise the floor of Bear Valley as well as the first low hills on the west side of the valley. The uplifted west side of Bear Valley is bounded by a series of faults that separates Great Valley sequence rocks to the east from rocks of the Franciscan Complex and Coast Range ophiolite to the west where these rocks form the high hills of Walker Ridge. The Rathburn and Petray Hg deposits are hosted in hydrothermally altered Coast Range ophiolite, however, the Hg deposits in the Sulphur Creek watershed are hosted in sedimentary rocks of the Great Valley sequence.

Sources of Mercury

Both natural and anthropogenic sources contribute Hg to Bear Creek and its tributaries. The natural sources consist of geothermal springs, cold carbonate springs, and hydrothermally altered rock associated with Hg and Au deposits, and unaltered rock. The anthropogenic sources include abandoned Hg mines, Au mines, and ore-processing facilities present in the Bear Creek and Sulphur Creek

watersheds. The geothermal springs are located within the Sulphur Creek watershed and include Wilbur Springs, and, farther upstream, Jones Fountain of Life, Elbow, Blank, and several hot springs within the Elgin Hg deposit. The Jones Fountain of Life and two smaller hot springs (Blank and Elbow) occur on the eastern margin of the Cherry Hill Au deposit and adjacent to the Manzanita Hg deposit. Cold carbonate springs are present throughout the Bear Creek watershed and are localized along faults that bound the east and west side of Bear Valley and the east side of the lower reach of Bear Creek. A large number of cold saline springs are localized along the Bear Fault (located on the west side of Bear Valley and to the east of the Rathburn and Petray Hg mines). Effluent from these springs, along with saline groundwater, significantly increases the conductivity of Bear Creek water (Slowey and Rytuba, 2007). Downstream of the input from the cold springs, the chloride (Cl^-) concentration of Bear Creek is 94 milligrams per liter (mg/L, ppm = parts per million) (Site 3, table 1) as compared to 30 ppm upstream of the input of the springs (Site 2, table 1), an increase of 300 percent. Because of the addition of saline groundwater, the Cl^- concentration of Bear Creek increases to 150 ppm just upstream of the confluence with Sulphur Creek (Site 4, table 1). However, sulfate concentration in the 6.5-km reach of Bear Creek from Site 2 to Site 4 remains about the same, at a relatively high concentration of 17–19 ppm. The conductivity of Bear Creek increases substantially downstream of its confluence with Sulphur Creek because of the effluent from high salinity hot springs in the Sulphur Creek watershed. During the dry season, Sulphur Creek waters are composed primarily of saline, hot spring effluent that also contains elevated concentrations of sulfate, Hg, W, B, and iron (Fe).

Geothermal Springs

In the lower part of the Sulphur Creek watershed, geothermal springs are localized along the Resort fault zone. At Wilbur Springs, several hot spring vents form a coalescing travertine terrace along the northern bank of Sulphur Creek (figs. 2 and 3). The temperature of the Wilbur Hot Springs geothermal waters ranges as high as 56°C, and the waters have very high concentrations of Cl^- (10,900 ppm) and B (280 ppm). The concentration of total Hg (TotHg) in the Wilbur springs ranges from 6.4 to 6.7 $\mu\text{g}/\text{L}$ (ppb = parts per billion) (Janik and others, 1994). Suchanek and others (2004) measured the geothermal waters where they feed the hot baths at the Wilbur Springs Resort and reported TotHg concentrations ranging from 3.5 to 7.3 ppb with 26 to 69 percent of the TotHg present in the dissolved fraction. Black sediment that precipitates from the hot spring water contains 27 ppm TotHg and 4.3 ppm Au (Peters, 1991). This Hg-enriched sediment enters Sulphur Creek from the hot spring vent area as the hot spring effluent cools and flows over the travertine terrace.

Table 1. Bear Creek watershed monitoring sites (NAD 83).

Site No.	Monitoring site	Latitude	Longitude	Distance from Cache Creek (km)
1	Milk Creek at Brim Road; upper watershed characterization above known mercury sources	39° 09' 46.90" N	122° 26' 50.20" W	34.80
2	Bear Creek at bridge above tributaries from Rathburn Petray; above all known mine input and to be used for comparison with site 3	39° 05' 51.40" N	122° 24' 48.90" W	25.78
3	Bear Creek downstream of Site 2; assess input from tributaries from Rathburn-Petray mines and cold saline springs along Bear Fault	39° 4' 50.27" N	122° 24' 48.1" W	23.65
4	Bear Creek upstream of Sulphur Creek (Hamilton); assess attenuation of input from Rathburn-Petray mines	39° 03' 24.00" N	122° 24' 41.00" W	20.74
5	Sulphur Creek above Wilbur Hot Springs and most mines; assess input from upper watershed and Elgin mine and geothermal springs	39° 02' 0.40" N	122° 25' 49.80" W	21.41
6	Sulphur Creek at USGS Gauge; assess input from geothermal springs and mines	39° 02' 19.0" N	122° 25' 8.0" W	19.92
7	Bear Creek downstream of Sulphur Creek; assess impact of input from Sulphur Creek	39° 02' 20.23" N	122° 24' 25.93" W	18.46
8	Bear Creek at Highway 20 Bridge; assess Hg methylation and transport from watershed impacted by mines and geothermal springs	39° 0' 41.78" N	122° 21' 40.34" W	12.33
9	Bear Creek at Thompson Canyon Bridge; assess Hg methylation in area of low gradient and cattle grazing	38° 58' 18.60" N	122° 20' 26.60" W	6.73
10	Bear Creek just upstream of the confluence with Cache Creek; assess Hg and MMeHg released from entire Bear Creek watershed	38° 55' 37.00" N	122° 20' 0.00" W	0.08

Elbow spring, located on the southern bank of Sulphur Creek (fig. 3), has the highest water Cl⁻ concentration (13,390 ppm) and TotHg concentration (61.0 ppb) of the geothermal springs in the Sulphur Creek watershed. The black precipitate at the vent contains 179 ppm TotHg and 12.1 ppm Au (Janik and others, 1994). Several unnamed hot spring vents occur in Sulphur Creek downstream of the Elbow spring and precipitate similar black sediment. Under low-flow conditions, the fine-grained precipitate accumulates in this section of Sulphur Creek until the first high-flow event of the wet season transports the Hg-enriched sediment downstream into Bear Creek. Upstream of the Elbow spring is Jones Fountain of Life, a spring that erupts about every 30 minutes with a maximum flow of 1.5 L/sec. The water has a Cl⁻ concentration of 11,260 ppm, a TotHg concentration of 22.0 ppb, and an estimated TotHg flux from this spring of 1.1 kg/yr (Janik and others, 1994). Suchanek and others (2004) reported that the TotHg concentration in this spring ranges from 24.3 to 39.7 ppb, with 14 to 35 percent of the TotHg in the dissolved fraction. As the geothermal water cools and flows from the vent, it precipitates black, fine-grained sediment that contains

157 ppm TotHg and 4 ppm Au. The black precipitate consists of an amorphous aluminum silicate that contains Fe, sulfur (S), and potassium (K). Crystals of cinnabar (up to 1 mm in size) and barite (up to 6 mm) occur within the amorphous black precipitate. Blank hot spring is located south of Sulphur Creek, and effluent and precipitate from the hot spring do not enter the creek except under very high-flow conditions. The hot spring water has a Cl⁻ concentration of 8,700 ppm and TotHg concentration of 6.9 ppb. However, because of its relatively low flow (0.25 L/sec), the estimated TotHg flux from this spring is only about 0.055 kg/yr (Janik and others, 1994).

In the upper part of the Sulphur Creek watershed, several hot springs and gas vents are present in and adjacent to the Elgin Hg mine. The Elgin hot spring, located within the open cut of the Elgin Hg mine, has the highest temperature, 67°C, of all geothermal springs in the Sulphur Creek watershed. The Cl⁻ concentration of the water is 11,400 ppm, and the TotHg concentration is 11.0 ppb. The flow from the hot spring vent is 1.07 L/sec, and the estimated TotHg flux is 0.15 kg/yr (Janik and others, 1994). Waters from other hot springs adjacent to the Elgin Hg mine have lower Hg concentrations, 0.7 ppb.

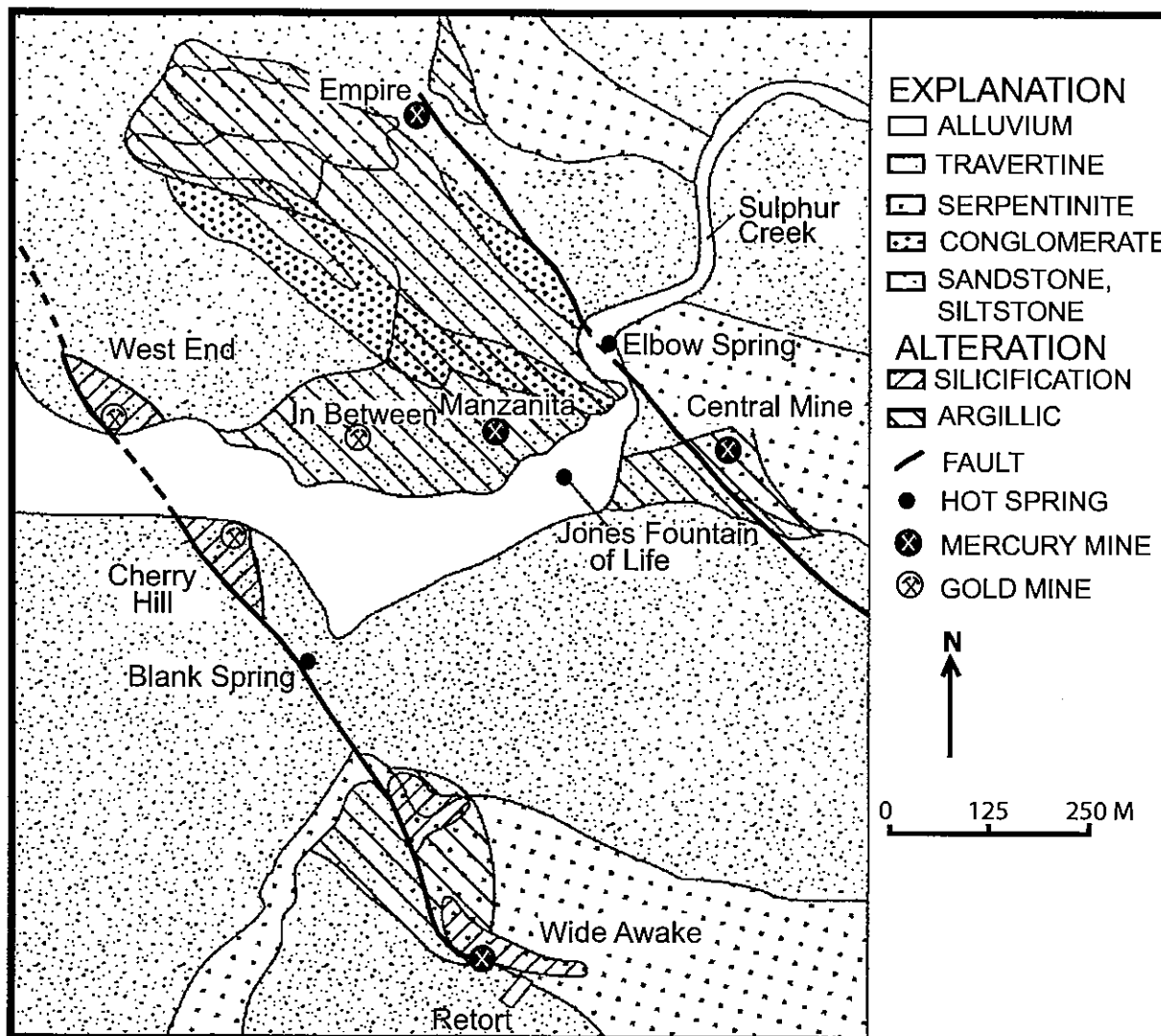


Figure 3. Geology and Hg and Au deposits located in the Sulphur Creek tributary to Bear Creek. Geothermal springs adjacent to the ore deposits are actively depositing Hg and Au and are sources of Hg-enriched sediment to Bear Creek.

All geothermal springs in the Sulphur Creek watershed are elevated in sulfate and sulfide concentration, resulting in $7-16 \times 10^3$ kg of sulfate being added to Sulphur Creek from these sources per year (Churchill and Clinkenbeard, 2002).

Sulphur Creek water downstream of all geothermal spring inputs has very high concentrations of TotHg, 1.3 ppb, 88 percent of which is in the particulate form (Suchanek and others, 2004). The geothermal springs and mine sources in the

Sulphur Creek watershed are significant sources of particulate TotHg to Sulphur Creek, with average estimates ranging from 0.6 to 10.7 kg/yr (Suchanek and others, 2004). The relative importance of the Hg–Au mine and geothermal Hg sources in Sulphur Creek has not been sufficiently documented, but under low-flow conditions and low rainfall years, the geothermal Hg source predominates.

Cold Carbonate Springs

Cold carbonate springs are present along several faults in the Bear Creek watershed. A large number of these springs are localized along the Bear Fault, which is located to the west of Bear Creek and east of the Rathburn-Petray mines (fig. 4). These springs consist of variable mixtures of meteoric water and saline groundwater derived from connate fluids in sedimentary rocks in the Great Valley sequence. The cold spring waters have a highly variable proportion of saline groundwater, ranging from 13 to 100 percent. Springs along the central part of the Bear Fault have the highest component of saline groundwater and have exceptionally high conductivities (9,400 and 19,000 $\mu\text{S}/\text{cm}$). The most saline cold spring waters, 6,065 mg/L Cl^- , are comparable to saline geothermal hot spring waters located in the Sulphur Creek watershed. The cold springs are characterized by high concentration of the cations sodium (Na), K, rubidium (Rb), lithium (Li), selenium (Se), strontium (Sr), and W, as well as nitrate, sulfate, and DOC. Plots of these cations against Cl^- for the various cold springs in the Bear Valley watershed define a two-component linear mixing line, indicating that the spring waters are mixtures of meteoric and saline groundwater. Alkalinity is relatively high in cold carbonate springs and surface waters that drain the Rathburn-Petray mine area. This results from release of carbonate from saline groundwater, and leaching of carbonate from serpentinite and mafic bedrock of the Coast Range ophiolite and the Franciscan Formation. The presence of alkaline pH (> 8.0) indicates that the cold carbonate springs and some surface waters, with a significant component of saline groundwater, are in aqueous equilibrium with calcium carbonate. The alkalinity of spring waters ranges from 2.8 meq/L as carbonate (less groundwater-dominated) to 29 meq/L in saline cold spring water that is actively depositing travertine. Bicarbonate is the dominant buffering agent, although organic acids also may buffer these waters.

High concentrations of TotHg, up to 0.7 ppb, occur in some cold carbonate springs and saline surface waters that drain the Rathburn-Petray mine area. In cold carbonate spring water, Hg is present primarily in the filtered fraction, typically comprising from 78 to 100 percent of the TotHg present. In saline surface waters that are dominantly meteoric with a small component of high salinity groundwater, the amount of TotHg in the filtered fraction is highly variable, ranging from 100 percent to less than 4 percent. The concentrations of TotHg in both filtered and unfiltered waters are not correlated with Cl^- concentration or any other major or minor element. Processes that control TotHg concentration in saline surface and spring waters are not conservative and may include precipitation and dissolution of carbonate, dissolution of HgS by DOC, and seasonal changes in surface-water flow. The highest TotHg concentration (0.9 ppb measured under dry

season low-flow conditions) occurs in surface water from a tributary that drains the north pit of the Petray mine (North fork of Tributary 1 in Slowey and Rytuba, 2008). The water in this tributary is dominantly meteoric (< 1.5 percent saline groundwater), and the creek sediment has a high concentration of TotHg (350 ppm), which is present as cinnabar and metacinnabar.

Bedrock

The Hg concentrations in unaltered bedrock exposed in the Bear Creek watershed are typically less than 154 ng/g (parts per billion = ppb), with higher Hg concentrations occurring in sedimentary rocks of the Great Valley sequence being higher in the range of Hg values (Smith and others, 2008). The Hg concentration in unaltered shales, siltstones, and sandstones in the Great Valley sequence ranges from 31 to 154 ppb. Much lower Hg concentrations, less than 24 ppb, occur in mafic rocks of the Coast Range ophiolite, serpentinite derived from the ophiolite, and mafic rocks in the Franciscan Formation. The Hg concentration in greywacke, blueschist, and cherty mudstone of the Franciscan Formation ranges from 35 to 88 ppb. Volcanic rocks in the Clear Lake volcanic field typically have low Hg concentrations (< 92 ppb). However, volcanic rocks are not present in the Bear Creek watershed, and only minor intrusive basaltic rock has been mapped in the Sulphur Creek watershed. Erosion of hill slopes composed of Great Valley sequence sedimentary rocks would be expected to produce sediment with a Hg concentration in the range of 30 to 150 ppb. Sediment derived from hill slopes composed of Franciscan and Coast Range ophiolite would produce sediment with lower Hg concentrations, ranging from 20 to 90 ppb.

An estimate of the annual TotHg flux of 0.45 to 9.8 kg from background soils in Sulphur Creek has been calculated by assuming erosion rates between 0.5 and 10 (tons/acre)/yr applied over the entire watershed (Churchill and Clinkenbeard, 2002), but the actual amount of regional background TotHg entering the watershed is unknown. No estimate has been made for the Bear Creek watershed.

Mercury and Gold Mines

Mines in the Bear Creek watershed include several Hg and Au mines in Sulphur Creek, and the Rathburn and Petray Hg mines located in the hills (Walker Ridge) on the western side of Bear Valley. All of these Hg mines have had relatively small production, but the surface disturbance and mine wastes at the mines are highly variable. Surface exposures of cinnabar mineralization in the Petray mine open pits have high TotHg concentrations (up to 2,490 ppm) and are a continuing source of Hg-enriched sediment that is released from the mine site resulting in high concentrations of Hg

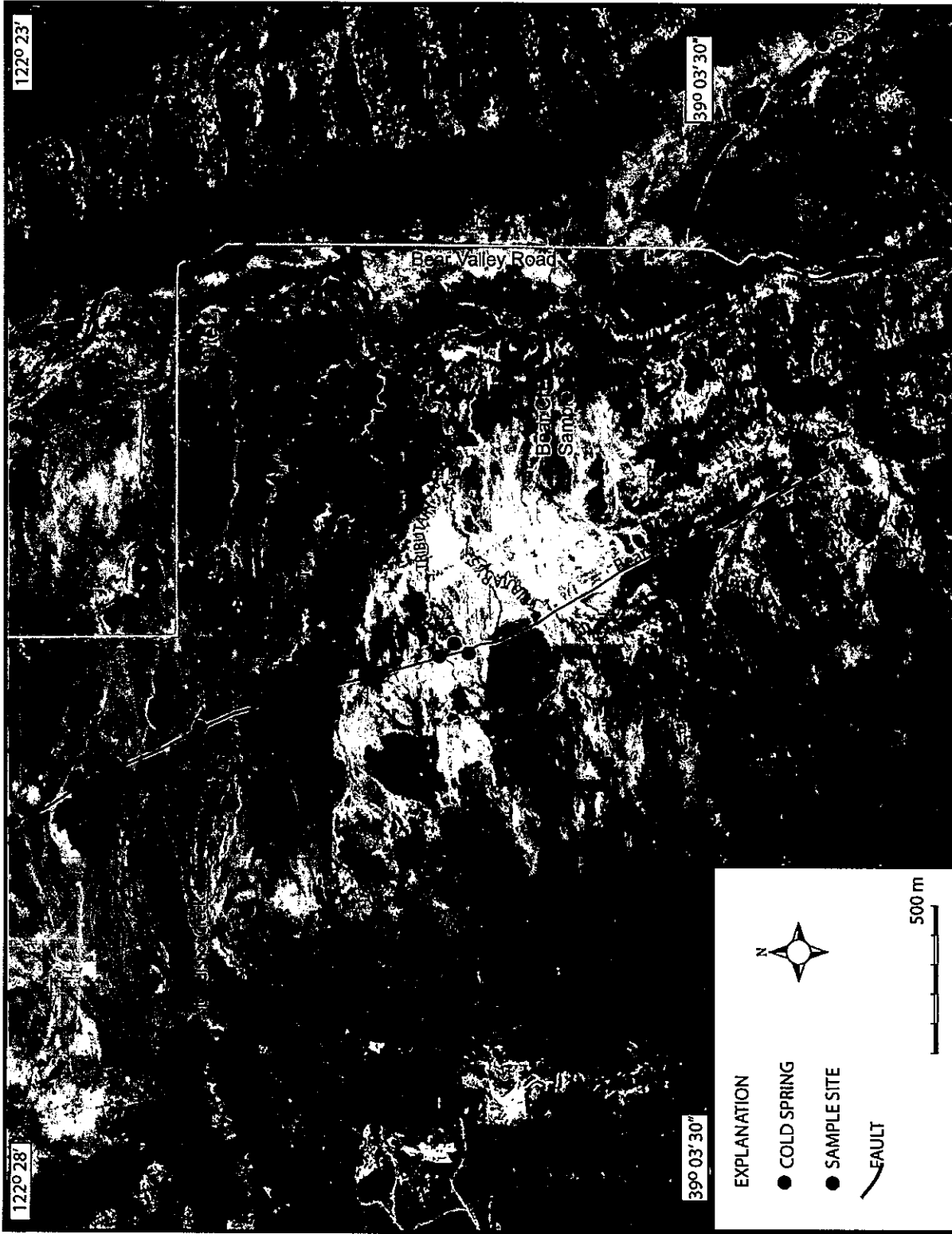


Figure 4. Location of the Rathburn and Petray Hg mines and tributaries 1- 4 that drain the mine area and release Hg-enriched sediment into Bear Creek. Some saline cold springs along the Bear Fault release Hg into Bear Creek. Cold carbonate springs east of the Petray Mine have relatively low concentrations of Hg as does the saline Cain Spring located east of Bear Creek. Bear Creek sample sites discussed in text and listed in table 1 are shown by red dots.

in tributaries that drain the mine area (Slowey and Rytuba, 2008). In Sulphur Creek, erosion of waste rock and tailings from the mine sites is a source of Hg-enriched sediment but Hg-enriched precipitates from geothermal springs located in and adjacent to the mines are likely more significant. Of the 10 major tributaries that enter Bear Creek, Sulphur Creek has the highest sediment Hg concentrations with 91.8 ppm in the grain size fraction $< 63 \mu\text{m}$ (Bosworth and Morris, 2009). In comparison, the other tributaries to Bear Creek have Hg concentrations in sediment that range from 0.04 to 0.53 ppm in the grain-size fraction $< 63 \mu\text{m}$ (Bosworth and Morris, 2009). The average background Hg concentration in sediment within the Cache Creek watershed is 0.06 ppm in the grain size fraction $< 63 \mu\text{m}$ (Foe and Bosworth, 2008). Mercury mine tailings (calcines) with TotHg concentrations up to 1,020 ppm are present at only three of the mines. Waste rock containing variable concentrations of TotHg ranging from 10 to 1,020 ppm, and Hg-enriched soils ranging in concentration from 10 to 300 ppm are present at all of these mines and are a volumetrically more significant potential source of Hg-enriched sediment to the Bear Creek watershed (Churchill and Clinkenbeard, 2002).

The Manzanita Hg-Au mine and the nearby West End Hg-Au mine and In Between Au prospect (fig. 3) were developed on the periphery of the larger Cherry Hill hot spring Au-Hg system that was discovered by Homestake Mining Company in 1977 (Nelson and others, 1993). The mines occur on either side of Sulphur Creek (fig. 3). The Manzanita Au-Hg mine was discovered in 1863 and operated until 1942. Total production was 2,500 flasks of Hg (U.S. Bureau of Mines, 1965). About 3,000 oz (about 85 kg) of Au was produced from the Cherry Hill and Manzanita mines from 1865 to 1891. The Au-Hg ores are hosted in silicified shales, sandstones, and conglomerates in the basal section of the Great Valley sequence. Cinnabar is the main Hg-bearing phase, but minor metacinnabar also was present. Where native Au was present, Hg also occurred as an amalgam (Churchill and Clinkenbeard, 2002). Other sulfides present in the ore included pyrite, marcasite, and stibnite. Bitumen and petroleum occur in some of the gold-quartz veins, especially at the In Between mine. The Manzanita mine workings include several adits and shafts and, in the upper part of the deposit, ores were mined from a glory hole and open cut. Various processing techniques were used at the Manzanita mine. These included stamp mills that introduced Hg to recover the Au by amalgamation, and mechanical concentration of cinnabar to create a cinnabar concentrate from which Hg was recovered by a retort (Churchill and Clinkenbeard, 2002). In the 1940s, the Hg concentrates from the mine were processed at the Wide Awake mine, located about 1 km to the south. There are presently no tailings at the Manzanita, West End, In Between, and Cherry Hill mines. There is a limited amount of waste rock at each of the mine sites, but exposures of altered rock are potential sources of Hg-enriched sediment.

The Central and Empire Hg mines have produced a small amount of Hg estimated to be about 170 flasks from ores that were processed primarily at the Wide Awake mine. There are small amounts of tailings and waste rock at the Central mine, and waste rock is present around and within a small retort at the Empire mine. The mine site is vegetated and does not appear to be a source of Hg-enriched sediment to Sulphur Creek (Tetra Tech, 2003).

The Wide Awake mine was discovered in the 1870s and produced 1,800 flasks of Hg until the mine was closed in the 1940s. Some of the production came from ores that were mined at the Manzanita and Empire mines. The Hg ore occurs in the basal section of the Great Valley sequence at the contact between shale and sediments composed of detrital serpentinite. Cinnabar is the main ore mineral and occurs in opalized serpentinite that locally contains abundant petroleum. Mine workings include several surface cuts and underground workings that were accessed by a 152-meter shaft (U.S. Bureau of Mines, 1965). Mercury ores were processed in a 24-ton Scott furnace and several smaller retorts. The pile of tailings that includes some waste rock is estimated to contain 11,000 tons of material (Churchill and Clinkenbeard, 2002) and is a source of Hg-enriched sediment during runoff in the wet season.

The Elgin Hg mine is located in the headwaters of Sulphur Creek, and several hot springs and gas vents are present in and adjacent to the mine workings. The mine was discovered in the early 1870s, and only a small amount of production, about 50 flasks, has been reported for the mine. The Hg ores occur along the contact of serpentinite and shale of the Great Valley sequence and are hosted in silicified serpentinite and in acid-leached serpentinite in the upper part of the ore body. Cinnabar is the primary ore mineral, and native sulfur occurs in the acid-leached part of the ore body. Pyrite is present in the lower part of the ore body. The mine workings consist of surface cuts, adits, and underground workings that were limited in development because the hot springs and associated sulfur and methane gases precluded extensive underground mining (U.S. Bureau of Mines, 1965). The small amount of ore was processed in a retort, and the amount of tailings on the mine site is minor, but waste rock in the open cuts is a potential source of Hg-enriched sediment. The Elgin hot spring vents in the central part of the main open cut, and effluent from the spring is collected in a small pond. A black precipitate that is enriched in Hg forms in the hot spring vent and collects in the pond but is only released to the watershed under high flows.

The Clyde Au mine (fig. 1) ore body was discovered in the early 1860s and has produced a small amount of Au. Native Au and pyrite occur in a silicified body of serpentine. The Au was recovered in a mill that apparently did not use Hg; more recent reprocessing of the tailings used gravity separation rather than Hg to recover the Au. This mine has only a small potential to release Hg-enriched sediment into Sulphur Creek.

Estimates of yearly TotHg flux from mine wastes into Sulphur Creek have been based on estimates of erosion rates from mine wastes with known Hg concentrations. The Hg flux into Sulphur Creek is estimated to range from 4.4 to 18.6 kg, while the range of Hg flux into Bear Creek is from 0.7 to 23.5 kg (Churchill and Clinkenbeard, 2002). However, there is high uncertainty in these estimates and only very limited data are available to quantify the Hg flux from the mine sites. Only two samples of water from the intermittent creek that drains the Wide Awake mine area have been collected, and the data indicate significant release of Hg from the mine site during the wet season. The concentration of TotHg in water from the Wide Awake mine drainage measured in February 2000 and 2001 was 2.5 and 4.3 ppb respectively, and from 52 to 58 percent of the TotHg was in the filtered fraction (Suchanek and others, 2004).

The Rathburn Hg mine ore body was discovered and initially mined in the early 1890s. The Rathburn and the more recently developed Petray open pit mines are localized along fault zones in serpentinite that has been altered and cut by quartz and chalcedony veins. Cinnabar is the primary ore mineral, and metacinnabar has been identified in sediment derived from the Petray mine. The Hg ores formed in a hot spring system in the steam-heated environment present above boiling groundwater table. However, no active hot springs are present in the deposits. The Rathburn Hg mine is relatively small, having produced 100 flasks of Hg. Mining in the late 1960s and early 1970s recovered about 400 flasks of Hg from the Petray open pit mine (U.S. Bureau of Mines, 1965). At the Rathburn Mine, Hg ores were processed in a brick retort, and small amounts of calcines are present that contain up to 1,020 ppm Hg (Churchill and Clinkenbeard, 2002; Slowey and Rytuba, 2008). Waste rock derived from open cuts (in altered serpentinite) contains less than 39 ppm TotHg. Ores from the Petray Mine were processed offsite in a rotary furnace at the Abbott Mine, and, as a result, there are no mine tailings at the Petray mine. However, waste rock and ore in altered serpentinite are sources of Hg-enriched sediment that are released from the mine during storm events. The Hg concentration in sediments of the two tributaries that drain the Petray mine is highly elevated for the sampled section extending 2 km from the mine site. Both cinnabar and metacinnabar are present in sufficient quantity to be panned easily from the sediment (Slowey and Rytuba, 2008). The relative importance of Hg-enriched sediment released from the Rathburn and Petray mines as compared with Hg released from cold carbonate springs along the Bear Fault has not been determined, but both sources contribute Hg to Bear Creek (Slowey and Rytuba, 2008). Sediment in Bear Creek just downstream of the input from tributaries that drain the Rathburn and Petray mines (Monitoring Site 3, [table 1](#)) has a highly elevated TotHg concentration, 9,290 ppb. The TotHg concentration in Bear Creek sediment is considerably lower, 80 ppb, upstream of the Rathburn and Petray input (Monitoring Site 2, [table 1](#)), which indicates a significant Hg release from the mine sites. Although the TotHg concentration

in Bear Creek water downstream of the Rathburn and Petray mine input under low-flow conditions is very low (2.2 ng/L; ppb = parts per billion), it is still higher than in water upstream of the mine input, which has a TotHg concentration of 0.45 ppb.

Mercury Assessments in the Bear Creek Watershed

Physical/Chemical Assessments

Water samples were collected during 2000–2001 from a number of sites within the Cache Creek watershed and analyzed for TotHg and monomethyl Hg (MMeHg) (Domagalski and others, 2004; Slotton and others, 2004; Suchanek and others, 2004). A subset of those sites was within the Bear Creek Watershed and their locations are identified below.

Upper Bear Creek

This site is located at the Bear Valley Road bridge crossing (N: 39°5.83', W: 122°24.71'). This site was believed to be upstream of all known mine loading of Hg, and it is located upstream of the Hg inputs into Bear Creek identified by Slowey and Rytuba (2008). Results from Slotton and others (2004) collections are presented below. For both unfiltered and filtered aqueous TotHg and MMeHg, the Upper Bear Creek site exhibited concentrations that were among the lowest in the entire Cache Creek and Bear Creek watersheds. At the Upper Bear Creek site, unfiltered aqueous TotHg ranged from ca. 0.5 to 4.0 ppb and filtered aqueous TotHg ranged from ca. 0.4 to 1.0 ppb, respectively. These data suggest that the TotHg at this site is mostly associated with particles. MMeHg in unfiltered aqueous samples ranged from ca. 0.05 to 0.11 ppb and filtered aqueous samples ranged from ca. 0.02 to 0.10 ppb, suggesting that a large proportion of MMeHg is found in the dissolved form. Because the Upper Bear Creek site is upstream of all known mining sites, these results could indicate a geothermal or saline spring (as opposed to a mining source) as the primary source of both TotHg and MMeHg in this region of Bear Creek.

Sulphur Creek

This site, located in Sulphur Creek upstream of the confluence with Bear Creek (N: 39° 2.21', W: 122° 24.56'), represents Hg inputs from Hg mines, Au mines, and geothermal springs along Sulphur Creek. Data from Slotton and others (2004) on aqueous TotHg and MMeHg in Sulphur Creek demonstrate a different result in comparison with the Upper Bear Creek site. Unfiltered and filtered TotHg ranged from ca. 0.3 to 1.1 ppb and from ca. 0.09 to 0.3 ppb, respectively, suggesting that at this site, the largest component of TotHg is found in the particulate form, not in the dissolved

form. MMeHg ranged from ca. 0.2 to 20 pptr in unfiltered samples and from ca. 0.09 to 1.5 pptr in filtered aqueous samples, again suggesting a significant component derived from particulate MMeHg. Although there are several large geothermal springs in and along Sulphur Creek, numerous adjacent Hg and Au mines erode into Sulphur Creek. Thus, although the dissolved fraction of both TotHg and MMeHg derived from the geothermal springs likely contribute significantly to Hg loading into Sulphur Creek, the particulate Hg found in the eroding soils from the surrounding mines likely overwhelms the contribution from the springs.

Within Sulphur Creek, Suchanek and others (2004) also analyzed unfiltered water collected during February 2000 and 2001. These data indicated that the highest TotHg concentrations were extremes observed from geothermal spring sites as follows: (1) The Jones Fountain of Life spring: 24.3 ppb in 2000 and 39.7 ppb in 2001, and (2) geothermal springs from which the Wilbur Hot Springs Resort draws hot water for their baths at 4.0–7.3 ppb in 2001. However, TotHg concentrations immediately downstream of the Resort at the USGS gaging station (Sulphur Creek Index Station) were considerably reduced to 1.0 ppb (90 percent of which was in particulate form) in 2000 and 1.3 ppb (88 percent of which was in particulate form) in 2001.

Middle Bear Creek Downstream of Sulphur Creek

This site, located about 10 km downstream of the confluence of Sulphur Creek (at approximately Monitoring Site 9 on [fig. 1](#)) (N: 38°58.88', W: 122°20.94'), represents a reach of Bear Creek that has approximately 10-fold dilution of Sulphur Creek inputs. Bear Creek exhibits TotHg and MMeHg concentrations that are intermediate between the Upper Bear Creek site and the Sulphur Creek site. TotHg in unfiltered and filtered aqueous samples exhibited ranges from ca. 11 to 150 pptr and from ca. 8 to 40 pptr, respectively. MMeHg in unfiltered and filtered aqueous samples exhibited ranges from ca. 0.2 to 1.5 pptr and from ca. 0.09 to 0.5 pptr, respectively. The distribution of these ranges of TotHg and MMeHg with respect to the proportions represented by filtered and unfiltered (that is, dissolved vs. particulate) components suggest a mixture of contributions between dissolved and particulate sources. This interpretation would be consistent with the multiple sources influencing the composition of the water mass at a site 10 km downstream of the confluence of Sulphur Creek with Bear Creek. Data on TotHg and MMeHg from the Upper Bear Creek site suggested contributions from a source that is primarily in a dissolved form. This source water would then be mixed with a Hg source that was primarily particulate from Sulphur Creek. As particulate material from the Sulphur Creek source is deposited downstream along the Bear Creek

streambed, the influence of particulate Hg diminishes, consistent with the greater overlap in the ranges of Hg in filtered and unfiltered samples for both TotHg and MMeHg.

A visual analysis of time-series data for TotHg and MMeHg at the Middle Bear Creek site from January 2000 to September 2001 revealed that TotHg peaks occurred during the winter rainy season (February) when maximum erosion typically would send Hg-laden particles downstream. MMeHg peaks at this site occurred during the summer (July/August) both years. A further analysis of the MMeHg:TotHg ratios¹ for water samples at these three sites reveals that this ratio is highest for the Upper Bear Creek site (0.1 for unfiltered water; 0.05 for filtered water), lowest for the Sulphur Creek site (0.001 for unfiltered water; 0.002 for filtered water), and intermediate for the Middle Bear Creek site (0.01 for unfiltered water; 0.01 for filtered water).

Biological Assessments

Several types of bacteria can convert naturally occurring inorganic Hg to its more toxic form, MMeHg, which is a neurotoxin and mutagen. MMeHg may affect several physiological functions, including vision, response to stimuli, growth, and reproduction in both vertebrates and invertebrates. In some cases, MMeHg can cause mortality. The effects of Hg toxicosis are exhibited most prominently in the egg or fetal stage, but may affect juvenile and adult stages as well. Thus, it is important to understand what concentrations of Hg are present, and evaluate whether corrective measures are feasible to lessen the impacts of Hg to wildlife and humans in this region.

Wildlife resources of significance in the Bear Creek watershed include wintering bald eagles (*Haliaeetus leucocephalus*), prairie falcons (*Falco mexicanus*), greater roadrunner (*Geococcyx mexicanus*), tule elk (*Cervus elaphus nannodes*), river otters (*Lontra canadensis*), and foothill yellow-legged frogs (*Rana boylei*) (Schwarzbach and others, 2001; Bureau of Land Management, 2004). An estimated 154 bird species have been documented in the watershed (Bureau of Land Management, 2004). BLM recognizes several sensitive species found in the watershed, including: Townsend's western big-eared bat (*Plecotus townsendii*), Pallid bat (*Antrozous pallidus*), burrowing owl (*Athene cunicularia*), St. Helena mountain king snake (*Lampropeltis zonata zonata*), foothill yellow-legged frog, and western pond turtle (*Actinemys marmorata*), and 17 sensitive plant species. Two of these species, foothill yellow-legged frog and the western pond turtle, are California Species of Special Concern (Jennings and Hayes 1994; California Department of Fish and Game, 2009).

¹MMeHg:TotHg ratios typically are regarded as a proxy for MMeHg bioavailability.

Invertebrates

Beginning in April 1995, Slotton and others (1997) conducted a survey of TotHg in benthic stream invertebrates at 38 sites along Cache Creek and the Bear Creek watershed (figs. 5, 6, 7). This survey involved collections of several trophic levels of benthic invertebrates including: Ephemerellidae (mayflies – herbivores), Siphonuridae (swimming mayflies – herbivores), Hydropsychidae (net-spinning caddisflies – drift feeders), Pteronarcidae (giant stoneflies – leaf shredders), Perlodidae (yellow sally stoneflies – small predators), Calopterygidae (damselflies – small predators), Sialidae (alderflies – small predators), Naucoridae (creeping water bugs – large predators), Aeshnidae (dragonflies – large predators), Libellulidae (dragonflies – large predators), Tipulidae (craneflies – large predators), and Corydalidae (hellgrammites – large predators).

Slotton and others (1997) found significant variability in the concentration of TotHg in invertebrate tissues among different sites within the Cache Creek watershed with a range of about 0.05–22.74 µg/g (parts per million = ppm) dry weight (dw). The highest TotHg concentrations were obtained from Harley Gulch at Highway 20 (up to 22.74 ppm, dw) and within Sulphur Creek (up to 2.69 ppm, dw) (note asterisks in fig. 6). Upstream of the confluence with Sulphur Creek, Bear Creek invertebrate whole body TotHg typically ranged from about 0.1 to 0.2 ppm (dw) but as soon as Sulphur Creek waters enter Bear Creek, invertebrate TotHg concentrations increased to about 1.2–1.5 ppm (dw). However, one site about 0.4 km upstream of the confluence of Sulphur Creek with Bear Creek had elevated invertebrate TotHg concentrations to about 0.3 ppm (dw). Although this increase appears to be real, it is from a single site at a single sampling point in time and its significance should not be over-interpreted. It is possible that there are additional Hg sources entering Bear Creek upstream of the confluence of Sulphur Creek, possibly from the Rathburn-Petray mine area described above. In addition, roadbed materials and/or grazing effects in Bear Valley could affect Hg concentrations upstream of Sulphur Creek. Schwarzbach and others (2001) also sampled invertebrates in Bear Creek near Hamilton Canyon, about 1.2 km upstream of the Slotton site, and found TotHg concentrations ranging from 0.02 to 0.04 ppm, ww (about 0.10–0.20 ppm, dw).

Further studies conducted from 1999 to 2003 by Slotton and others (2004) provided additional Hg data from water, invertebrates, and fish (where present) at three sites in the Bear Creek watershed (in addition to other sites along the entire Cache Creek watershed). Their findings mirror the relative ranges of TotHg and MMeHg found in aqueous samples presented in section, “Physical/Chemical Assessments.” Average TotHg in aquatic insects ranged from ca. 19–41 ppb, wet weight (ww) at the Upper Bear Creek site to ca. 168–465 ppb (ww) at the Middle Bear Creek site, and ca. 416–1,987 ppb (ww) at the Sulphur Creek site. MMeHg ranged from ca. 18–33 ppb (ww) at the Upper Bear Creek site, to ca. 138–359 ppb (ww) at the Middle Bear Creek site, and ca. 139–290 ppb (ww) at Sulphur Creek. Interestingly, the

proportion of MMeHg in these samples was lowest (17–33 percent) at the Sulphur Creek site, intermediate at the Middle Bear Creek site (66–84 percent), and highest at Upper Bear Creek (81–97 percent). A visual analysis of time-series data for MMeHg concentrations in these invertebrates at the Middle Bear Creek site exhibited trends similar to water, with MMeHg peaks occurring during the summer (July/August) both years. That same analysis at the Upper Bear Creek site was not as conclusive, but exhibited a maximum in MMeHg during the summer of 2001 only.

Schwarzbach and others (2001) also analyzed aquatic insects (e.g., Trichoptera, Zygoptera, Anisoptera, and Megaloptera) in Bear Creek as well as other locations within the Cache Creek watershed. Their data revealed a pattern of lower TotHg concentrations (< 0.5 ppm dw) in the North Fork of Cache Creek, Mill Creek, and Bear Creek upstream of Sulphur Creek, but much higher concentrations at sites in Bear Creek downstream of Sulphur Creek (0.5–5.2 ppm dw) and in Sulphur Creek proper (5.0–8.7 ppm dw). In general, their results agreed with those of Slotton and others (1997) for comparable taxa and sites.

Fish

Slotton and others (2004) focused their fish Hg analyses from their wider Cache Creek watershed study primarily on California roach (*Hesperoleucus symmetricus*), speckled dace (*Rhinichthys osculus*), and red shiner (*Notropis lutrensis*), all three of which exhibited average MMeHg concentrations as a percentage of TotHg of 90 percent or greater. However, only California roach were abundant enough within the Bear Creek watershed to obtain sufficient samples to analyze trends. No fish were found in Sulphur Creek. However, an analysis of the MMeHg:TotHg ratio was conducted on California roach from Upper Bear Creek and Middle Bear Creek. Upper Bear Creek roach (N = 29) exhibited a MMeHg percentage of 97.66 percent, whereas the roach at the downstream site, Middle Bear Creek (N = 31), yielded a MMeHg percentage of 86.77 percent. These results are similar to those from analyses on water and invertebrates from those same sites. Time-series data for California roach at the Upper Bear Creek site and the Middle Bear Creek site demonstrated MMeHg peaks in summer June/July/August time periods for both 2000 and 2001.

Schwarzbach and others (2001) also collected California roach from Bear Creek sites upstream and downstream of the confluence with Sulphur Creek in April and August 1997. Results were consistent with Slotton and others (2004), with TotHg concentrations in roach that were significantly higher downstream than upstream of the confluence with Sulphur Creek: 3 times greater in April (upstream = 0.1 ppm, ww; downstream = 0.3 ppm, ww) and 4 times greater in August (upstream = 0.4 ppm, ww; downstream = 1.7 ppm, ww). Sacramento pikeminnows (*Ptychocheilus grandis*) also were collected in Bear Creek in 1998 and exhibited the highest TotHg concentrations among all pikeminnows from a total of five sites throughout the entire Cache Creek watershed.

**CACHE CREEK WATERSHED
INVERTEBRATE MERCURY BIOINDICATOR
SAMPLING SITES -- 1995-1997**

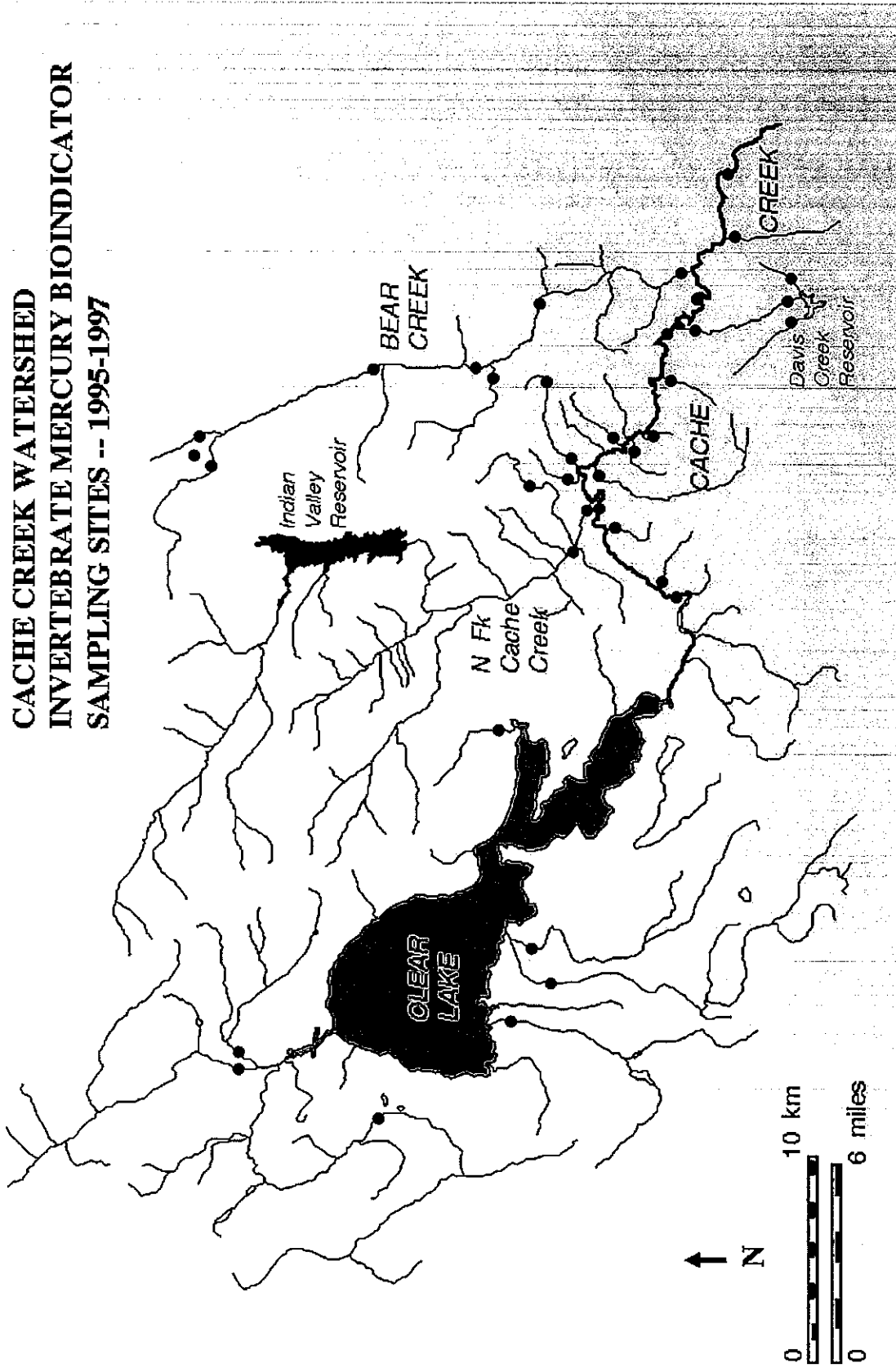


Figure 5. Cache Creek Watershed, including its two major tributaries, Bear Creek and North Fork Cache Creek; red dots indicate invertebrate mercury bioindicator sampling sites used by Slotton and others during 1995-97 (Slotton and others, 1997).

**CACHE CREEK INVERTEBRATE MERCURY
MAIN STEM INPUTS --MAGNIFIED SCALE**

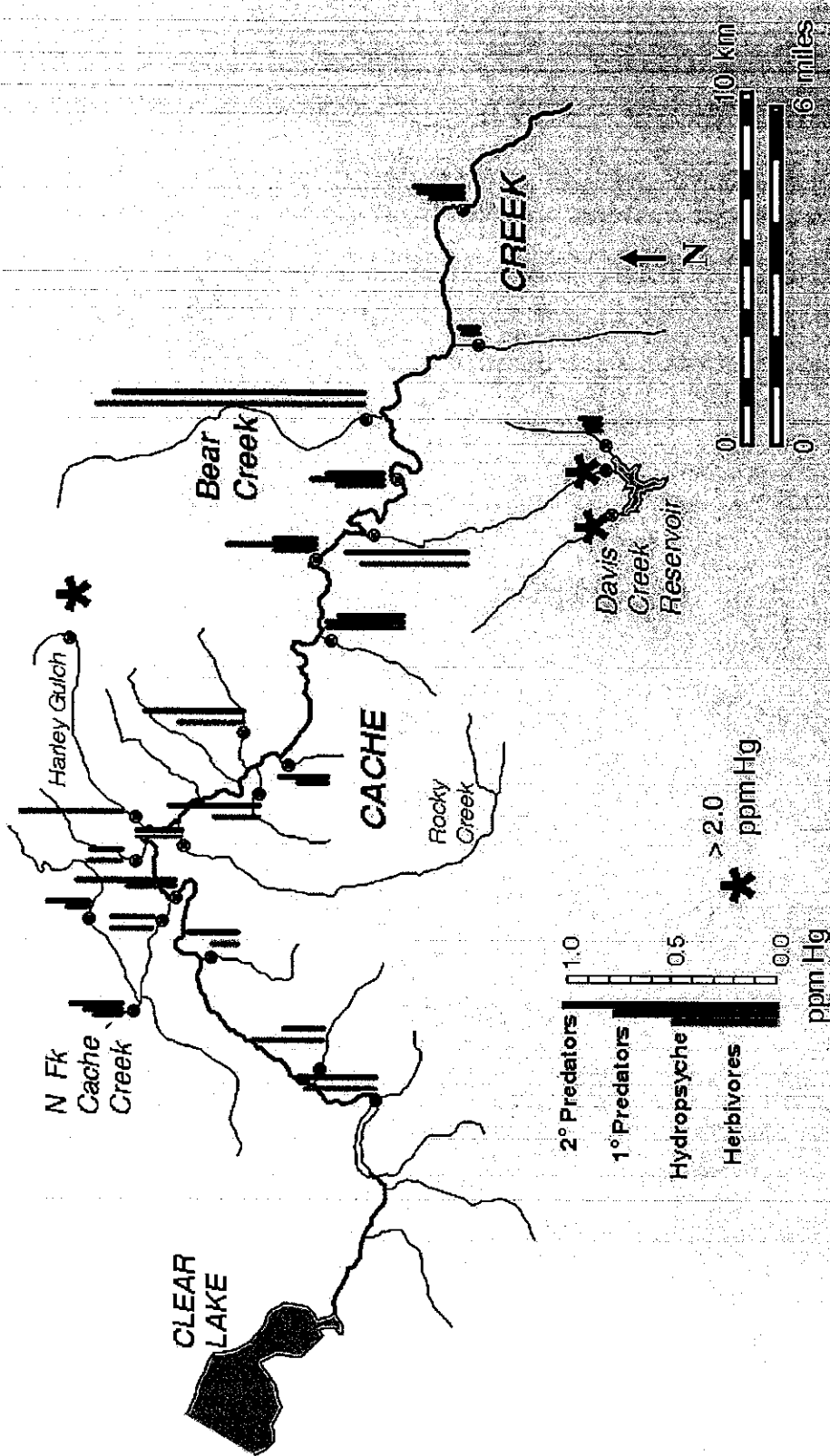


Figure 6. Mercury concentrations (ppm dw) in stream invertebrates from the Cache Creek watershed in 1995. (Slotton and others, 1997).

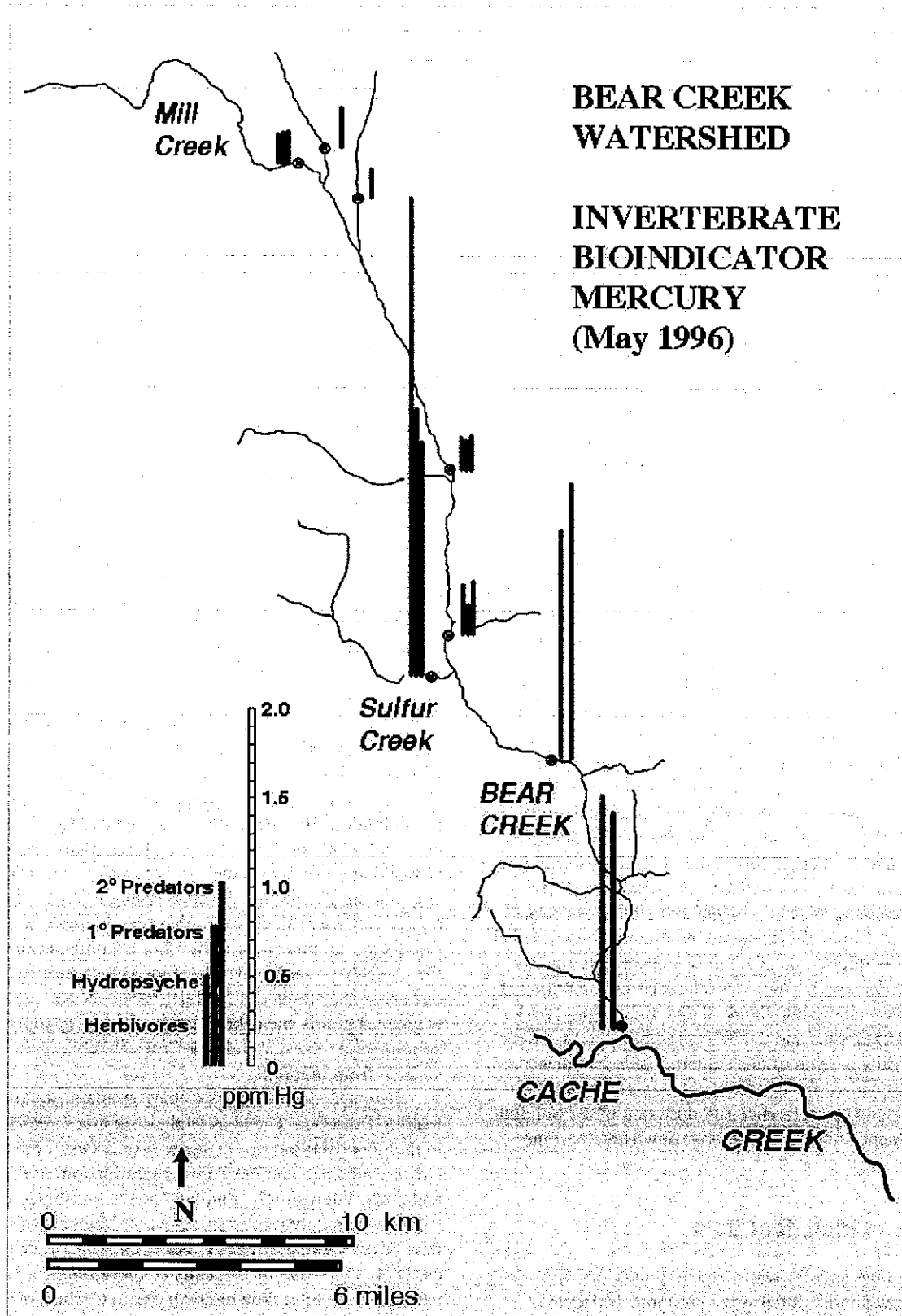


Figure 7. Mercury (ppm dw) in stream invertebrates in the Bear Creek Watershed from D. Slotton collections in 1996 (Slotton and others, 1997).

Amphibians and Birds

Schwarzbach and others (2001) collected six foothill yellow-legged frogs (*Rana boylei*) from Bear Creek, three from upstream, three from downstream of the Sulphur Creek confluence, and a sample from Bear Creek at Highway 20. The range of TotHg concentrations was 0.075–0.538 ppm (ww) with the highest value obtained at the Highway 20 site. The mean TotHg was 0.11 ppm (ww) in upstream samples and 0.31 ppm (ww) in downstream samples.

At 22 sites in 1997 and 19 sites in 1998, Hothem and others (in press) collected and analyzed TotHg in three anuran species from the Cache Creek watershed, including sites within the Bear Creek watershed: American bullfrogs (*Lithobates catesbeianus*), Foothill yellow-legged frogs (*Rana boylei*), and Pacific chorus frogs (*Pseudacris sierra*). Results were comparable between 1997 and 1998. Pooling data for both years, the geometric means for TotHg in Bear Creek bullfrogs in 1997 were 0.032–0.390 ppm (ww) at sites upstream of Sulphur Creek and 0.423–0.561 ppm (ww) for sites downstream of Sulphur Creek. For yellow-legged frogs, the pattern was similar; using pooled data, TotHg ranged from 0.082 to 0.159 ppm (ww) upstream of the confluence with Sulphur Creek, and 0.328 to 0.846 ppm (ww) downstream of Sulphur Creek. Similarly, Pacific chorus frog TotHg at a single site was 0.166 ppm (ww) upstream of Sulphur Creek and 0.258 ppm (ww) downstream of Sulphur Creek.

In 1997, Schwarzbach and others (2001) collected and analyzed three killdeer (*Charadrius vociferus*) eggs from separate nests in the Bear Creek region. One from a nest near the Jones Fountain of Life yielded a TotHg concentration of 0.26 ppm (ww) and eggs from two nests on Bear Creek ca. 0.4 km downstream of the Sulphur Creek confluence contained TotHg concentrations of 0.10 and 0.90 ppm (ww).

Hothem and others (2008) reported TotHg concentrations from cliff swallow (*Petrochelidon pyrrhonota*) eggs and nestling carcasses collected in 1997 and 1998 from nests within the Cache Creek watershed, including the Bear Creek watershed. Geometric mean values for egg TotHg ranged from 0.02 to 0.04 ppm (ww) at a reference site upstream of the confluence of Sulphur Creek, 0.097–0.208 ppm (ww) at Sulphur Creek sites and 0.070–0.118 ppm (ww) for Bear Creek sites downstream of the Sulphur Creek confluence. TotHg geometric means in nestling carcasses ranged from 0.047 ppm (ww) at a reference site upstream of the Sulphur Creek confluence to 0.116 ppm (ww) downstream of the confluence.

Overview of Historical Data

Cumulative data for water, invertebrates, and fish matrices show similar patterns of minimum TotHg and MMeHg concentrations at the Upper Bear Creek site,

maximum concentrations at the Sulphur Creek site (no fish data available for Sulphur Creek), and intermediate concentrations downstream of the confluence of Sulphur Creek with Bear Creek at the Middle Bear Creek site. In addition, the ratio of MMeHg:TotHg (or the percentage of TotHg as MMeHg) exhibited similar trends for all matrices; i.e., the highest ratios were found at the Upper Bear Creek site, the lowest ratios at Sulphur Creek, and intermediate ratios at the Middle Bear Creek site (Slotton and others, 2004). As discussed above, because no known mining sites are located near or upstream of the Upper Bear Creek site, the Hg source influencing this site is most likely a geothermal spring, which could easily be undetected if it lies within the stream bed itself. In addition, evidence from the Sulphur Creek site suggests that the Hg source for that site is dominated by Hg mines.

Several recent publications provide evidence that cinnabar and/or metacinnabar, the primary forms of Hg at Hg mines, are more refractory and less bioavailable than other forms of Hg (Kim and others, 2000; Bloom and others, 2003; Suchanek and others, 2008b). Thus, the Bear Creek watershed data also are consistent with an interpretation that Hg derived from springs is more bioavailable and thus could be bioaccumulated more efficiently than Hg derived from mining sources. That is, despite the absolute concentrations of Hg, if the primary source of Hg at the Upper Bear Creek site is primarily from springs (see discussions above for water), and the primary source of Hg at Sulphur Creek was mining (see discussion above for water), this would result in a higher proportion of MMeHg to TotHg in water, invertebrates and fish from the Upper Bear Creek site (which may derive its Hg from springs), a lower proportion of MMeHg:TotHg at the Sulphur Creek site (which is dominated by mines), and an intermediate proportion at the Middle Bear Creek site (which has a mixture of the two types of sources). Therefore, sites having geothermal or saline spring influence may play a relatively more significant role in producing MMeHg than those sites dominated by mines. For example, even though the absolute amount of TotHg at the Upper Bear Creek site is quite low, the amount of MMeHg produced per unit of TotHg is greatest at this site (likely dominated by Hg sources from springs) and lowest at Sulphur Creek (likely dominated by Hg sources from mining).

Domagalski and others (2004) estimated annual TotHg loading from Bear Creek as well as Sulphur Creek in relation to their contributions to the water discharges of the Cache Creek watershed and the Yolo Bypass for water years 2000 and 2001. Interestingly, Sulphur Creek contributed ca. $1.8\text{--}2.8 \times 10^6 \text{ m}^3$ annually (representing ca. 1–2 percent of the total flow of downstream Cache Creek) and Bear Creek contributed ca. $18.3\text{--}33.3 \times 10^6 \text{ m}^3$ annually (representing ca. 12–19 percent of the total flow of downstream Cache Creek).

Mercury Monitoring Protocol

Objective

The objective of this monitoring protocol is to document procedures for collecting and processing water, sediment, and biota for estimation of TotHg and MMeHg in the Bear Creek watershed. Concurrent sampling of TotHg and MMeHg in biota as well as water and sediment will provide information regarding the relative bioavailability of Hg released from Hg sources in the watershed and identify environments of Hg methylation.

These protocols will assist landowners, land managers, water-quality regulators, and scientists in detecting whether restoration/mitigation actions lead to significant progress toward achieving water-quality goals to reduce Hg in Bear Creek and Sulphur Creek to meet total maximum daily load (TMDL) standards established by the Central Valley Regional Water Quality Control Board (CVRWQCB).

Sampling

Water, sediment, and biota should be sampled for a minimum of 2 years before any remediation activity (Pre-R). Because of potentially significant inter-annual variability in precipitation events that drive erosion of Hg-laden sediments from the landscape into streams within the Bear Creek watershed, as well as inter-annual variability in the production of Hg-charged fluids from cold or hot springs, at least 2 years is needed to provide adequate baseline data prior to the commencement of remediation. However, if time and funding allow, it would be advantageous to collect Pre-R data for up to 5 years to confirm trends from past studies. Following remediation, water, sediment, and biota should be sampled for several years (Post-R). For a number of reasons, including the physical disturbance effects of remediation, reduction in loading, the inter-annual variability factors discussed above, and changes in bioaccumulation rates, it is unknown how long it will be before potential changes in Hg concentrations occur in abiotic and biotic matrices after remediation. Therefore, the length of time needed to detect changes will most likely be longer than the time needed to establish a reliable baseline. Up to 10 years of Post-R sampling would be desirable to account for those factors identified above. At a minimum, Post-R sampling should be conducted for 5 years. If additional remediation projects are begun or completed during the initial Post-R phase, then the sampling plan should revert to the Pre-R protocol, which would start a new Post-R phase after that subsequent remediation was completed.

Seasonality

Summer (June-August) appears to be the season when MMeHg production reaches a maximum at all sites within the Bear Creek watershed as evidenced by data from water, sediments, invertebrates, and fish. During Pre-R monitoring, water, sediment, and biota should be sampled in the spring and late summer/early fall and analyzed for TotHg and MMeHg. This would serve two purposes. First, it would provide information to assess what concentrations of TotHg and MMeHg are present in spring during typical breeding periods for many wildlife species. Second, it would confirm that late summer/early fall is a period of higher MMeHg concentrations (based on data from previous studies). If these results are consistent with data from previous studies, water, sediment, and biota could be collected only in the late summer in subsequent Pre-R years. During Post-R years for any of the mine sites in the watershed, water, sediment, and biota should be collected in the spring and late summer and analyzed for both TotHg and MMeHg. If these results also are consistent with previous data, water, sediment, and biota could be collected only in the late summer.

Physical/Chemical Matrices

Based on existing data, and the need to identify potential changes in Hg loading and bioaccumulation in relation to remediation actions, we recommend 10 monitoring sites for physical and biological matrices ([table 1](#)). Sampling sites for the Bear Creek watershed were selected based on spatial relationships to known natural and anthropogenic sources of Hg within the watershed ([fig. 1](#)), and the justification for each sample site is provided in [table 1](#). The frequency and timing of water and sediment sampling should be coordinated with biota sampling. All samples at a site should be collected on the same day during similar flow and weather conditions in the watershed. It is important that water and sediment samples be collected prior to biota sampling to avoid any changes in water quality that arise from disturbance of the stream during biota collection. Water should be collected for analysis of TotHg and MMeHg in unfiltered and filtered samples. Sediment should be collected for analysis of TotHg and MMeHg. The unfiltered water sample provides information on TotHg and MMeHg associated with particulate phases in the water. The filtered water sample provides information on Hg that is dissolved as well as TotHg and MMeHg present in colloids that pass through a 0.45- μm filter (Babiarz and others, 2001). Based on results from historical studies (see above), late summer to early fall appears to be the season during which maximum MMeHg concentrations were observed in water, sediments, and biota. Because this is the most critical toxic form of Hg

in this system, it is advisable that samples be collected during periods when MMeHg is highest in order to relate results to impacts on biota. However, it is possible that different weather or precipitation conditions from those that were present during the previous studies could alter the seasonality of maximum MMeHg. Therefore, some sampling at other seasons (for example, spring) should be incorporated into this monitoring plan. In order to relate physical/chemical data to biological data, it is recommended that for the first 2 years, physical/chemical data be collected in both spring and late summer/early fall.

Episodic transport of TotHg and MMeHg caused by high flows associated with storm events has been documented for several watersheds (Babiarz and others, 1998; Hurley and others, 1998; Scherbatskoy and others, 1998; Balogh and others, 2005). Because most Hg transported in a watershed moves during a few high-flow events, it also is necessary to sample Bear Creek during at least one high-flow event per year in order to monitor Hg dynamics in stream water and assess Hg transport from both natural and mine impacted areas.

Sample Collection and Processing

Water and sediment should be collected using standard ultra-clean sampling and handling protocols (Gill and Bruland, 1990; Bloom, 1995) to avoid introduction of extraneous Hg into the samples. Sampling personnel must wear clean, non-powdered gloves made of polyethylene, latex, or PVC at all times when handling sampling equipment and containers, and gloves must be changed between sample collection sites. At a sampling site, one person is designated as “dirty hands” and the other person who is sampling is designated as “clean hands.” The dirty hands person is responsible for all activities that do not involve direct handling of the sample and its container, such as handling all other potentially contaminated equipment, clothing, etc. The clean hands sampler is involved in direct handling of the sample container and transfer of the sample from the collection device to the sample container. Water samples should be collected in ultra clean 250-mL FLPE bottles. A Hg laboratory with experience in low level Hg analysis, such as the USGS Mercury Research Laboratory or Brooks Rand LLC, should provide sample bottles. Grab samples should normally be taken near the centroid of flow, but during high flow, grab samples may occasionally be taken from the streambank. Care should be taken not to disturb bed sediments before sample collection. For TotHg, the sample container should be filled partially and emptied 3 times prior to its final filling. The sample container should then be rapidly submersed, filled, and capped while submersed so that there is no headspace of air. Water samples for Hg and MMeHg analysis should be preserved with 2 mL of Ultrex 6N HCl (Olson and DeWild, 1999).

For collection of filtered water for TotHg and MMeHg analysis, water should be filtered in the field during collection through an in-line 0.45- μ m filter pack assembly using a peristaltic pump with Teflon® tubing. Water samples should be acidified with ultra-pure 6N HCl in the field immediately after collection (Olson and DeWild, 1999). Samples should be kept on ice until shipped. Water samples should be shipped on wet ice to arrive the next morning at the analytical facilities at temperatures ranging from 1 to 4°C; the temperature specified by EPA Method 1631E to minimize biologically induced phase changes and MMeHg degradation.

Water-quality parameters, including pH, conductivity, dissolved oxygen, oxidation-reduction potential (ORP), and temperature should be measured in the field with a multi-probe metering device (for example, Hydrolab™ or YSI™), either by placing the probe directly into the flowing stream water, or by filling a container and placing it over the probe. If a multi-probe metering device is not available, the following meters are recommended. Values of pH should be determined using an Orion 250A or 290A meter with a gel-filled Triode electrode, or comparable pH meter. The pH meter should be calibrated using commercially available pH 10 and 7 buffers. Water temperatures should be measured using a thermometer that was checked against a thermometer certified by the American Society for Testing and Materials (ASTM). Specific conductance should be determined using a Cole-Parmer meter and probe; a one-point calibration should be done with a standard in the approximate concentration range of the unknown water. Dissolved oxygen should be determined using a YSI meter and probe, calibrated using standard procedures.

High-Flow Event Sampling

The high flow sampling should be carried out using the same protocol used for the seasonal sampling of water under low flow conditions. The high flow sampling should be carried out by starting at the upper part of the watershed and continuing to the lowest sample site in the watershed. It is important to collect the sample in the centroid of the stream, if possible. In order to assess Hg release from the Rathburn and Petray mines, Tributary 1 (fig. 4) should be sampled just above its intersection with the Bear Fault. Water samples should be collected for analysis of Hg and MMeHg on unfiltered and filtered fraction. It is not necessary to collect a sediment sample. Automated samplers should be considered for use because staff may not always be available for a high-flow event. The automated ISCO samplers with Teflon® tubing are suggested for use to collect stream water samples. Control studies using ISCO samplers have documented only minimal contamination of sample bottles from dry deposition of airborne Hg, and reliable results are obtained when Hg concentrations are greater than 5 ppb (Riscassi and others, 2008).

Sediment Collection and Analysis

Sediment samples collected using polycarbonate or Teflon® spoons should be transferred to Teflon® or acid-washed glass containers, following the protocols described by Shelton and Capel (1994). Representative sediment should be collected from in-stream sites, avoiding large pebbles, twigs, and roots. Excess water should be decanted from the container. Sediment samples collected for analysis of TotHg and MMeHg are frozen with dry ice immediately after collection, kept frozen, and shipped on dry ice so that they are received frozen at the analytical facility, and kept frozen there until analysis is initiated. Sediment should be analyzed for TotHg and MMeHg, and percent solids should be determined for reporting results on a dry weight basis. Analysis of TotHg should be carried out according to USEPA method 1631 and for MMeHg according to USEPA method 1630.

Biological Matrices

This protocol documents procedures for collecting and processing aquatic invertebrates and fish for estimation of Hg bioaccumulation in biota of the Bear Creek watershed. Concurrent sampling for Hg and MMeHg in water and sediments will provide information regarding sources and relative bioavailability of Hg at each site (see above).

Clean techniques are essential to minimize potential contamination, including contact with personnel and equipment. The field methods described here are based on guidelines developed in conjunction with the National Water-Quality Assessment (NAWQA) Program, the Toxic Substances Hydrology Programs, and researchers from other disciplines in the USGS as described by Scudder and others (2008).

This protocol will focus on smaller individuals of upper trophic level predatory fish whenever possible. Smaller fish provide a more short-term representation of changes in Hg concentrations of prey species, which in turn will reflect short-term changes in Hg in water and sediments. Fish of lower trophic levels also will be collected, especially where predominantly piscivorous species are not available. TotHg and MMeHg will be analyzed in individual samples of fish during the first year of the study to confirm the percentage of TotHg as MMeHg. If, as predicted, the percentage of TotHg that is MMeHg is high (> 95 percent) in the sampled fish, then it will be sufficient in subsequent years to analyze the fish samples only for TotHg. Once the percentage of TotHg as MMeHg is established for those species, only TotHg need to be analyzed. Previous studies have shown that about 95 percent of TotHg in fish muscle tissue is MMeHg (Huckabee and others, 1979; Bloom, 1992; Wiener and Spry, 1996). Skin-off filets of top-level piscivores will be analyzed as well as individual whole bodies (less gut contents) of the lower trophic level fish. In addition, because the cost for MMeHg analyses greatly exceeds that for TotHg, the elimination of the redundant MMeHg analyses will provide significant cost savings yet will not compromise the validity of the

data. Whole-body aquatic invertebrates, however, should be analyzed for both TotHg and MMeHg every year, because the ratios of MMeHg to TotHg tend to be inconsistent among invertebrate taxa, among sites and among years (Mason and others, 2000; Haines and others, 2003; Wiener and others, 2007).

Biological samples, as well as water and sediment samples, need to be collected concurrently or within a short time period (2 weeks for invertebrates and forage fish; 4 weeks for top predator fish) to minimize changes that might affect relative Hg concentrations in the various media collected. In addition, sample collection of each media type must be coordinated to minimize risk of site disturbance and sample contamination. For example, collection of biota at a given site before water and sediment will likely stir up bottom sediment producing conditions unsuitable for water and sediment sampling. At each site, a typical order for sample collection would be water, followed by sediment, then invertebrates, and finally fish. Protocols for sample collection, processing, labeling, submission, and for data management should be reviewed by all field personnel prior to sample collection. See Scudder and others (2008) for examples.

Sampling sites for the Bear Creek watershed ([table 1](#), [fig. 1](#)) were selected based on spatial relationships (both above and below) to known natural and anthropogenic sources of Hg within the watershed and potential for bioaccumulation by biota. In addition, data from previous biological studies (Schwarzbach and others, 2001; Slotton and others, 2004; Hothem and others, in press) were used to assess the most useful sites for a comprehensive, but cost-effective, evaluation of Hg bioaccumulation before and after restoration.

Invertebrates

The target macroinvertebrates for this study (Merritt and Cummins, 1995) should be predatory or filter-feeding insects, depending on their abundance and availability at sampling sites. Aquatic invertebrates can serve as excellent bioindicators of metals contamination (Cain and others, 1992). At least three key invertebrate taxa should be targeted for sampling ([table 2](#)). As feasible, these taxa should represent different functional feeding categories (for example, scrapers, shredders, grazers, collectors/gatherers) and should be taxa and sizes that are considered important prey items for target fish. For the lotic habitats (streams and flowing channels) of the Bear Creek watershed, preferred macroinvertebrates should be larval caddisflies (Trichoptera, family Hydropsychidae), larval dragonflies (Odonata, Anisoptera, family Gomphidae, Aeshnidae, and Libellulidae), and adult water striders (Hemiptera, family Gerridae). Invertebrates should be sorted to the lowest practical taxon, normally family, and processed as single-taxon composites. For example, one or more species of net-spinning caddisfly larvae in the family Hydropsychidae could form a composite sample. If available, water striders might represent a good sentinel species because they have been found to quantify accurately the food chain entry of Hg

Table 2. Available and Target* invertebrate families, Bear Creek.

Order	Common name	Family name	Trophic level	Previously sampled
Hemiptera	Water strider adult*	Gerridae	Large predator	No
	Creeping water bug adult	Naucoridae	Large predator	Slotton and others 1997, 2004
Odonata	Dragonfly larvae*	Gomphidae	Large predator	Schwarzbach and others 2001; Slotton and others 2004
	Dragonfly larvae*	Aeshnidae	Large predator	No
	Dragonfly larvae*	Libellulidae	Large predator	Slotton and others 1997, 2004; Schwarzbach and others 2001
	Damselfly larvae	Calopterygidae	Small predator	Slotton and others 1997; Schwarzbach and others 2001
	Damselfly larvae*	Coenagrionidae	Small predator	Slotton and others 2004
Trichoptera	Net-spinning caddisfly larvae*	Hydropsychidae	Drift feeder	Slotton and others 1997, 2004; Schwarzbach and others 2001
Ephemeroptera	Mayfly larvae	Ephemerellidae	Herbivore	Slotton and others 1997, 2004
	Mayfly larvae	Siphonuridae	Herbivore	Slotton and others 1997
Diptera	Crane fly larvae	Tipulidae	Large predator	Slotton and others 1997, 2004
	Soldier fly larvae	Stratiomyidae	Small predator	Slotton and others 2004
Plecoptera	Golden stonefly larvae	Perlidae	Small predator	Slotton and others 1997
Megaloptera	Alderfly larvae	Sialidae	Small predator	Slotton and others 1997
	Dobsonfly larvae	Corydalidae	Large predator	Slotton and others 1997, 2004
Coleoptera	Riffle beetle adult	Elmidae	Large predator	Slotton and others 2004

(Jardine and others, 2005). However, because of the high variability of Hg in water striders from aquatic systems, especially among different seasons, care should be taken to understand the potential short-term variations in Hg sources to the streams being sampled (see Jardine and others 2009). For all sites, alternate species of invertebrates should be identified and collected the first year to serve as functionally equivalent substitutes in case adequate numbers of primary target species are not available. Some invertebrates may be unsuitable because of their small size (for example, Chironomidae), because expending the time needed to collect sufficient mass for chemical analyses may not be feasible.

Fish

Black basses (Centrarchidae: *Micropterus spp.*) are excellent target species (May and others, 2000), but previous studies have not been successful at collecting black bass from Bear Creek sites. Predatory fish can serve as good bioindicators of metals contamination in the long term (Wiener and Spry, 1996), but considering the ephemeral nature of the streams in parts of the Bear Creek watershed, other fish should be collected wherever possible. One or two other species will need to be identified that can be collected across all study sites. Species that have been collected in previous studies (Slotton and others, 1997, 2004; Schwarzbach and others, 2001) include Sacramento pikeminnow, Sacramento sucker, and California roach. The species of fish that is most likely to be collected is the California roach. The collection of the same species at each site allows for comparison among

sites across geographical areas. The use of target taxa allows for comparison among sites across geographical areas. Alternate species will be identified for each site. Two species of forage fish and one species of top predator fish (table 3) will be collected, as available, at each site; these will be identified in the field to the lowest possible taxonomic category and processed individually. Alternate species of acceptable forage fish and top predator fish also will be identified for all sites to serve as functionally equivalent substitutes in the case that adequate numbers of primary target species are not collected.

Preference should be given to fish that are resident (for example, speckled dace), avoiding whenever possible sampling areas where fish are likely to move in and out of other major water bodies. Although speckled dace represent a good potential target species because they have relatively limited movements, short lifespan, and are benthically dependent foragers (for example, on insects), they have not been documented during previous collections and may not be available. Collections during the first year will determine the size ranges available for various fish species and provide guidance for future collections. Depending on the fish species, all individuals used in composite samples should be as similar in size as possible. If large variation in fish size affects the variation in Hg concentrations, then size should be used as a covariate during statistical analysis to control for this effect while comparing differences in Hg concentrations among sites.

Table 3. Available and Target* fish species, Bear Creek.

Family name	Common name	Scientific name	Previously sampled
Centrarchidae	Smallmouth bass	<i>Micropterus dolomieu</i>	No
	Bluegill	<i>Lepomis macrochirus</i>	No
	Green sunfish	<i>Lepomis cyanellus</i>	Slotton and others 2004
Cyprinidae	Sacramento pikeminnow*	<i>Ptychocheilus grandis</i>	Slotton and others 2004; Schwarzbach and others 2001
	California roach*	<i>Hesperoleucus symmetricus</i>	Slotton and others 2004; Schwarzbach and others 2001
	Speckled dace*	<i>Rhinichthys osculus</i>	No
Catastomidae	Sacramento sucker*	<i>Catostomus occidentalis</i>	Slotton and others 2004; Schwarzbach and others 2001

Table 4. Summary of invertebrate and fish sample collections for Bear Creek Watershed.

Collection Season	Pre Cleanup				Post Cleanup			
	Year 1		Years 2-5		Year 1		Years 2-5	
	Fish	Inverts	Fish	Inverts	Fish	Inverts	Fish	Inverts
Spring (April –May)	3 species	3 taxa			2 species	2 taxa		
Fall (Sept. – Oct.)	3 species	3 taxa	3 species	3 taxa	2 species	2 taxa	3 species	3 taxa

Preparation for Collections

Suggested equipment and supplies for use in these biological studies are listed in [tables 5 and 6](#). Equipment and supplies need to be properly prepared to minimize the potential for sample contamination. New, sealed supplies such as zip-seal plastic bags and plastic vials with plastic caps do not need pre-cleaning. However, reusable equipment will need to be cleaned properly prior to field collections (see Scudder and others, 2008, for techniques). After tools are cleaned, supplies and smaller equipment will be double-bagged in new plastic bags and stored in sealed containers to minimize contamination; supplies should be cleaned and packed separately for each site to minimize the need for field cleaning (Brumbaugh and others, 2001). In the field, all equipment should be cleaned between sites.

Field forms ([appendixes A and B](#)), sample labels ([appendix C](#)), and laboratory submission forms ([appendix D](#)) should be prepared prior to collecting samples and should be printed on durable water-proof paper (for example, Rite-In-The-Rain™ paper). Field forms and labels should be preprinted with station name, analyte, medium code, and contact information (name and telephone number). For other examples of such forms, see Scudder and others (2008).

California scientific collection permits, obtained from the California Department of Fish and Game, will be required for collections of invertebrates and fish. Landowner permissions will be required for access to sites located on private property or when site access requires crossing private property.

A consultation with local U.S. Fish and Wildlife Service personnel with regard to Section 7 of the Endangered Species Act is recommended and may be required in some locations if a threatened or endangered species is known or thought to be present (<http://www.fws.gov/endangered/factsheets/consultations.pdf>).

Quality Assurance and Quality Control (QA/QC)

Quality-assurance samples are collected to investigate field and laboratory variability. Triplicate invertebrate composite samples (three individuals per species) and multiple individual fish samples in this protocol serve as quality-assurance replicates for field variability. Quality assurance for laboratory analyses will include duplicate runs, blanks, spikes, and use of certified or standard reference sample materials. Voucher specimens for taxonomic confirmation should be preserved in 70-percent ethanol (invertebrates). Techniques used for biota must ensure that tissues are not contaminated during collection or during sample processing. Processing on site or at a nearby outdoor area is acceptable if a stable, clean work area is available. However, processing in an enclosed facility, such as a field laboratory, is preferred. Disposable, powder-free latex gloves must be worn during all sample processing and must be changed frequently, particularly after touching any unclean surface.

Table 5. Equipment checklist (modified from Scudder and others 2008).

Carboys, 5-gallon (2, tap; 2, DI water; 1, 5 percent HCl)
Camera, digital
Chairs, folding
Clipboard(s)
Coolers (4, wet ice; 2, dry ice)
Collection permits/licenses
Detergent, phosphate-free
Field data sheets (pre-printed, water-resistant paper)
First aid kit
Flashlights and headlamps
Garbage bags, large, plastic
Global Positioning System (GPS) unit
Ice, dry (about 15 lb per day of trip)
Ice, "wet"
Insect repellent
Keys, identification, for invertebrates and fishes
Labels, (waterproof, pre-printed)
Maps
Markers, fine-tip, alcohol/solvent resistant
Markers, wide-tip, alcohol/solvent resistant
Personal Flotation Device (1 per person)
Phone, cell
Phone numbers, emergency
Protocol (on water-resistant paper)
Sunscreen
Table, folding
Tape, flagging, biodegradable
Tape, clear, 2", for shipping
Tray or tub, large (for dishwashing/storage)
Trays, plastic, large (for cleaning equipment)
Trays, plastic, shallow (for weighing fish)
Towels, paper rolls
Trash bags, heavy duty
Waders/hip boots/wading boots
Wader repair kit
Wash Bottles (500 mL, Teflon®; 1, tap water; 1, DI water; 1, dilute HCl; 1, dilute detergent)
Water, high-purity DI
Water, tap

Sample Collection and Processing

A summary of invertebrate and fish sample-collection plans is provided in [table 4](#). Additional taxa may be collected as available.

Invertebrates

Invertebrate sampling should be conducted in spring (April–May) and late summer/fall (August–September) in the first year of the study (Pre-R) and the first year after restoration (Post-R) to evaluate inter-seasonal differences in Hg bioaccumulation. Invertebrates may be collected using dip nets, kick nets, or by hand and placed into labeled plastic bags or containers. At least 1 g wet weight of each taxon will be required to ensure sufficient biomass for analyses (minimum

Table 6. Fish and invertebrate collection checklist (modified from Scudder and others, 2008).

Dipnets, D-frame
Forceps, plastic
Counters, hand-held
Gloves, powder-free (nitrile, vinyl, other non-latex)
Vials with caps, plastic, 20 mL
Magnifying glass/hand lens/binocular microscope
Scale, top-loading, accuracy to 0.01 g
Trays, plastic, shallow (for picking invertebrates)
Batteries or fuel for electrofishing unit
Buckets, 10 gallon
Electrofishing unit (backpack)
Gloves, rubber, safety (insulated)
Polarizing sunglasses
Nets, large dipnet
Nets, small
Anesthetic CO ₂ tablets (e.g., AlkaSeltzer®)
Bags, plastic, heavy-weight, zipper-seal, 1 L
Bags, plastic, heavy-weight, zipper-seal, 4–8 L
Cutting sheet/mat/board, plastic
Knives, filleting
Measuring board (non-metallic)
Pliers, needle-nose
Rulers, 6-inch plastic
Scale, top-loading, accuracy to 0.01 g
Scale, top-loading, accuracy to 0.1 g
Scale, hanging or hook, for large fish
Scalpels, high-grade stainless
Scissors, dissecting, high-grade stainless steel
Vials with caps, plastic, 20 mL

of 0.1 g dry weight) (Hall and others, 1998). Depending on the size of the invertebrates collected, the number of individuals needed to obtain 1 g wet weight will vary but, in any case, will likely not be less than three individuals. Small invertebrates, such as caddisfly larvae, may require up to 150 individuals. Collectors should attempt to be consistent with selection of species and size classes within a species and should collect each taxon from as broad a range of locations within a reach as possible. Because the number of individuals comprising each sample will drive Hg concentration variability, that number should be held constant for each species being sampled. This will be determined most easily after the first Pre-Remediation sampling and attempts should be made to maintain this number of individuals throughout the study period.

Invertebrates should be processed as three replicate composite samples for each taxon with the same number of organisms, of similar size, in each composite sample. Holding (deuration) times should typically range from a few to 24 hours per site, depending on the time of day collected. Voucher specimens of each uncertain taxon should be collected for taxonomic confirmation. Within 24 hours, individuals should be sorted by family and placed in disposable dishes using Teflon®-coated forceps or gloved-hand. Organisms are to be

rinsed clean with DI water and patted dry with a clean paper towel. Composite samples, consisting of 3–150 individuals of the same family (1–5 g, wet weight), should then be weighed and placed into chemically cleaned glass jars with Teflon[®]-lined lids. Processed samples should then be preserved immediately on dry ice for transport to a freezer where they should be kept frozen for no more than 6 months until they can be shipped to an approved analytical laboratory. Each composite sample of invertebrates should be analyzed for TotHg and MMeHg. If sample mass is insufficient for both analyses, the priority analysis is MMeHg.

Fish

A variety of fish-collection procedures may be appropriate, depending on site conditions and target species. General fish-collection procedures are described elsewhere (Meador and others, 1993; Moulton and others, 2002), and rely primarily on backpack electrofishing. Other methods in combination with or in lieu of electrofishing, such as seining or rod-and-reel (with artificial lures), or passive gear, such as traps or nets, may be more effective at some sites and would be acceptable. After capture, fish should be placed in a large plastic bucket in native water until they can be processed. Guidelines for live specimen handling and care are provided in Walsh and Meador (1998). Fish can be anesthetized using carbon dioxide from carbon dioxide-producing tablets, such as Alka-Seltzer[®] (2–4 tablets per gallon of water in bucket or other container). After anesthetization, fish can be euthanized by additional carbon dioxide (recommended by Walsh and Meador, 1998). Fish that are to be processed in a location other than the collection site should be placed in clean zip-seal bags on wet ice and processed within 24 hours. If they cannot be processed within 24 hours, they should be placed in a cooler on dry ice and kept frozen until they can be processed.

Fish should be collected both in spring and fall in the first Pre-R year of the study and in the first Post-R year of the study. Fish should be collected from the same sites as the water, invertebrates, and sediments and at each site, a typical order for sample collection would be water, followed by sediment, then invertebrates, and finally fish. Three species of fish, depending on availability, should be collected from each sample site. Initially, at each site, the goal is to collect five individuals of each species of similar size/length. Fish should be analyzed for MMeHg and TotHg during year 1 of Pre-R sampling and TotHg only during subsequent years. Detailed procedures for processing fish are provided by Scudder and others (2008). Upper trophic level fish are longer lived with slower tissue turnover than forage fish, so they do not have to be collected at exactly the same time as the rest of the biota. At each site, five similar-sized mature individuals of the target top predator fish should be collected. This size should be

maintained throughout the entire study. A second species of piscivorous fish may be sampled if availability of the primary target species is limited.

As indicated earlier, additional species of fish should be collected wherever possible. The preferred fish that may be collected is the California roach. Captured fish should be held in native water in buckets until they are weighed and measured for standard and total length. Each individual fish should then be labeled, placed in a polyethylene zip-lock bag and placed on dry ice in a cooler. Samples should be stored frozen until they can be processed further. Each fish should be measured for standard and total length (± 0.5 mm) and the total mass determined (± 0.5 g) on an electronic balance. In the laboratory, fillet tissue from top-level predatory fish should be dissected following procedures described by May and others (2000). The whole bodies of small fish should be analyzed, after removing the contents of the gastrointestinal tract. Tissues to be analyzed should be placed in chemically clean glass sample jars with Teflon[®]-lined lids. Processed samples should be preserved immediately on dry ice for transport to a freezer or analytical laboratory and analyzed as soon as possible, preferably within 6 months.

Sample Shipment

Before they are shipped to the contract laboratory for analysis, all sample data must be entered on the appropriate sample chain-of-custody forms (included in the packaging), and the analytical laboratory must be notified to ensure that they can receive the samples. Ship frozen samples for next-day delivery (for example, FedEx[®]); ensuring that sufficient dry ice is included in the packaging so that a 1-day delay will not adversely affect the samples. Samples should be shipped on Mondays or Tuesdays to minimize the likelihood of a shipping error causing samples to sit over a weekend.

Statistics

TotHg and MMeHg concentrations in all matrices (water, sediments, invertebrates, fish) should be compared statistically among sites and sampling periods. However, limited availability of certain invertebrate and fish taxa at some sites and limited replication may restrict the statistical power (probability) for detecting certain effects, in which case only qualitative inter-site comparisons may be useful. Using the scientific literature, potential impacts of the observed Hg concentrations on the reproduction, growth, metamorphosis, and survival of each taxon should also be evaluated for the species sampled as well as other species present in the watershed.

To avoid biasing the results of the data analysis towards spurious patterns in the data, any hypotheses intended for statistical evaluation should be developed *a priori*. For

example, if a simple assessment of change is desired, the following hypotheses can be developed *a priori*:

H_0 = Hg concentrations for [matrix] during Post-R year(s) are statistically indistinguishable from Hg concentrations during Pre-R year(s).

H_1 = Hg concentrations for [matrix] during Post-R year(s) are statistically different from Hg concentrations during Pre-R year(s).

If desired, these hypotheses can be generalized to include trends characterized by relatively sustained rates of continuous change. For example, if an analysis of change in Post-R years is desired, then a linear regression model could be applied and the following hypotheses developed:

H_0 = The slope of Hg concentrations for [matrix] over time during Post-R year(s) is statistically indistinguishable from zero (that is, no change).

H_1 = The slope of Hg concentrations for [matrix] over time during Post-R year(s) is statistically different than zero (that is, indicating an increase or decrease in Hg concentration).

These hypotheses can be evaluated with a wide variety of models ranging from simple (that is, two-sample t-test and simple linear regression) to complex models depending on additional sampling factors that could influence and/or confound with the variation in Hg concentrations (such as site, year, flow events, and fish size). However, complex models require larger sample sizes in order to reliably identify and account for the effects associated with these additional factors. Therefore, even if additional factors were to confound with the difference between Pre-R and Post-R periods, small sample sizes could reduce the ability to account for them and this would diminish the interpretability of the comparisons.

Because the extent to which variation in the data exists cannot be determined *a priori*, then the specific appropriate statistical model might best be chosen after patterns in the initial data are evaluated. At a minimum, a one-factor ANOVA model comparing Pre-R and Post-R, essentially equivalent to a two-sample t-test, can evaluate the first hypothesis. Ideally, a Repeated Measures ANOVA model (for example, based on a linear mixed effects model structure) should be considered, using data from multiple sites as the repeated measures sampling units at each time interval. Covariates such as site, timing, water flow, and fish size should be added to this type of model as appropriate. With sufficiently abundant data, multiple comparisons tests (for example, Student-Newman-Keuls or Tukey's Multiple Comparisons Tests) can be used to compare Pre-R data from 1 or 2 years versus multiple years of Post-R data. This would allow statistical comparisons between and among individual year pairs as well as groupings of years. However, if data are limited, this approach would have less statistical power than using simpler and more direct statistical approaches.

Because inter-annual variability, especially with respect to the frequency and intensity of rainfall events (and possibly the flow rates of Hg-laden cold or hot springs), may result in significant variations in the Hg concentrations observed in water, sediments, and biota, it is important to assess multiple years for both the Pre-R Phase and Post-R Phase. In order to account for inter-annual variability in rainfall and natural spring activity, it is recommended that 5 years of Pre-R and 5–10 years of Post-R sampling should be conducted, with preference for more years when possible.

Power and Sample Size for Testing Percent Difference Between Pre-R and Post-R Periods

Because the statistical power to detect changes in Hg concentrations for all matrices would be enhanced by increasing sample sizes, to offset the uncertainty associated with sampling variation, a formula for determining adequate sample size to detect specific levels of change is provided below. This formula only applies to situations where the two-sample t-test will be used. A comparable formula for repeated measures ANOVA would require more variables and is difficult to express without yet having a detailed specification for that model. Therefore, this formula is intended only to provide a starting point for determining the adequacy of the protocol sample size after initial data has been gathered.

The minimum sample size for detecting an effect is determined by sampling variation (to be determined from initial data), the anticipated size of the effect, and the desired power for detecting that effect. A percent change in Hg between two periods can be expressed as an absolute difference in log-transformed Hg. For example, a hypothetical change of D percent (for example, $D = -15$ would be a 15 percent decrease) in Hg concentrations from Pre-R to Post-R treatment periods is equivalent to having the ratio of Hg from Post-R to Pre-R treatment periods = $1+(D/100)$ (for example, 0.85). Equivalently, this ratio can be expressed in terms of the difference $\delta = \ln(\text{Post}) - \ln(\text{Pre}) = \ln(\text{Post}/\text{Pre}) = \ln(1+(D/100))$, where $\ln(\text{Post})$ and $\ln(\text{Pre})$ correspond to average natural log transformed Hg levels from Post-R and Pre-R periods respectively. The minimum sample size (n) required for a minimum prescribed power $(1-\beta)$ of detecting a D percent change sample when testing at the a significance level should satisfy the following inequality (Zar, 1999, section 8.4):

$$n \geq \frac{2s^2}{\delta^2} \left(t_{\alpha(1),\nu} + t_{\beta(1),\nu} \right)^2,$$

where s^2 = within-period variance among samples (within-Pre-R and within-Post-R sampling variance are assumed to be equal), $\nu = 2(n-1)$, and $t_{\alpha(1),\nu}$ and $t_{\beta(1),\nu}$ are 1-sided critical values of the t-distribution with ν degrees of freedom and α and β tail probabilities respectively (Zar, 1999, table B.3 in appendix B).

This formula can be rearranged algebraically to determine, for a given sample size, the power of detecting an effect, $1-\beta$, where β satisfies the following inequality:

$$t_{\beta(1),v} \leq \frac{\delta}{\sqrt{2s^2/n}} - t_{\alpha(1),v}$$

Power, significance level, and sample size are interrelated such that by enhancing any one of the three, then one or both of the other two will be compromised. For example, an effect detected at the $\alpha=0.10$ significance level would provide a reasonable confidence that a change occurred (as opposed to being a spurious statistical pattern). Comparatively, an effect detected at the $\alpha=0.05$ significance level would provide even greater confidence that a change had occurred, but there will be either a reduced power of making that detection, or an increased sample size will be required to maintain the same power as for detecting effects at the $\alpha=0.10$ significance level.

Analytical Costs

The estimated prices for chemical analyses of water, sediment, and biota are listed in [table 7](#). The prices are based on a minimal sampling protocol, with 1 year of Pre-R and 5 years of Post-R sampling. These prices do not include any potential volume discounts or other discounts that individual laboratories might offer. The cost of sampling at each site is based on analysis of TotHg and MMeHg on an unfiltered and filtered water sample and a sediment sample. The percent solids also will be determined for the sediment sample so that results can be reported on a dry weight basis. The high-flow sampling event includes analysis of TotHg and MMeHg analysis on an unfiltered and filtered water sample at each site but no collection of a sediment sample. A summary of costs for water and sediment per site is presented in [table 8](#).

The estimated costs for chemical analyses of biotic samples are shown in [table 7](#). These prices do not include any

Table 7. Estimated costs of individual analyses.¹

	Unit	Unit Price
Water samples for total Hg analyses	EA	\$80
Water samples for MMeHg analyses	EA	\$160
Sediment samples for total Hg analyses	EA	\$110
Sediment samples for MMeHg analyses	EA	\$210
Sediment percent solids for result on dry weight basis	EA	\$10
Biological samples for total Hg analyses	EA	\$110
Biological samples for MMeHg analyses	EA	\$160
Determination of tissue percent solids	EA	\$10
Sample homogenization	EA	\$20
Total cost for total Hg only		\$140
Total cost for total and MMeHg		\$300

¹ Based on November 2008 cost estimate from Brooks Rand Laboratories, Seattle, WA.

potential volume or other discounts that individual laboratories might offer. The proposed numbers of samples of fish and invertebrates by year for 10 sites and the estimated costs per year are shown in [table 9](#). The total numbers of samples collected in the first year are not all proposed for analysis ([table 2](#)). Instead, those collections are intended to determine the taxa available at each site. The taxa that are most common at the most sites are those that should be proposed for analyses in the first and subsequent years. Seasonal availability will be a factor to consider the first year as well. As discussed above, sampling during subsequent years should be performed during the season that is determined to be optimal for evaluation of Hg bioaccumulation in the Bear Creek watershed, likely the season with the highest production of MMeHg.

The total costs, with the assumptions listed in the footnotes, are presented in [table 10](#). No cost of living or inflationary factors were included in the cost estimates. In addition, costs will vary depending on the availability of “in-kind” services, available equipment and supplies, and travel costs.

Table 8. Summary of water and sediment chemical analyses per site for Bear Creek watershed.

Collection Season	Pre Cleanup				Post Cleanup			
	Year 1		Years 2-5		Year 1		Years 2-5	
	Water ¹	Sediment ²	Water ¹	Sediment ²	Water ¹	Sediment ²	Water ¹	Sediment ²
Spring (April –May)	\$530	\$330			\$530	\$330		
Fall (Sept. – Oct.)	\$530	\$330	\$530	\$330	\$530	\$330	\$530	\$330
Cost per site per year	\$1,060	\$660	\$530	\$330	\$1,060	\$660	\$530	\$330
Cost per 10 sites per year	\$10,600	\$6,600	\$5,300	\$3,300	\$10,600	\$6,600	\$5,300	\$3,300
High flow 10 Sites per year	\$5,300		\$5,300		\$5,300		\$5,300	
Total cost per year	\$22,500		\$13,900		\$22,500		\$13,900	
Cost per period	\$22,500		\$55,600		\$22,500		\$55,600	
10-year total							\$156,200	

¹ Based on one water sample per site per collection season for filtered and unfiltered Hg, and filtered and unfiltered MMeHg.

² Based on one sediment sample per site for Hg, MMeHg, and determination of percent solids for reporting concentration on a dry weight basis.

Table 9. Summary of invertebrate and fish chemical analyses per site for Bear Creek watershed.

Collection Season	Pre Cleanup				Post Cleanup			
	Year 1		Years 2-5		Year 1		Years 2-5	
	Fish ¹	Inverts ²	Fish ³	Inverts ⁴	Fish ³	Inverts ⁴	Fish ³	Inverts ⁴
Spring (April – May)	15	9			10	6		
Fall (Sept. – Oct.)	15	9	10	6	10	6	10	6
Cost per site per year	\$9,000	\$5,400	\$1,400	\$1,800	\$2,800	\$3,600	\$1,400	\$1,800
Cost per 10 sites per year	\$90,000	\$54,000	\$14,000	\$18,000	\$28,000	\$36,000	\$14,000	\$18,000
Total cost per year	\$144,000		\$32,000		\$64,000		\$32,000	
Cost per period	\$144,000		\$128,000		\$64,000		\$128,000	
10-year total							\$464,000	

¹ Based on three species and five individual fish samples per species (whole bodies for forage fish; fillets for larger piscivorous species) per site; analyze for TotHg and MMeHg in years 1 and TotHg in subsequent years.

² Based on three composite samples of each analyzed taxon per site; all samples analyzed for both TotHg and MMeHg.

³ Based on two species and five individual fish samples per species (whole bodies for forage fish; fillets for larger piscivorous species) per site; analyze for TotHg only.

⁴ Based on two composite samples of each analyzed taxon per site; all samples analyzed for both TotHg and MMeHg.

Table 10. Estimated budget (in dollars) for Federal staff to conduct Bear Creek sampling based on 2009 costs.

	Year 1 Pre	Year 2-5 Pre (per yr)	Year 1 Post	Year 2-5 Post (per yr)	Total
Personnel:					
Biologist ¹	6,140	3,070	6,140	3,070	
Geologist ¹	6,140	3,070	6,140	3,070	
2 technicians ²	5,590	2,795	5,590	2,795	
Travel	1,800	900	1,800	900	
Equipment ³	11,000	1,000	1,000	1,000	
Supplies ⁴	2,000	1,000	1,000	1,000	
Shipping Costs ⁵	400	200	400	200	
Chemical Analyses: biota	144,000	32,000	64,000	32,000	
Chemical Analyses: water & sediments	22,500	13,900	22,500	13,900	
Per year totals	199,570	57,935	108,570	57,935	
10-year totals	199,570	231,740	108,570	231,740	\$771,620

¹ Based on research scientist (GS-12/1) for 4 weeks/year in first years and 2 weeks/year in 2-5 years (not adjusted for COLA).

² Based on technician (GS-5/1) for 4 weeks/year in first years and 2 weeks/year in 2-5 years (not adjusted for COLA).

³ Includes one-time purchase of backpack electrofisher: \$10,000. Delete if one can be borrowed.

⁴ Includes chemically cleaned jars, dissecting equipment, nets, waders, etc.

⁵ Based on one 40-lb cooler per season FedEx priority overnight to contract laboratory.

Summary and Conclusions

This report summarizes the known information on the occurrence and distribution of Hg in physical/chemical and biological matrices within the Bear Creek watershed. Multiple sources, both natural and anthropogenic, contribute Hg to Bear Creek and its tributaries. Previous studies of water, sediment, and biota from the Bear Creek watershed have revealed elevated concentrations of Hg and MMeHg in certain areas, notably downstream of sources of Hg that include both abandoned Hg and Au mines, ore-processing facilities or natural hot and cold springs. Cumulative data for water, invertebrates, and fish matrices show similar patterns of minimum TotHg and MMeHg concentrations at Upper Bear Creek sites, maximum concentrations in the Sulphur Creek area, and intermediate concentrations downstream of the confluence of Sulphur Creek with Bear Creek.

Based on these data, a matrix-specific monitoring protocol was developed to be used for the evaluation of the effectiveness of Hg remediation activities in the Bear Creek watershed. The monitoring protocol documents procedures for collecting and processing samples of water, sediment, and biota for estimation of TotHg and MMeHg in the Bear Creek watershed. It also details timing of sampling before and after site remediation and techniques for evaluation of the results of chemical analyses and estimated costs for sampling and analyses.

The concurrent sampling of TotHg and MMeHg in biota as well as water and sediment from 10 monitoring sites will provide information on the relative bioavailability of Hg released from Hg sources in the watershed and identify environments conducive to Hg methylation. The sampling sites were selected based on spatial relationships (both above and below) to known natural and anthropogenic sources of Hg within the watershed and potential for bioaccumulation by biota. In addition, data from previous biological studies were used to assess the most useful sites for a comprehensive, but cost-effective, evaluation of Hg bioaccumulation before and after restoration.

This protocol is designed to assist landowners, land managers, water-quality regulators, and scientists in determining whether specific restoration/mitigation actions lead to significant progress toward achieving water quality goals to reduce Hg in the Bear Creek watershed.

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Appendix D. Example Chain of Custody Form.

Chain of Custody Record

Page _____ of _____

BROOKS RANDAL LABS
 MEANINGFUL METALS DATA www.brooksrand.com
 3958 6th Avenue NW
 Seattle, WA 98107
 Phone: 206-632-6206
 Fax: 206-632-6017
 samples@brooksrand.com

White: LAB COPY
 Yellow: CUSTOMER COPY

Client:		Address:		COC receipt confirmation? Y / N														
Contact		Phone #:		if so, by: email / fax (circle one)														
Client project ID:				Email:														
PO #:				Fax #:														
Sample ID	Collection		Miscellaneous		Field Preservation		Analyses required				Comments							
	Date	Time	Sampler (initials)	Matrix type	# of containers	Field filtered? (Y/N)	Unpreserved / ice only	HCl / HNO ₃ (circle one)	Other (specify)	Total Hg, EPA 1631		Methyl Hg, EPA 1630	ICP-MS Metals (specify)	As / Se species (specify)	% Solids	Filtration	Other (specify)	Other (specify)
1																		
2																		
3																		
4																		
5																		
6																		
7																		
8																		
9																		
10																		
Relinquished by:		Date:	Time:	Relinquished by:		Date:	Time:	Received at BRL by:		Date:	Time:	BRL project ID:						
Received by:		Date:	Time:	Received at BRL by:		Date:	Time:	BRL work order ID:										
Shipping carrier:		# of coolers:																

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Modoc Hall, Room 3006
Sacramento, CA 95819
<http://www.werc.usgs.gov/>**

EXHIBIT D

Laboratory Report from FGL Environmental for
Wilbur Hot Springs in Williams, CA 95987,
Results for Mercury and Lithium, June 18, 2010



Analytical Chemists
June 18, 2010

Wilbur Hot Springs
3375 Wilbur Springs Road
Williams, CA 95987

Lab ID : CH 1072500
Customer : 7-8348

Laboratory Report

Introduction: This report package contains total of 3 pages divided into 3 sections:

Case Narrative (1 pages) : An overview of the work performed at FGL.
Sample Results (1 page) : Results for each sample submitted.
Quality Control (1 page) : Supporting Quality Control (QC) results.

Case Narrative

This Case Narrative pertains to the following samples:

Sample Description	Date Sampled	Date Received	FGL Lab ID #	Matrix
Geothermal Spring Hotel	06/02/2010	06/02/2010	CH 1072500-001	SW

Sampling and Receipt Information: The sample was received, prepared and analyzed within the method specified holding times. All samples arrived on ice. All samples were checked for pH if acid or base preservation is required (except for VOAs). For details of sample receipt information, please see the attached Chain of Custody and Condition Upon Receipt Form.

Quality Control: All samples were prepared and analyzed according to the following tables:

Inorganic - Metals QC

200.8	06/16/2010:207211 All analysis quality controls are within established criteria
245.1	06/08/2010:206743 All analysis quality controls are within established criteria
3010	06/08/2010:205717 All preparation quality controls are within established criteria
7470	06/08/2010:205742 All preparation quality controls are within established criteria

Certification: I certify that this data package is in compliance with NELAC standards, both technically and for completeness, except for any conditions listed above. Release of the data contained in this data package is authorized by the Laboratory Director or his designee, as verified by the following electronic signature.

KD:DMB

Approved By **Kelly A. Dunnahoo, B.S.**

Digitally signed by Kelly A. Dunnahoo, B.S.
Title: Laboratory Director
Date: 2010-06-18



Analytical Chemists
June 18, 2010

Lab ID : CH 1072500-001
Customer ID : 7-8348

Wilbur Hot Springs
3375 Wilbur Springs Road
Williams, CA 95987

Sampled On : June 2, 2010-09:30
Sampled By : Richard Davis
Received On : June 2, 2010-14:15
Matrix : Surface Water

Description : Geothermal Spring Hotel
Project : Surface Water Monitoring

Sample Result - Inorganic

Constituent	Result	PQL	Units	Note	Sample Preparation		Sample Analysis	
					Method	Date/ID	Method	Date/ID
Metals, Total ^{P:15}								
Lithium	11.9	0.05	mg/L		3010	06/08/10:205717	200.8	06/16/10:207211
Mercury	0.0011	0.0001	mg/L		7470	06/08/10:205742	245.1	06/08/10:206743

ND=Non-Detected. PQL=Practical Quantitation Limit. Containers: (P) Plastic Preservatives: HNO3 pH < 2 #Surrogate.



Analytical Chemists

June 18, 2010
Wilbur Hot Springs

Lab ID : CH 1072500
Customer : 7-8348

Quality Control - Inorganic

Constituent	Method	Date/ID	Type	Units	Conc.	QC Data	DQO	Note
Metals								
Lithium	200.8	06/16/2010:207211	CCV	ppb	120.0	97.0 %	90-110	
			CCB	ppb		0.03	1	
			CCV	ppb	120.0	98.1 %	90-110	
			CCB	ppb		0.12	1	
Mercury	245.1	06/08/2010:206743	CCV	ppt	199.8	92.2 %	90-110	
			CCB	ppt		5.1	20	
			CCV	ppt	199.8	92.2 %	90-110	
			CCB	ppt		5.3	20	
Lithium	3010	06/08/2010:205717 (SP 1005221-002)	Blank	ug/L		ND	<1	
			LCS	ug/L	40.00	93.0 %	85-115	
			MS	ug/L	40.00	95.0 %	75-125	
			MSD	ug/L	40.00	98.2 %	75-125	
			MSRPD	ug/L	39.94	2.6 %	≤20.0	
			PDS	ug/L	40.00	91.7 %	75-125	
Mercury	7470	06/08/2010:205742 (CH 1073276-001)	Blank	ug/L		ND	<0.02	
			LCS	ug/L	0.1998	92.7 %	85-115	
			MS	ug/L	0.1998	92.3 %	75-125	
			MSD	ug/L	0.1998	92.8 %	75-125	
			MSRPD	ug/L	0.1998	0.5 %	≤20	
Definition								
CCV	: Continuing Calibration Verification - Analyzed to verify the instrument calibration is within criteria.							
CCB	: Continuing Calibration Blank - Analyzed to verify the instrument baseline is within criteria.							
Blank	: Method Blank - Prepared to verify that the preparation process is not contributing contamination to the samples.							
LCS	: Laboratory Control Standard/Sample - Prepared to verify that the preparation process is not affecting analyte recovery.							
MS	: Matrix Spikes - A random sample is spiked with a known amount of analyte. The recoveries are an indication of how that sample matrix affects analyte recovery.							
MSD	: Matrix Spike Duplicate of MS/MSD pair - A random sample duplicate is spiked with a known amount of analyte. The recoveries are an indication of how that sample matrix affects analyte recovery.							
MSRPD	: MS/MSD Relative Percent Difference (RPD) - The MS relative percent difference is an indication of precision for the preparation and analysis.							
ND	: Non-detect - Result was below the DQO listed for the analyte.							
DQO	: Data Quality Objective - This is the criteria against which the quality control data is compared.							



EXHIBIT E

Mercury and Methylmercury Concentrations and Loads in the Cache Creek Watershed, California, by Joseph L. Domagalski, published in the Science of the Total Environment, International Journal for Scientific Research 327 (2004) 215-237



Mercury and methylmercury concentrations and loads in the Cache Creek watershed, California

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Shaun M. Ayers^b

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Received 16 September 2003; accepted 13 January 2004

Abstract

Concentrations and loads of total mercury and methylmercury were measured in streams draining abandoned mercury mines and in the proximity of geothermal discharge in the Cache Creek watershed of California during a 17-month period from January 2000 through May 2001. Rainfall and runoff were lower than long-term averages during the study period. The greatest loading of mercury and methylmercury from upstream sources to downstream receiving waters, such as San Francisco Bay, generally occurred during or after winter rainfall events. During the study period, loads of mercury and methylmercury from geothermal sources tended to be greater than those from abandoned mining areas, a pattern attributable to the lack of large precipitation events capable of mobilizing significant amounts of either mercury-laden sediment or dissolved mercury and methylmercury from mine waste. Streambed sediments of Cache Creek are a significant source of mercury and methylmercury to downstream receiving bodies of water. Much of the mercury in these sediments is the result of deposition over the last 100–150 years by either storm-water runoff, from abandoned mines, or continuous discharges from geothermal areas. Several geochemical constituents were useful as natural tracers for mining and geothermal areas, including the aqueous concentrations of boron, chloride, lithium and sulfate, and the stable isotopes of hydrogen and oxygen in water. Stable isotopes of water in areas draining geothermal discharges showed a distinct trend toward enrichment of ¹⁸O compared with meteoric waters, whereas much of the runoff from abandoned mines indicated a stable isotopic pattern more consistent with local meteoric water.

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Keywords: Mercury; Methylmercury; Abandoned mines; Water quality

1. Introduction

The Cache Creek watershed (Fig. 1) is an important source of total inorganic mercury to

downstream areas including the San Francisco Bay, and the region known as the Delta of the Sacramento and San Joaquin rivers (Domagalski, 1998, 2001; Domagalski and Dileanis, 2000; Foe and Croyle, 1999). Although the Cache Creek drainage basin covers only approximately 4% of the area drained by the Sacramento River (Fig. 1), the

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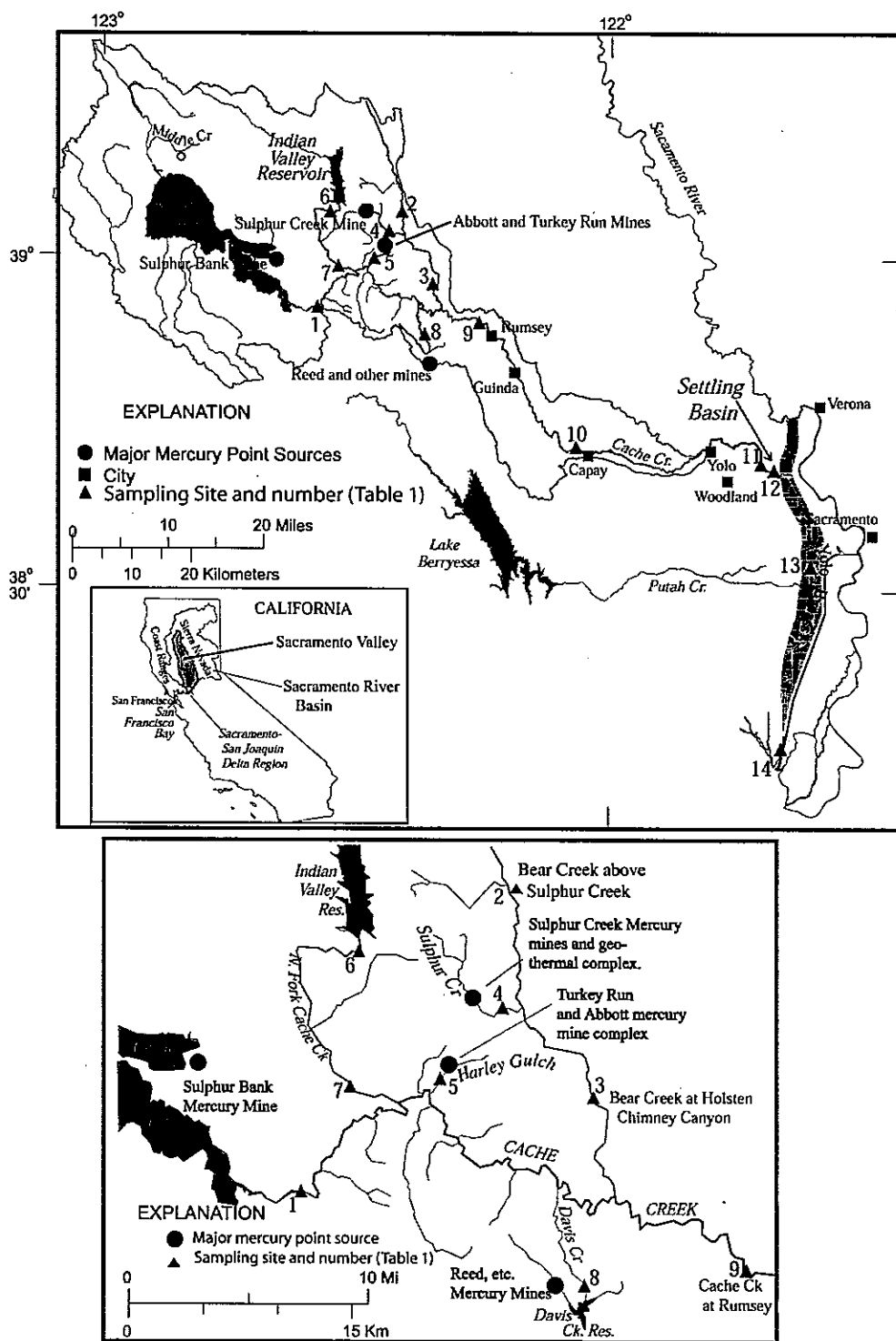


Fig. 1. Map of study area and location of sampling sites.

amount of total mercury transported downstream can be as high as 50% of the total annual load of the Sacramento River (Foe and Croyle, 1999). Sources of mercury within the Cache Creek watershed include natural geothermal springs, abandoned and inactive mercury mines, and mercury prospects (Fig. 1). Sulphur Creek (Fig. 1) has several active geothermal springs within its drainage.

Mercury was mined at several locations in the Cache Creek basin. The mercury–sulfide mineral, cinnabar (HgS), occurs in deposits near the Clear Lake area (Fig. 1) and other locations within the Cache and Putah creek drainages. The mercury deposits in the region near Clear Lake are hydrothermal in origin, of Cenozoic Age, and are the most northern part of a group of similar deposits associated with volcanism and the migration of a transform fault system within the central portion of the California Coast Ranges (Rytuba, 1996). Production of mercury in California was especially high during the period after 1850 following the discovery of placer gold deposits in the California Sierra Nevada. Peak production of mercury occurred in 1877 when the various mines of the California Coast Ranges produced approximately 2776 metric tons of elemental mercury that were primarily used in gold recovery operations (Bradley, 1918). Residues from the abandoned mercury mines remain a source of total mercury to Cache Creek and downstream receiving bodies of water (Foe and Croyle, 1999; Domagalski, 1998). Mining wastes can enter streams primarily through runoff associated with rain, and the highest observed concentrations and loads of total mercury in Cache Creek have followed rainfall events (Domagalski, 1998, 2001). Mercury from geothermal sources enters the creeks year-round.

The mercury transported from the Cache Creek basin to receiving waters may pose a human health problem if that mercury enters the aquatic food web and eventually bioaccumulates as methylmercury in fish to levels above health guidelines. Currently, the potential for the mercury of the Cache Creek basin to change to the methylated form, either within the Cache Creek basin or when transported to a downstream receiving body of water such as the Delta, is largely unknown. Most

of the mercury transported through Cache Creek is presumably in the form of cinnabar as a suspended solid. The cinnabar must dissolve to liberate aqueous Hg (II) before the mercury can be transformed to methylmercury. No studies have yet documented the fraction of mercury present as methylmercury at various locations within the Cache Creek watershed.

The present study was designed to determine local sources of total mercury and methylmercury within the Cache Creek watershed and to determine the mass loadings from those sources. It was hypothesized that the greatest loadings would occur from previously mined regions where little or no removal of mine wastes have occurred, and that loads from geothermal sources would be stable, but minor compared to those of mine wastes. Furthermore, it was hypothesized that stable isotopes of hydrogen and oxygen in water, or other geochemical tracers such as boron and lithium could be used to help relate mercury concentrations or loads in water to source areas. The study determined the concentrations and loadings during a time frame from January 2000 through May 2001 and assessed the seasonal effects on concentrations and loadings. The study is part of a larger investigation on mercury and its effects both within the Cache Creek watershed and downstream in the Delta of the Sacramento and San Joaquin rivers. The larger investigation is examining mercury bioaccumulation, the potential of mine remediation within the Cache Creek watershed to reduce mercury loads, and mercury bioaccumulation-related issues associated with ecosystem restoration projects within the Delta of the Sacramento and San Joaquin rivers.

2. Study area and methods

The Cache Creek Basin occupies approximately 3000 km² in Northern California (Fig. 1). The area upstream of Rumsey is characterized by the low hills of the California Coast Ranges whereas the area downstream of Rumsey flattens out to become part of the Sacramento Valley. Land cover in the upstream portion of the basin is mainly forest and grazing land with minor amounts of orchards and cropland. The amount of land used

Table 1
Site names and numbers from Fig. 1

Site number	Site name
1	Cache Creek near Lower Lake
2	Bear Creek above Sulphur Creek
3	Bear Creek above Holsten Chimney Canyon
4	Sulphur Creek at Wilbur Springs
5	Harley Gulch near Wilbur Springs
6	North Fork Cache Creek near Clearlake Oaks
7	North Fork Cache Creek at Highway 20
8	Davis Creek Reservoir at dam, near Knoxville
9	Cache Creek at Rumsey
10	Cache Creek near Highway 505
11	Cache Creek into Settling Basin
12	Cache Creek out of Settling Basin
13	Yolo Bypass at Interstate 80 near West Sacramento
14	Lower Yolo Bypass

for crops increases downstream of Rumsey. Former mine sites represent a relatively small amount of the total land cover. Cache Creek has its origin as outflow from Clear Lake. The largest tributary to Cache Creek, the North Fork of Cache Creek, has its origin in the northern part of the basin and includes the Indian Valley Reservoir. Another major tributary to Cache Creek is Bear Creek. The Bear Creek watershed does not have a reservoir. Both Clear Lake and Indian Valley Reservoir are managed to supply irrigation water to farmers in the lower parts of the Cache Creek basin. In fact, summertime flows in Cache Creek and the North Fork of Cache Creek are entirely managed for irrigation usage, and essentially no water reaches the Sacramento River during the summer and fall months (Domagalski et al., 2000a). Fall and early wintertime flows tend to be low because releases from Clear Lake and Indian Valley Reservoir are very low. Higher flows occur in winter in response to seasonal rainfall. In addition, the level of Clear Lake or Indian Valley Reservoir is occasionally lowered during the winter months for flood protection. The rainy season occurs from November through March, although each year is variable with respect to timing and amount of rainfall. The water from Cache Creek that leaves the basin enters a seasonal flood-control channel of the Sacramento River system known as the Yolo Bypass (Fig. 1), which is designed to reduce the potential of flood-

ing in adjacent areas and cities. The Yolo Bypass discharges very little water during the dry season.

There are numerous smaller tributaries to Cache Creek; some draining abandoned mining sites and geothermal areas. One of these smaller tributaries is Harley Gulch (Fig. 1), which drains an abandoned mercury mine complex (the Turkey Run and Abbott mines). Another is Davis Creek (Fig. 1), which drains the Reed Mine. The Sulphur Creek (Fig. 1) drainage includes both natural sources of mercury from geothermal springs and some mine wastes, including both mercury and gold mines. Sulphur Creek drains into Bear Creek, a tributary to Cache Creek above Rumsey.

Sampling sites (Fig. 1 and Table I) were selected to assess representative locations of potential sources of mercury within the Cache Creek watershed. Stream sites immediately downstream of the dams on both Clear Lake and Indian Valley Reservoir were sampled to determine mercury and methylmercury concentrations from either the lake or reservoir. Sampling sites were situated on small tributaries or other water bodies near mercury mines or natural mercury sources. There were two sites on Bear Creek which included an upper site, Bear Creek above Sulphur Creek (Fig. 1, site 2); and a lower site, Bear Creek above Holsten Chimney Canyon (Fig. 1, site 3). There was one site on Sulphur Creek (Fig. 1, site 4), one on Harley Gulch (Fig. 1, site 5), and one on Davis Creek

Reservoir at its spillway (Fig. 1, site 8). The upper Bear Creek site is situated above the mercury mines and geothermal springs. Additional sites situated on Cache Creek included a site at Rumsey (Fig. 1, site 9), which is centrally located in the Cache Creek Basin, and sites just upstream of the point where Cache Creek discharges to the Yolo Bypass (Fig. 1, sites 10, 11 and 12); these latter two sites bracket the Cache Creek Settling Basin, which is designed to trap sediment transported out of the Cache Creek watershed. Finally, two sites were situated in the Yolo Bypass (Fig. 1, sites 13 and 14): one in the central portion of the Yolo Bypass (Yolo Bypass at Interstate 80 near West Sacramento) and the second site (Lower Yolo Bypass) just upstream of where the Yolo Bypass discharges into the Delta region.

In addition to the sites listed in Table 1, two mine-site areas in the Cache Creek watershed were sampled in more detail by a separate team from the University of California, Davis (UCD). The location of several sampling sites in both the Abbott–Turkey Run mine-site area and the Sulphur Creek mine-site area are described in detail by Suchanek et al. (2002).

The US Geological Survey (USGS) sampled some sites, including the Yolo Bypass sites and the site immediately downstream of the dam on Indian Valley Reservoir, and the UCD team sampled some sites, such as the Bear Creek above Sulphur Creek and Cache Creek near Highway 505. Other sites were sampled by both the USGS and UCD.

Water samples collected by the USGS were width- and depth-integrated and were collected with a sampler designed for the collection of isokinetic samples (Shelton, 1994; Edwards and Glysson, 1988; Ward and Hair, 1990; US Geological Survey, 1999). The water samples were collected in 3-l Teflon bottles that had been cleaned for the purpose of collecting water samples for mercury and trace metals. The Teflon bottles were originally cleaned by immersion in 10% hydrochloric acid at 65° C for a period of 3 days. After thorough rinsing with ultra-clean water, the bottles were tightly capped and double-wrapped in plastic for transport to a field site. After collection of a water sample, the bottles were rinsed with ultra-

clean water and then field-cleaned with a dilute detergent, followed by thorough rinsing with ultra-clean water, a rinse with 5% hydrochloric acid, and a final series of rinses with ultra-clean water. One set of sampling bottles was only used for geothermal or mercury mine sites expected to have higher mercury concentrations; while another set was only used for downstream sites on the larger creeks and rivers expected to have lower mercury concentrations. After collection, the water samples were composited in an 8-l Teflon-lined stainless-steel churn. The cleaning procedure for a churn involved washing with dilute detergent followed by thorough rinsing with ultra-clean water, a thorough internal rinse with 5% hydrochloric acid, and a final series of rinses with ultra-clean water. Similar to the procedure with the 3-l Teflon sampling bottles, one churn was used only for mining or geothermal sites, and a second churn was used only for the sites on the larger creeks and rivers.

Water samples were taken from the churn for various analyses of whole-water (unfiltered) samples such as suspended sediment concentration, mercury and methylmercury in unfiltered water, trace elements in unfiltered water, and measurement of pH and specific conductance. Water samples were then collected for analyses of filtered samples with a 0.45 µm, high-capacity capsule filter. The filtration order for samples was total mercury, methylmercury, other trace metals, and finally alkalinity.

Water samples collected by UCD differed from those taken by the USGS in that the UCD samples were grab samples collected in that part of the river or stream judged to have the greatest discharge. The UCD group did not filter samples in the field, but rather transported the samples by overnight courier or ground transport to the corresponding laboratory, where samples were immediately filtered and preserved. Samples taken for mercury and methylmercury were collected in 1 l, pre-washed glass bottles. Samples for trace metals, alkalinity and stable isotopes were taken in 4-l polyethylene bottles that were cleaned with the same procedure described above for the Teflon-lined churns.

Water samples collected by the USGS for the measurement of total mercury in water were ana-

lyzed according to the method of Roth (1994), which utilizes cold vapor atomic fluorescence spectrometry. Water samples collected by UCD were also analyzed with a cold vapor atomic fluorescence methodology, and complete details are given in Puckett and van Buuren (2000). The method was based on that of the US Environmental Protection Agency (US EPA, 1996). Methylmercury in water was measured by a similar method following distillation and ethylation of aqueous samples (Puckett and van Buuren, 2000). Selected trace elements in water were analyzed by inductively coupled plasma mass spectroscopy (Alpers et al., 2000).

Full details of laboratory and field quality assurance requirements are given by Puckett and van Buuren (2000). Field-level quality assurance consisted of the collection of blanks and replicates. Seven field blanks were collected for total mercury in unfiltered and filtered water during the three sampling events completed by the USGS. The concentrations of total mercury in unfiltered water blanks ranged from less than detection (0.5 ng/l) to 1.2 ng/l. The median level was 0.6 ng/l. The median was estimated by setting the concentrations of non-detected values to one half the detection limit. The concentrations of total mercury in filtered blank samples ranged from less than detection (0.5 ng/l) to 1.2 ng/l. The median value was less than the detection limit. Therefore, bias caused by contamination does not affect the data set, as the levels of mercury measured in environmental samples are much higher than those measured in blank samples. The range in measured concentrations of total mercury in environmental samples was less than the detection limit to 3070 ng/l, and 98% of all measured concentrations exceeded a concentration of 1 ng/l.

Six field blanks were collected for methylmercury in unfiltered and filtered water during the three sampling events completed by the USGS. Most of the measurements were less than the detection limit of 0.02 ng/l. Two samples of methylmercury in unfiltered water had concentrations just slightly above the detection limit, and the highest concentration was 0.03 ng/l. Therefore, bias caused by contamination does not affect the measurements of methylmercury.

All samples collected for total mercury in unfiltered and filtered water by the USGS were taken in duplicate, and each of the duplicate samples was analyzed in triplicate. The median relative percent difference (RPD) for the values of total mercury in unfiltered water samples was 3.5%, whereas that for filtered water samples was 6.4%. The higher RPD for the filtered water samples may be attributed to the relatively lower concentrations of total mercury in filtered water. A total of six replicates were collected by the USGS for methylmercury analysis. The median RPD for methylmercury in whole water samples was 8.5%, whereas that in filtered water was 4.5%.

The UCD sampling team also collected field blanks and replicates. The median concentration of total mercury in unfiltered water blanks was 0.32 ng/l. The median concentration of methylmercury in unfiltered water blanks was less than the detection limit of 0.02 ng/l. The median concentration for the field blanks taken by the UCD team and filtered at the Batelle Laboratory was 0.072 ng/l for filtered total mercury, and below the detection limit of 0.024 ng/l for filtered methylmercury. The median RPD of total mercury in unfiltered water for the UCD sampling team was 8.6% and that for methylmercury in unfiltered water was 13.3%. The RPD for methylmercury in filtered water for the samples collected by UCD was 7.5% and that for methylmercury was 20.1%.

A separate laboratory quality assurance program was used for the analysis of oxygen and hydrogen isotope ratios in unfiltered water samples. Isotopic analyses of oxygen and hydrogen atoms in water were recorded as ratios relative to Standard Mean Ocean Water (SMOW-V, O'Neil, 1986). Isotope ratios of oxygen ($^{18}\text{O}/^{16}\text{O}$, expressed as $\delta^{18}\text{O}$) and hydrogen ($^2\text{H}/^1\text{H}$, expressed as δD) in water were measured with a light stable isotope ratio mass spectrometer. Oxygen isotope measurements were done on CO_2 after equilibration with the water at 25 °C. Hydrogen isotope measurements were done on H_2 after reduction of the water with zinc with a platinum catalyst (Bigeleisen et al., 1952; Kendall and Coplen, 1985). The laboratory uses a calibration procedure with three unique standards, with each standard analyzed in duplicate with each analytical run. In all cases, the laboratory

was able to calibrate the instruments according to the known values of isotope ratios in the standards. The laboratory also completed 18 duplicate measurements of $\delta^{18}\text{O}$ and 16 duplicate measurements of δD during the time when the environmental samples from this study were analyzed. The average differences in the replicates for $\delta^{18}\text{O}$ were 0.03 per mil and that for δD were 0.4 per mil. Another quality assurance check was made by including 13 samples of de-ionized (DI) water as blind replicates. The S.D. for 13 measurements of the DI water were 0.07 per mil for $\delta^{18}\text{O}$ and 0.8 per mil for δD .

3. Results and discussion

The general strategy for determination of mass loads was two-fold: (1) to collect samples of storm water run-off because of the higher river flows and the greater potential for transport of mercury and methylmercury; and (2) to collect samples at pre-planned intervals during the dry season. The rainy season and peak river flows generally occur between November and March, with little or no rainfall and low river discharge during the remainder of the year. Rainfall was below normal during the period of this study, and discharge from Cache Creek was relatively low compared to historical records. The discharge for water year 2000 (1 October 1999 through 30 September 2000) for the Cache Creek at Yolo was only 55% of the long-term average based on data from 1903 to 2000 (Anderson et al., 2001). Discharge during water year 2001 was even less than that of water year 2000. Therefore, the results of this study reflect low-flow conditions in these streams and rivers.

Concentrations of total mercury in whole and filtered water samples are shown in Fig. 2 for the larger stream sites, and in Fig. 3 for the smaller stream sites. As expected, the mining and geothermal sites had the highest concentrations, and most of the total mercury was associated with suspended sediment, especially for the sites on Cache Creek downstream of Bear Creek. The fraction of total mercury associated with particles increased downstream from the mining sites. The median ratio for the filtered to unfiltered total mercury for the Cache Creek at Rumsey site was 0.13, while that

for the inflow to the Cache Creek Settling Basin was 0.1, and that for the Yolo Bypass was 0.12. In contrast, the median ratio of filtered to unfiltered total mercury for the Sulphur Creek at Wilbur Springs site was 0.26, while the median ratio for the Harley Gulch site was 0.45, and that for the Bear Creek above Holsten Chimney Canyon site was 0.43. Therefore, soluble mercury enters the streams near the mine or geothermal sites, but then either precipitates or becomes associated with particles as the water from those tributaries and its associated load of mercury, discharge into Cache Creek. Concentrations of total mercury were lower at most of the downstream locations than at the mining and geothermal sites, because of their distance from these sources and because of dilution from the two largest sources of water, Clear Lake and Indian Valley Reservoir, or precipitation of the dissolved mercury.

Concentrations of methylmercury in whole water and filtered water samples for selected sites are shown in Figs. 4 and 5. The highest concentrations were measured in water from Sulphur Creek at Wilbur Springs, Bear Creek above Holsten Chimney Canyon, and Harley Gulch near Wilbur Springs. Concentrations of methylmercury were generally higher in whole water samples than in filtered samples. The ratio of methylmercury in the filtered water samples to that for total methylmercury in unfiltered water was higher than the corresponding ratio for total mercury. The ratio of methylmercury in filtered water samples to whole water samples ranged from approximately 0.1 to greater than 1, and the median ratio ranged from 0.29 to 0.78 for all sites. These ratios for methylmercury were considerably more variable than the corresponding ones for total mercury, at all sites.

Tables of instantaneous daily loads of total mercury for selected sites are given for data from February and March 2000 (Table 2), and February 2001 (Table 3). The periods of time presented in Tables 2 and 3 correspond to when samples of storm water runoff were collected at the sites. For the year 2000 sampling, the total instantaneous mercury loads were relatively low near the mining and geothermal sites relative to the downstream sites because of the lower discharges from the mining and geothermal sites. Loads of total mer-

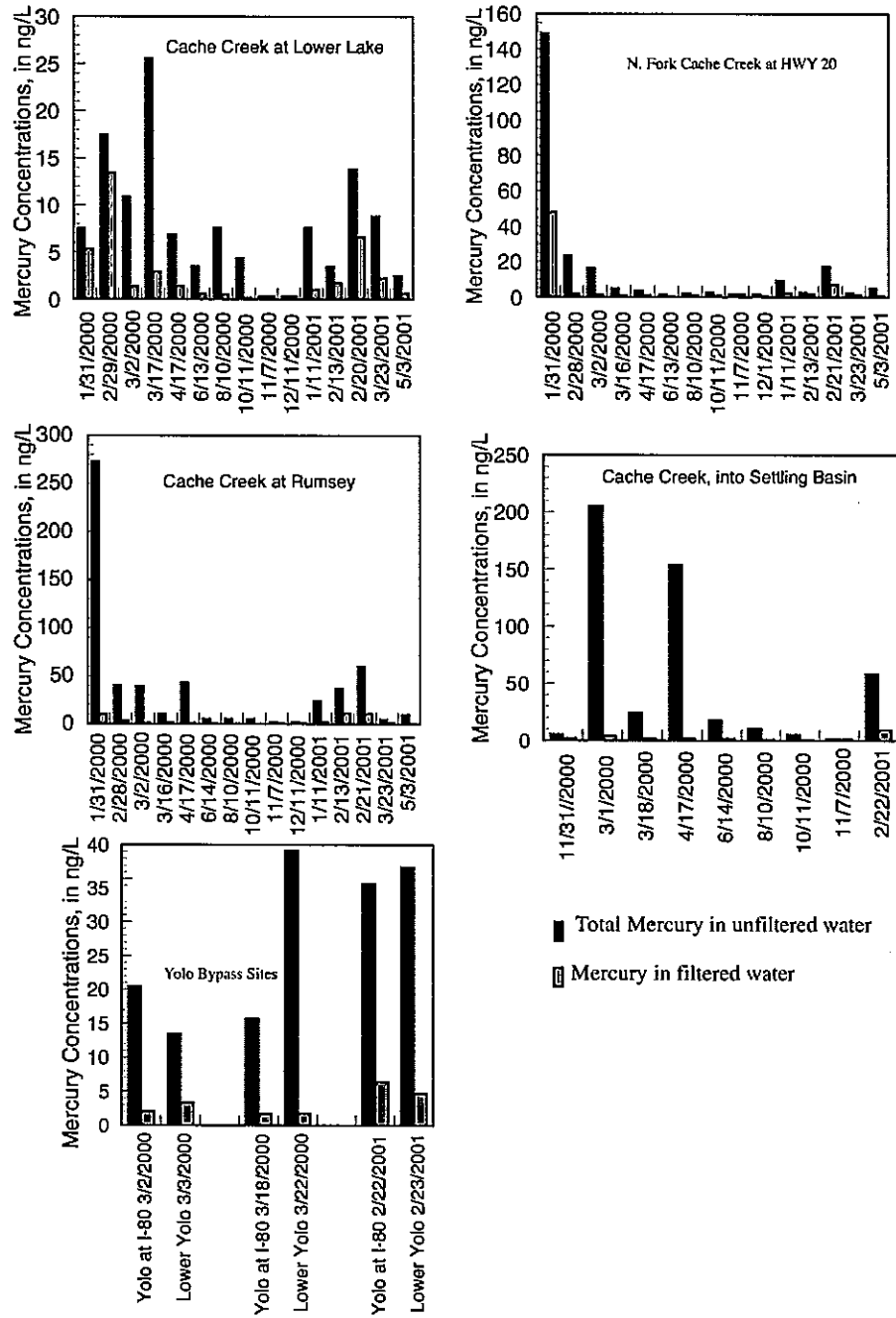


Fig. 2. Mercury concentrations at large river sites.

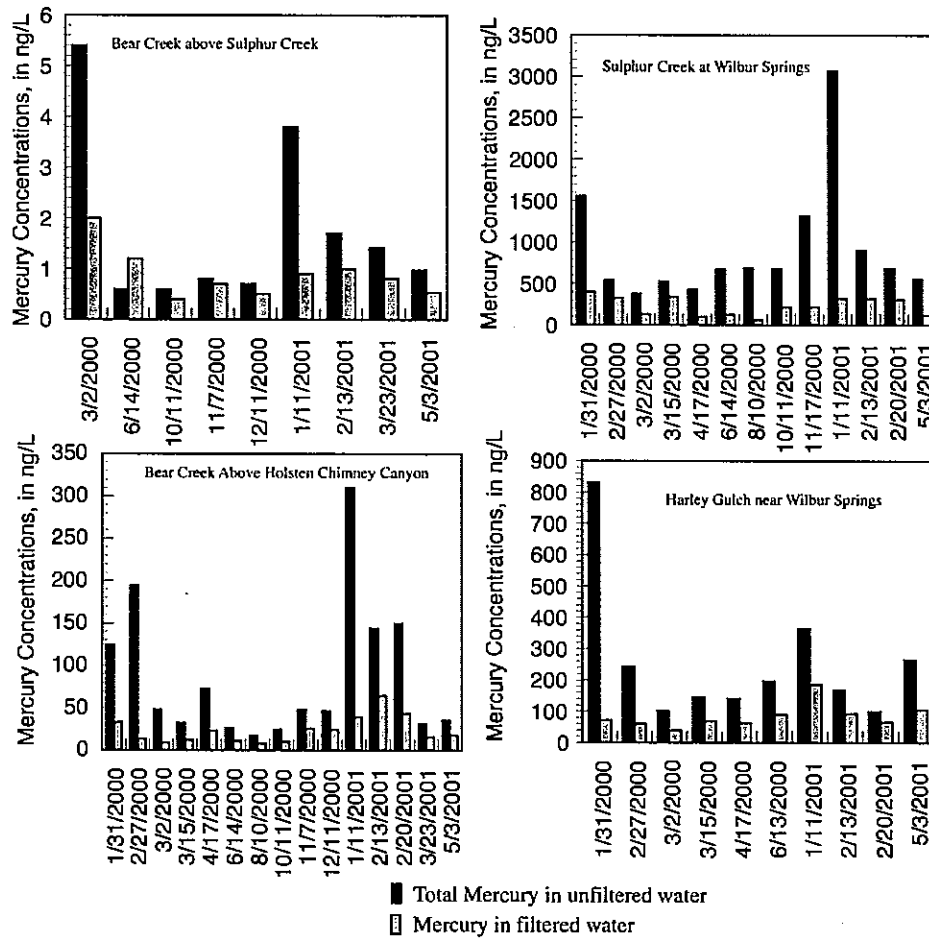


Fig. 3. Mercury concentrations at small stream sites.

cury increased downstream during the February–March 2000 storm, and the downstream loads exceeded the sum of the loads from the mining and geothermal sites. For the samples collected during February 2000, part of the downstream increase could be attributed to hydrological or water management factors. Midway during the period of time that samples were being collected, on 28 February 2000, water began to be released from the Clear Lake dam to lower water levels of Clear Lake to reduce the risk of flooding to lakeside property. The discharge of Cache Creek at Rumsey and at downstream sites during sampling, for example, contained both storm-water runoff and released water from Clear Lake, where-

as discharge at the time of sampling at the mining and geothermal sites, as well as the sites on the North Fork of Cache Creek, contained only storm-water runoff. Therefore, the higher loads at the Cache Creek at Rumsey, and downstream at the settling basin can be logically attributed primarily to re-suspension of previously deposited mercury in the bottom sediments as a result of higher flows from the released water. The load of total mercury at the sites furthest downstream, i.e. the Yolo Bypass at Interstate 80 near West Sacramento and the Lower Yolo Bypass resulted from combined flows from Cache Creek and the Sacramento River. No attempt was made, nor are data available, to discriminate between these sources.

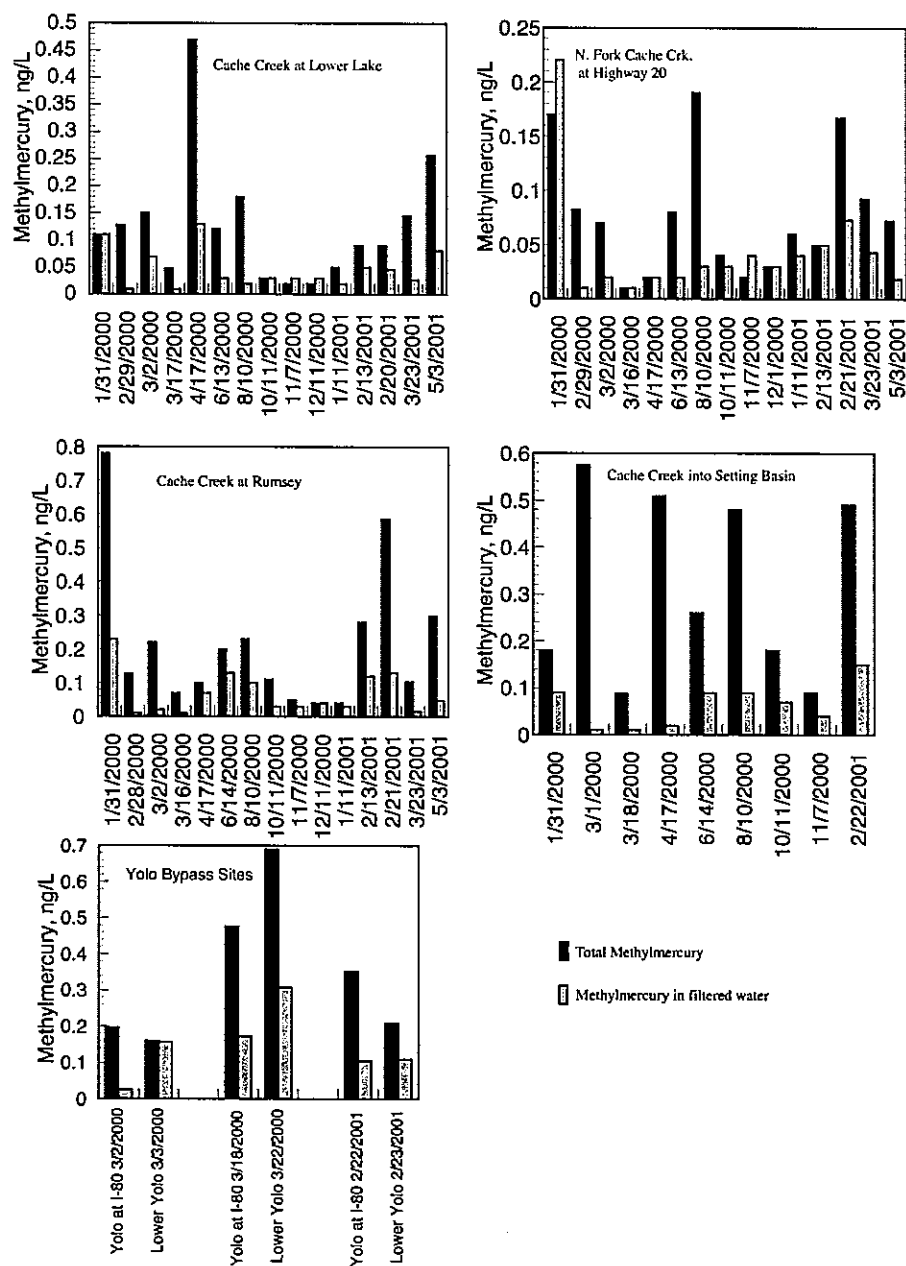


Fig. 4. Methylmercury concentrations at large river sites.

The loads of mercury and methylmercury from the storm of late February and March 2001 were much less than those during the storm of Febru-

ary–March 2000 (Tables 2 and 3). The sum of the loads originating from the mining and geothermal sites, as measured on the storm of February

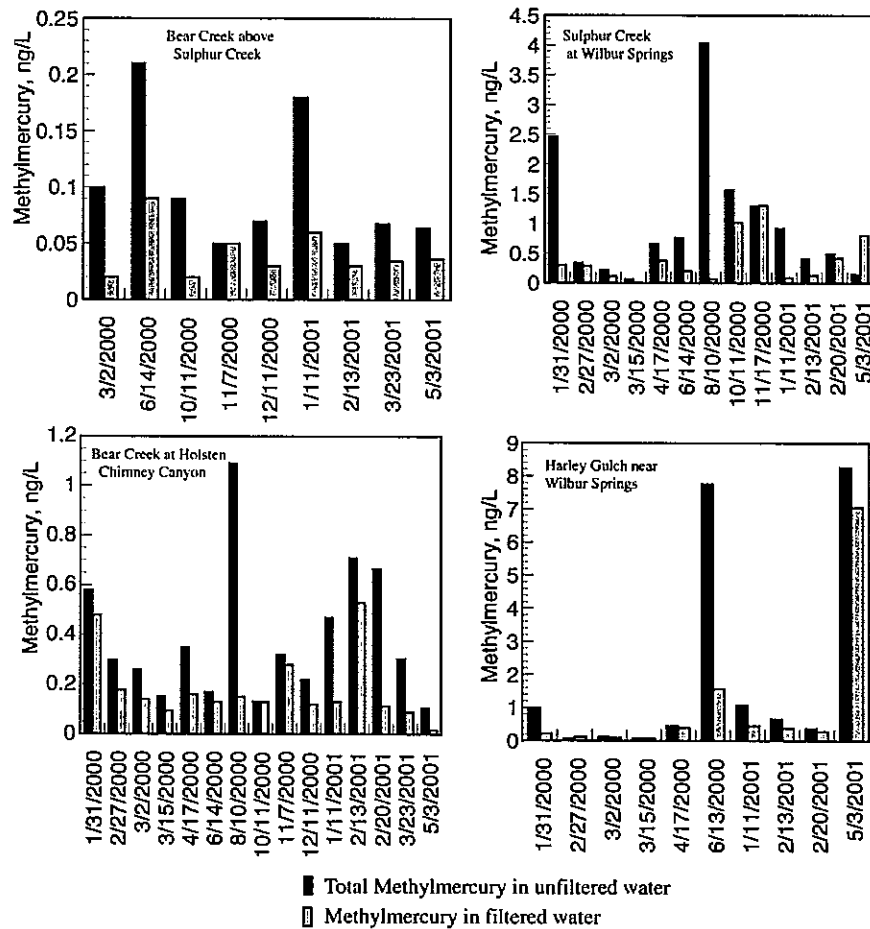


Fig. 5. Methylmercury concentrations at small stream sites.

2001 was close to that measured at the Cache Creek at Rumsey and downstream. During that storm, there was very low discharge of water from both Clear Lake and Indian Valley Reservoir. As a result, the mercury loads measured downstream at Cache Creek were more representative of the loads from the mining and geothermal sites.

Patterns of instantaneous loads of total methylmercury for individual sites were generally similar to those for total mercury. The upstream loads of total methylmercury during the February–March 2000 sampling were less than the loads at the downstream sites. During the February 2001 sampling, however, the highest load of total methyl-

mercury occurred at the Cache Creek at Rumsey site, with two upper-watershed streams, Bear Creek and the North Fork of Cache Creek, contributing most to the load at Rumsey.

It was not possible to calculate accurate annual discharge or annual loads of mercury from all of the sampling sites, or at all times at individual sites. Continuous records of discharge were only available for Sulphur Creek at Wilbur Springs, Bear Creek above Holsten Chimney Canyon, Harley Gulch near Wilbur Springs, outflow from Clear Lake (Cache Creek near Lower Lake), North Fork Cache Creek near Clearlake Oaks (outflow from Indian Valley Reservoir), and the Yolo Bypass.

Table 2
Mercury mass loadings during two storm events

Site name	Hg load (g/day)	
	Storm 1 ^a	Storm 2 ^b
Cache Creek near Lower Lake	86	0.2
Bear Creek above Holsten Chimney Canyon	280	67
Sulphur Creek at Wilbur Springs	51	35
Harley Gulch near Wilbur Springs	5	0.009
North Fork Cache Creek near Clearlake Oaks	29	0.1
North Fork Cache Creek at Highway 20	129	12
Davis Creek Reservoir at dam, near Knoxville	5	Not sampled
Cache Creek at Rumsey	213	149
Cache Creek into Settling Basin	2386	134
Cache Creek out of Settling Basin	1864	122
Yolo Bypass at Interstate 80 Near West Sacramento	2267	119
Lower Yolo Bypass	1496	128

^a Storm 1, Sampling occurred from 27 February 2000 through 30 March 2000.

^b Storm 2, Sampling occurred from 20 February 2001 to 23 February 2001.

Discharge for the input to the Cache Creek Settling Basin (Lower Cache Creek) was estimated from the discharge record of a nearby gauging station.

Annual discharge and percentage of discharge for the entire Cache Creek watershed and Yolo Bypass for water years 2000 and 2001 for the sites with continuous records are given in Tables 4 and 5.

A significant relationship between concentration and discharge is required to calculate an accurate annual load of any constituent in a river with few

observations of the concentration of that constituent and a continuous record of discharge. Linear least-squares regression of the data on stream discharge and total mercury concentrations for the mining or geothermal sites and the input to the Cache Creek Settling Basin had generally poor fits (r^2 between 0.008 and 0.14). The best relation between stream discharge and total mercury was for the Cache Creek into Settling Basin site ($r^2=0.7$), but the regression equation had poor predictive value with a positive y-intercept. This lack of

Table 3
Methylmercury mass loadings during two storm events

Site name	Methylmercury load (g/day)	
	Storm 1 ^a	Storm 2 ^b
Cache Creek near Lower Lake	0.63	0.002
Bear Creek above Holsten Chimney Canyon	0.43	0.3
Sulphur Creek at Wilbur Springs	0.03	0.03
Harley Gulch near Wilbur Springs	0.001	0.00003
North Fork Cache Creek near Clearlake Oaks	0.16	Not detected
North Fork Cache Creek at Highway 20	0.45	0.11
Davis Creek Reservoir at Dam, near Knoxville	0.05	Not sampled
Cache Creek at Rumsey	0.67	1.45
Cache Creek into Settling Basin	6.7	1.12
Cache Creek out of Settling Basin	5.1	0.75
Yolo Bypass at Interstate 80 near West Sacramento	21.8	1.22
Lower Yolo Bypass	17.7	0.73

^a Storm 1, sampling occurred from 27 February 2000 through 30 March 2000.

^b Storm 2, sampling occurred from 20 February 2001 to 23 February 2001.

Table 4

Annual discharge for selected sites for water year 2000 (1 October through 30 September), and percent of Cache Creek and Yolo Bypass discharge

Site	Annual discharge (m ³)	Percent of Cache Creek Watershed discharge	Percent of Yolo Bypass discharge
Sulphur Creek	2 784 930	1	0.1
Bear Creek	33 270 770	12	1
Harley Gulch	395 290	0.15	0.01
Lower Cache Creek	268 342 150	100	8

Table 5

Annual discharge for water year 2001 (1 October through 30 September), and percent of Cache Creek and Yolo Bypass discharge

Site	Annual discharge (m ³)	Percent of Cache Creek Watershed discharge	Percent of Yolo Bypass discharge
Sulphur Creek	1 834 700	2	<1
Bear Creek	18 267 000	19	9
Harley Gulch	5020	0.005	<0.01
Lower Cache Creek	93 931 500	100	45

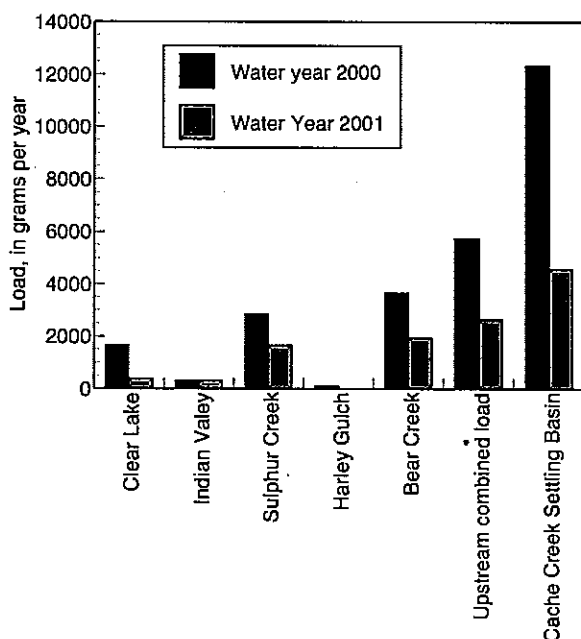


Fig. 6. Annual mercury loads at sites with continuous stream-flow records.

a clear relation between discharge and mercury concentration limited our ability to calculate annual loads of mercury for these streams.

A crude estimate of annual mercury loading at select sites may be obtained with an estimated average mercury concentration of the dry season and an average mercury concentration for the wet season, or runoff events, combined with flow data for sites that have reliable records of discharge. For the Clear Lake outflow, a dry-season estimated average of 4 ng/l of total mercury and a wet-season estimated average of 12 ng/l of total mercury was used. For the Indian Valley Reservoir, an estimated average of 2 ng/l of total mercury for the dry season and 5 ng/l during the wet season were used. For Harley Gulch, an estimated average of 169 ng/l for the dry season and 279 ng/l for the wet season were used. For Bear Creek, similar concentrations of 38 ng/l and 131 ng/l were used, respectively. For Sulphur Creek, values of 758 and 1095 ng/l were used. For the Cache Creek Settling Basin, concentrations of 1.3 and 51.3 ng/l were used.

Annual loads for each year of the study were calculated for sites that have continuous stream-flow records. These annual loads are shown in Fig. 6. For both water years, the loads from Sulphur Creek are greater than those from either Clear Lake or the Indian Valley Reservoir. Loads from Sulphur Creek are also much greater than those

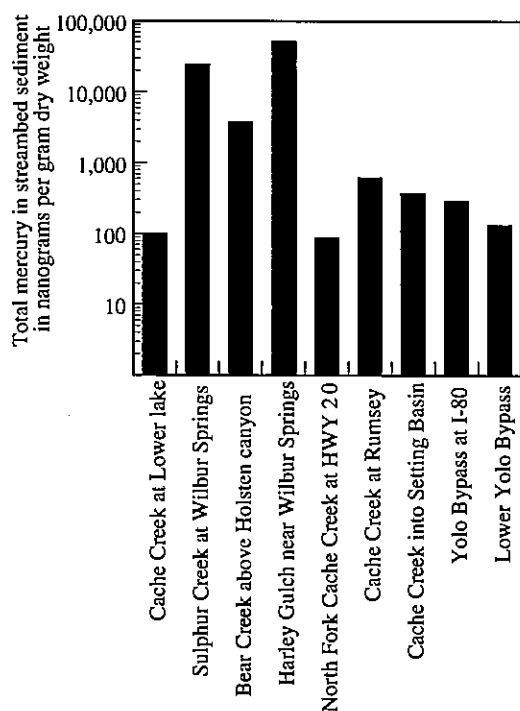


Fig. 7. Total mercury in streambed sediment at selected sites.

from Harley Gulch, which is immediately downstream of a large mercury mine. Because of the lower than normal rainfall amounts, mercury loads from Harley Gulch were relatively low. Mercury loads from Bear Creek increase slightly from those of Sulphur Creek, probably from re-suspension of previously deposited mercury from Sulphur Creek. When the combined loads of the upstream tributaries are summed, the resulting combined load is less than that calculated for the most downstream site, the Cache Creek Settling Basin. This increase in loads between the mine and geothermal sites and the most downstream site can be logically attributed to re-suspension of previously deposited mercury. Erosion of mercury from these mine waste piles has been ongoing for over 100 years. As a result, the bed sediments of Cache Creek are a source of mercury to downstream water bodies.

Concentrations (dry weight) of total mercury in streambed sediments collected during the late fall of 2000 are shown on Fig. 7. As expected, concentrations were considerably higher in the sedi-

ments from the mining or geothermal sites relative to the sites downstream on Cache Creek or the North Fork of Cache Creek.

Mercury mining began approximately 150 years ago at locations in the Cache Creek basin, and the wastes from those operations remain a continuing source to downstream locations. Because these sites are impacted by mining activities, there is no way of determining what the concentration of mercury in streambed sediment would be in the absence of mining. Mercury concentrations were 100 ng/g of dry sediment in streambed sediment taken just below Clear Lake and 87 ng/g of dry sediment in the North Fork of Cache Creek near Highway 20. It is to be expected that mercury concentrations in sediment from the Cache Creek at Rumsey site would be higher than those at the Clear Lake site because of runoff from geothermal sources and of naturally occurring mercury in upstream soils. Although no 'pre-mining background' concentration of mercury in sediment could be derived for the Cache Creek at Rumsey site, the present concentrations have probably been influenced by human activities for more than 150 years and almost certainly exceed the pre-mining levels. Because of the anthropogenic influences on the Cache Creek at Rumsey site, the streambed sediments along Cache Creek can be considered as an additional source of mercury to downstream areas.

The aqueous chemistry at various locations within the Cache Creek Basin can vary seasonally because of chemical differences among the inflowing waters from different sources. These variations in chemistry, related to water source, may be useful in relating the sources of mercury or methylmercury at downstream locations if the water associated with these mercury sources have distinguishable geochemical signatures. Some potentially useful chemical tracers include the aqueous concentrations of chloride (Cl), sulfate (SO₄), boron (B), and lithium (Li), the relative amounts of dissolved or suspended mercury, and the stable isotopes of hydrogen and oxygen in water.

An example of a chemical signature for the Cache Creek at Rumsey site is aqueous chloride and sulfate. A 2-year profile of Cl/SO₄ ratios with data from a previous study is shown in Fig. 8

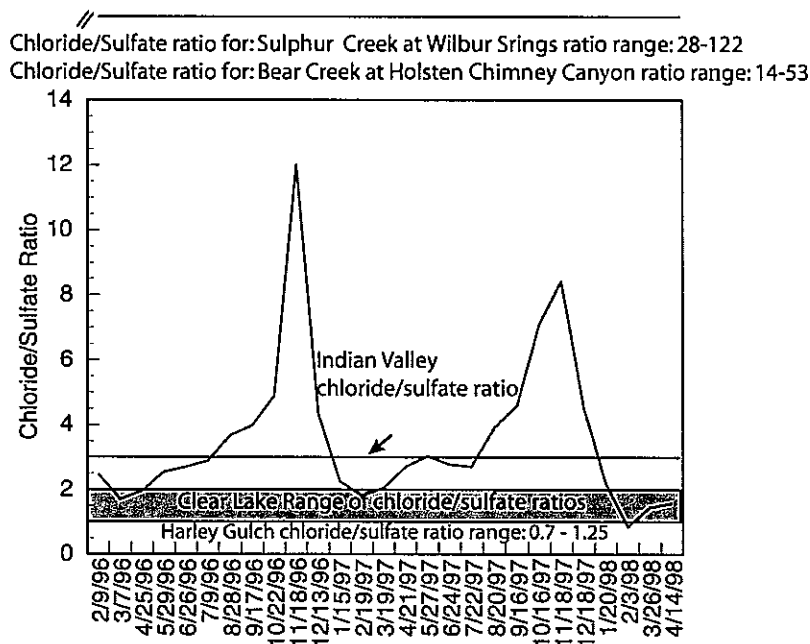


Fig. 8. Ratio of chloride to sulfate at the Cache Creek at Rumsey site and at other selected sites within the Cache Creek basin.

(Domagalski et al., 2000b). Also, shown in that figure are Cl/SO₄ ratios from select sites using data collected during the present study. The Cl/SO₄ ratio is mostly dependant on whether Clear Lake or the Indian Valley Reservoir is the primary source of water (typically during the irrigation season and wet season), or whether Bear and Sulphur creeks dominate the flow (typically during late fall to early winter). Because of the higher chloride content in the geothermal springs within the Sulphur Creek drainage, the Cl/SO₄ ratio increases as the percentage of water from Sulphur Creek increases. The Harley Gulch samples have a low Cl/SO₄ ratio because of their higher concentrations of sulfate derived from the mine waste. As a result of the higher sulfate concentrations, the Cl/SO₄ ratio is relatively low in Harley Gulch water. Winter storm water runoff indicates a mixed source. The water chemistry changes significantly in the fall, with large changes in the Cl/SO₄ ratio. As the irrigation season ends, and flows from Clear Lake and Indian Valley Reservoir are decreased, the percentage of Sulphur Creek and

Bear Creek water in Cache Creek increases, resulting in the large increase in the Cl/SO₄ ratio.

It was hypothesized that systematic changes in the differences in select element ratios in water, from upstream mining and geothermal sources, to downstream locations, might be useful as tracers of which locations (abandoned mines or geothermal springs) are important sources of mercury or methylmercury to downstream locations. Geochemical tracing of mercury transported to downstream areas to specific source areas would provide a powerful tool for mine re-mediation and clean-up efforts. Erosion of geologic material at the mine or geothermal sites, for example, might differ from that of the surrounding geologic material at other locations such that runoff from the mine or geothermal sites would have characteristic signatures with respect to element ratios. An analysis of whole-water samples was completed by computing the ratios of the amounts of various elements in whole water samples to the amount of aluminum. Aluminum has low solubility, but is a major constituent of the rock types found in the Cache

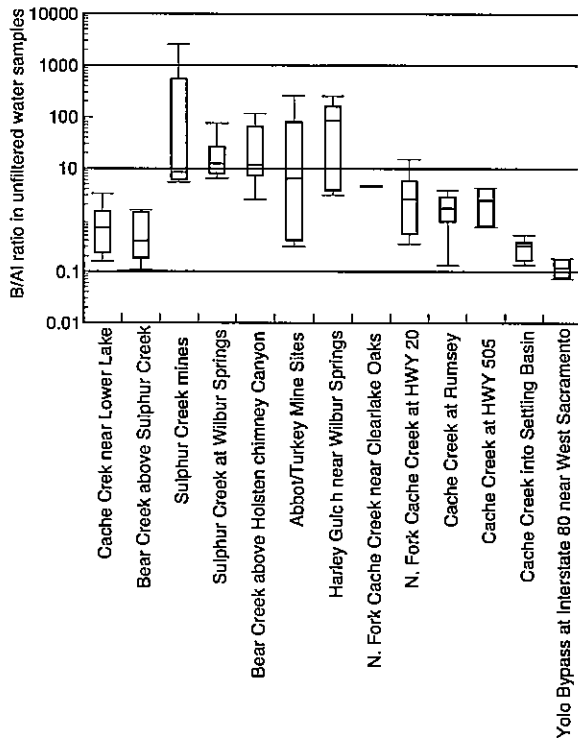


Fig. 9. Boron to aluminum mass ratios at selected sites of the Cache Creek Basin and Yolo Bypass.

Creek basin. Therefore, it was reasoned that normalizing the element concentrations in whole-water samples to that of aluminum might provide useful chemical signatures.

Boron concentrations were found to differ among various locations throughout the Cache Creek Basin. A plot of the ratios of boron to aluminum (B/Al) for mining and other sites within the Cache Creek Basin is shown in Fig. 9. Many of the mining and geothermal sites, such as those of the Abbott and Turkey Run mines, the Sulphur Creek mines, sites that are downstream of mines, such as Harley Gulch, and sites downstream of geothermal streams, such as Sulphur Creek, generally have higher B/Al ratios relative to other non-mining or non-geothermal sites. The outflow from Clear Lake (Cache Creek at Lower Lake) and the Upper Bear Creek (Bear Creek above Sulphur Creek) has relatively low B/Al ratios. The median values of the B/Al ratio for the

outflow from Clear Lake and the Upper Bear Creek did not differ statistically, according to the Mann–Whitney non-parametric test. The upper Bear Creek and the lower Bear Creek (Bear Creek above Holsten Chimney Canyon) sites are different ($P=0.0001$) by the same statistical test. Water from Sulphur Creek probably has the greatest impact on the B/Al ratio at the Bear Creek above Holsten Chimney Canyon site. The B/Al ratio for the Bear Creek above Holsten Chimney Canyon and the Sulphur Creek at Wilbur Springs site are similar and well above that of the Bear Creek above Sulphur Creek site.

The B/Al ratios for Sulphur Creek, the Sulphur Creek mines, Bear Creek above Holsten Chimney Canyon, Harley Gulch near Wilbur Springs, and the Abbott–Turkey mine sites were statistically similar ($P>0.05$). The B/Al ratio of Indian Valley Reservoir was higher than that of Clear Lake and that had an influence on the chemistry of the Cache Creek. Although relatively few water samples were collected at the outlet of Indian Valley Reservoir (North Fork Cache Creek near Clearlake Oaks), the B/Al ratio appeared to be higher than that of Clear Lake, and this higher ratio probably affected the chemistry of the downstream site of Cache Creek at Rumsey. The B/Al ratios were similar at the Cache Creek sites near Highway 505 and Rumsey, but the ratio at the Cache Creek Settling Basin was much lower and similar to that at Clear Lake. Therefore, the mine and geothermal chemical signature of boron to aluminum was distinctive in the upper part of the watershed, but was lost before Cache Creek discharges into the Yolo Bypass.

Although the B/Al ratio in water is similar at the geothermal and mining sites, boron and lithium might co-vary, and the concentrations of both boron and lithium might be highest in geothermal water (Goff et al., 1993a,b). A plot of boron and lithium concentrations in water from the study sites is shown in Fig. 10. There is a very good relation between these two elements and the regression coefficient (r^2) for all sites was 0.99. As expected, the concentrations of boron and lithium were highest in water from the Sulphur Creek at Wilbur Springs and nearby Sulphur Creek mine sites. There was considerable overlap in

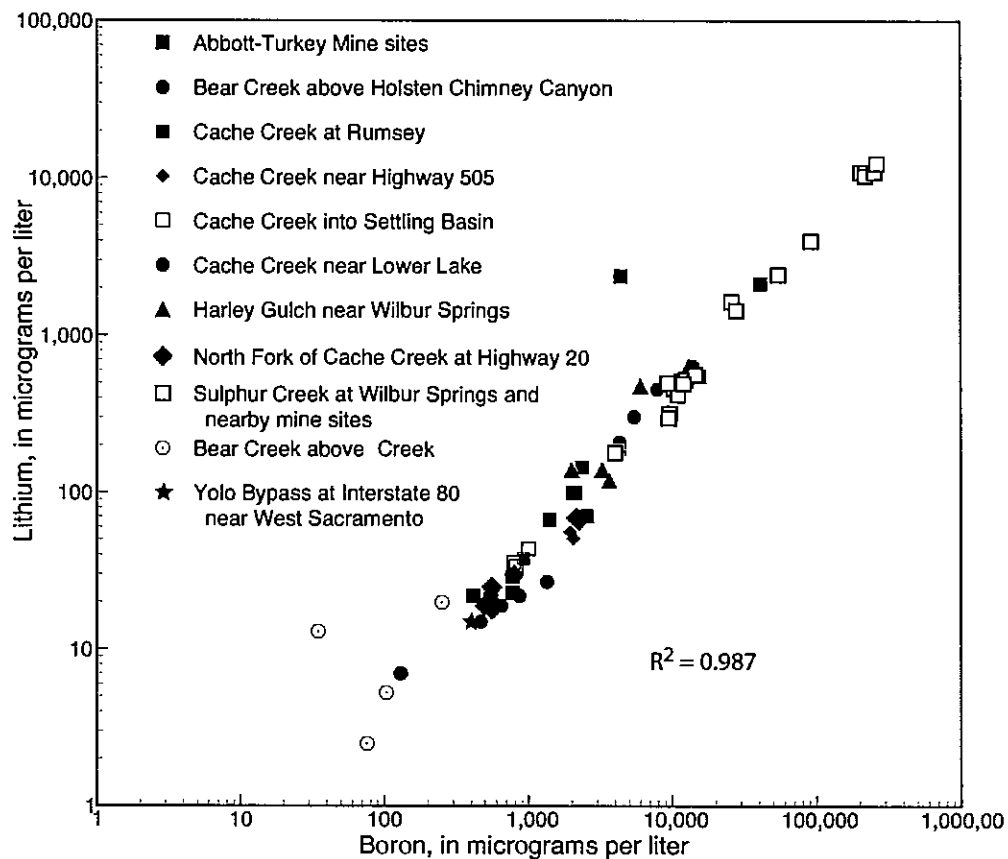


Fig. 10. Plot of boron and lithium concentrations at selected sites within the Cache Creek watershed.

ranges of concentrations between Sulphur Creek and waters from Abbott and Turkey Run Mine and Harley Gulch. Because of the discharge of Sulphur Creek into Bear Creek, the boron and lithium concentrations of Bear Creek above Holsten Chimney Canyon water samples partially overlapped with those of Sulphur Creek or Sulphur Creek mine samples. The boron and lithium concentrations of water from Bear Creek upstream of its confluence with Sulphur Creek, which is above the mining and geothermal influence, were the lowest of all samples. As with the Cl/SO_4 ratio, the concentrations of boron and lithium tend to be low in water from Clear Lake and Indian Valley Reservoir, which partially dilute the concentrations from mine waste or geothermal water in Cache Creek. Boron and lithium were elevated at the

Cache Creek at Rumsey, relative to the concentrations in either Clear Lake outflow or the North Fork of Cache Creek, but it is unclear whether the source is from geothermal or the mine sites. Similar relations were found for boron and chloride (Donnelly-Nolan et al., 1993; Goff et al., 1993a,b).

The relation among boron, chloride and sulfate is also shown with a ternary plot (Fig. 11). In this plot, the relative amounts are shown on a molar basis. A mixing relation of Sulphur Creek water, Bear Creek at Holsten Chimney Canyon, and in some cases, the Cache Creek at Rumsey, and the Cache Creek near Highway 505, is apparent from the plot. The water of the Cache Creek at Rumsey had a similar chemistry to that of Sulphur and Bear Creeks, as seen by the ratio of chloride to sulfate in water, when the outflows from the Indian

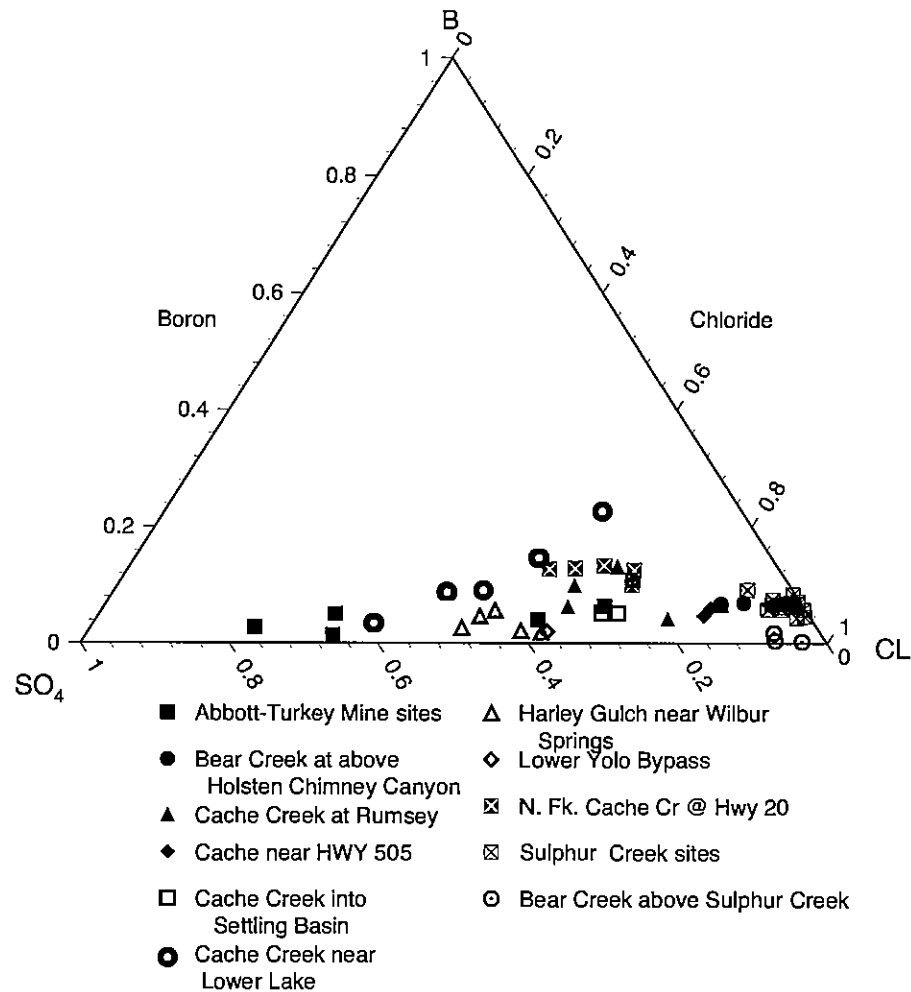


Fig. 11. Ternary plot of boron, chloride and sulfate for selected sites within the Cache Creek watershed.

Valley Reservoir and Clear Lake were low. That happens in the fall, after the irrigation season and before the rainfall/runoff season. At other times of the year, the water of the Cache Creek at Rumsey is more similar to that of either Indian Valley Reservoir, or Clear Lake. The water at Cache Creek had a lower relative amount of boron, or higher chloride and sulfate, relative to that of the Indian Valley Reservoir or Clear Lake. The Abbott–Turkey Run mine and Harley Gulch water samples plot along a range of chloride and sulfate levels. It is not possible to distinguish any mixing trend of the Abbott–Turkey Run Mine and Harley

Gulch waters with downstream sites, such as the Cache Creek at Rumsey.

Another useful signature is the stable isotopic composition of water. Hydrogen and oxygen isotope ratios were measured in samples collected from most of the sites of the present study (Fig. 12). Stable isotope signatures of the geothermal waters have also been previously reported (Goff et al., 1993a,b). Many of the water samples collected during this study had isotopic distributions that plot away from the global meteoric water line, which is based on worldwide stable isotope patterns ($\delta^{18}\text{O}$ and δD) in rainfall. Stable isotope

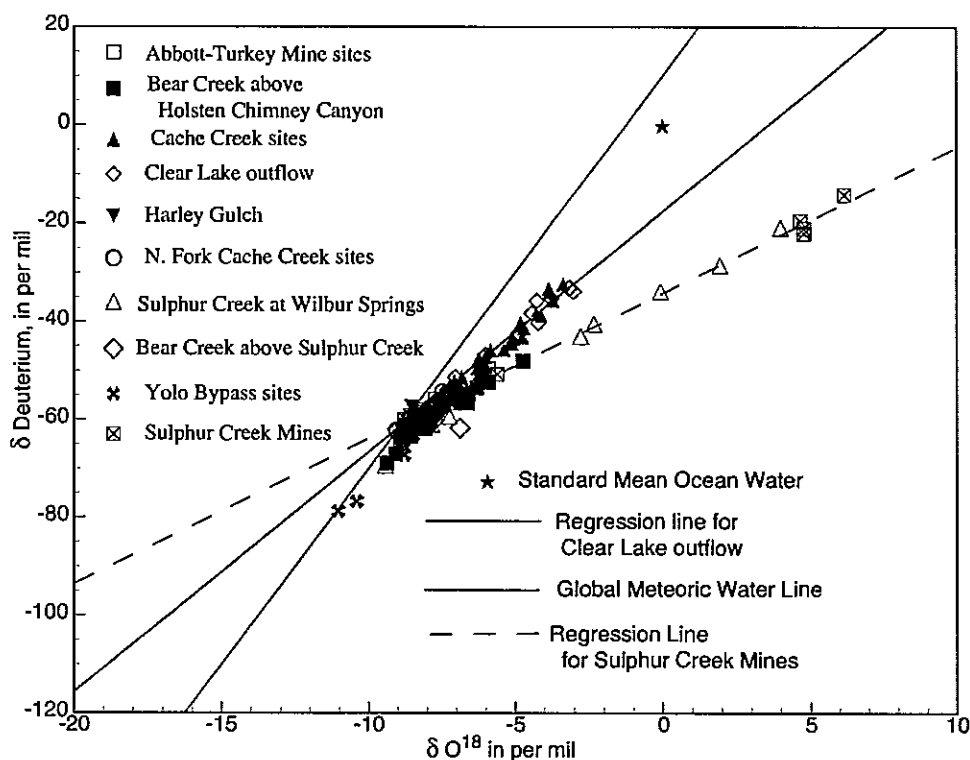


Fig. 12. Plot of stable isotopes (δ deuterium and $\delta^{18}\text{O}$) for selected sites within the Cache Creek watershed.

ratios of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ in rain become progressively smaller as air masses leave the ocean and move inland and towards the poles. By definition, ocean water has values of $\delta^{18}\text{O}$ and δD equal to 0.0. Water that plots away from the global meteoric water line usually indicates some type of isotopic fractionation such as may occur during evaporation or certain types of water–rock interactions (Drever, 1982).

The waters from the Sulphur Creek and the Sulphur Creek mines had the greatest deviation from the global meteoric water line. The samples from the Sulphur Creek mine sites were most enriched in ^{18}O . The samples from the Bear Creek above Holsten Chimney Canyon plotted along a mixing line from the Sulphur Creek waters. The large deviation from the global meteoric water line was a unique geochemical signature for the waters of this study. In contrast, the waters from the Abbott–Turkey Run mines and those from Harley

Gulch were more depleted in ^{18}O and plotted closer to the global meteoric water line. The runoff from the Abbott–Turkey Run mines and the water in Harley Gulch are generally not affected by geothermal discharge, and therefore their isotopic distribution is more typical of rain.

A second prominent feature of the isotope plot shown in Fig. 12 is the regression line for the Clear Lake outflow. The isotopic signature from that site was similar to those for Cache Creek at Rumsey, Cache Creek near Highway 505, and the Cache Creek Settling Basin. The Clear Lake mixing line is indicative of the isotopic composition of Clear Lake water, which resulted from the long-term evolution of lake water caused by evaporation and local geothermal input over geologic time. The water that is most depleted in the heavier isotopes is that of the Yolo Bypass. That water plots on or just below the global meteoric line. Much of the water in the Bypass was from the

Sacramento River, which is depleted in the heavier isotopes, and also plots on the global meteoric water line (Domagalski et al., 2001). Therefore, the isotopic patterns of the geothermal waters are very distinct in the small streams in the upper part of the Cache Creek Basin, but the signature of Clear Lake water dominates at locations on Cache Creek downstream of the mining and geothermal sites.

Plots of chemical constituents and stable isotopes of water molecules can be used to show mixing relations and to evaluate whether or not constituent transport is conservative. Plots of lithium vs. $\delta^{18}\text{O}$, and total mercury vs. $\delta^{18}\text{O}$ are shown in Fig. 13, for sites along a flow path from Sulphur Creek through Bear Creek. The water samples from Sulphur Creek with the highest enrichment in the heavier isotope of oxygen were the result of mine drainage or a higher percentage of geothermal discharge into Sulphur Creek. Elevated concentrations of both lithium and mercury in Sulphur Creek water plotted across a range of oxygen isotope signature. Dissolved lithium shows a continuous mixing line from the Sulphur Creek mines to the Sulphur Creek near Wilbur Springs waters, for the samples that are most enriched in ^{18}O ($\delta^{18}\text{O} > -2$). In contrast, for mercury, there is no suggestion of a continuous mixing line from the Sulphur Creek mines to the water of Sulphur Creek near Wilbur Springs. Mercury in the mine waters probably sorbs to sediment particles and precipitates to the streambed. Lithium is probably transported more or less conservatively in these waters because it is dissolved, and does not precipitate as a mineral along this flow path or become absorbed to other sediment particles. This non-conservative transport of mercury limits our abilities to trace mercury deposited in downstream areas to source areas using geochemical or isotopic tracers.

4. Summary and conclusions

A 17-month study of mercury and methylmercury concentrations and loads was completed in the Cache Creek watershed. Tributaries to Cache Creek located downstream of abandoned mercury mines and in proximity of geothermal discharges

were sampled for mercury and methylmercury and other aqueous constituents. Other major tributaries to Cache Creek and Cache Creek itself were also sampled in several locations, as was the Yolo Bypass, which receives water from Cache Creek and the Sacramento River during flood conditions. The study period was one of relatively low stream discharge in this watershed compared with historical records, because of relatively low rainfall. Consequently, observed loads of mercury and methylmercury were probably less than that occur during years of normal or above-normal precipitation. Geothermal springs were the source of the highest loads of mercury during this study. This was attributed to the lower than normal rainfall, which failed to produce large run-off events capable of eroding mine wastes. The largest instantaneous loads of mercury and methylmercury occurred in the winter months in response to rainfall-induced runoff. Loads of mercury and methylmercury were generally low in the summer months because of low stream discharge. Release of water from either Clear Lake or Indian Valley Reservoir, for the purpose of either flood control or to supply irrigation water to downstream farms, may also increase the loads of mercury and methylmercury by re-suspension of previously deposited streambed sediment containing elevated amounts of mercury or methylmercury. Although the loads of mercury and methylmercury can be low during the dry season, concentrations can be elevated at other times of the year. This was particularly true for methylmercury, which tends to have elevated concentrations in April–May, July–August, and January.

Water from the geothermal and mining locations had relatively unique geochemical signatures, especially for stable isotopes of water and other aqueous constituents such as boron, chloride, sulfate and lithium. The ratio of chloride to sulfate in water samples from Cache Creek at Rumsey shows strong seasonal variations that can be attributed to different sources of water in the watershed. The aqueous constituents are also useful as tracers for geothermal sources of water and for evaluation of the extent to which mercury is transported conservatively. Concentrations of lithium, a conservatively transported ion, correlate well with

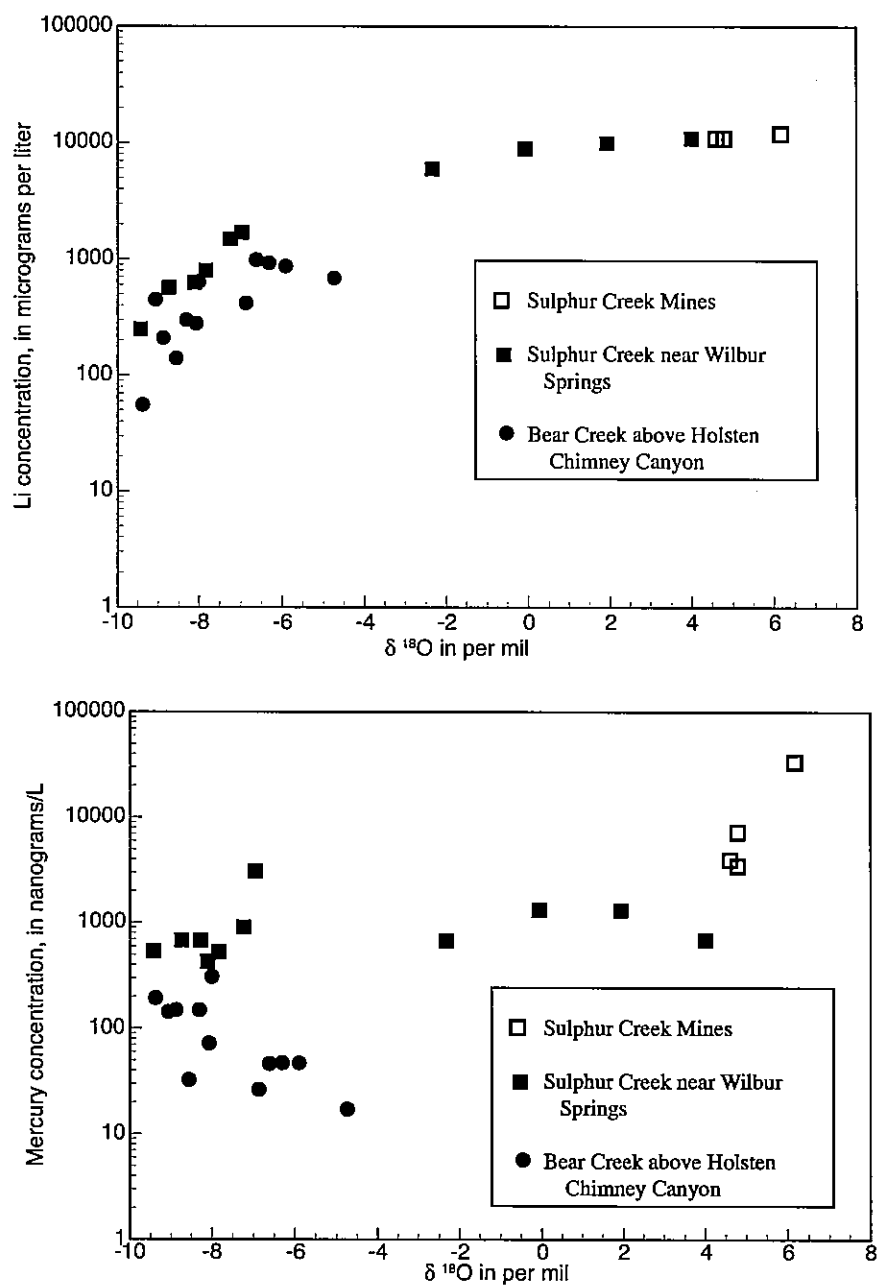


Fig. 13. Plots of lithium and total mercury vs. $\delta^{18}\text{O}$ for selected sites within the Cache Creek watershed.

oxygen isotopes along a mixing and dilution flow path from Sulphur Creek through Bear Creek, indicating that all of these constituents are transported conservatively. In contrast, total mercury

does not correlate well with oxygen isotopes or the other aqueous constituents, indicating that mercury transport is non-conservative. It is hypothesized that dissolved mercury from the geothermal

sources is largely adsorbed onto fine-grained sediments in Sulphur Creek and lower Bear Creek, or further downstream in Cache Creek. Mercury transport in the tributaries dominated by geothermal sources is highly episodic, with much of transport related to the re-suspension of previously deposited sediment. Mercury transport in tributaries dominated by mining sources such as Harley Gulch is also related to sediment transport mechanisms, as the main form of mercury is hypothesized to be particles of mercury sulfide (cinnabar and metacinnabar).

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