SUBTASK 5A: SOURCE BIOAVAILABILITY AND MINE REMEDIATION FEASIBILITY IN THE CACHE CREEK WATERSHED

Thomas H. Suchanek[a,b], Darell G. Slotton[c], and Douglas C. Nelson[d,b], Shaun M. Ayers[c], Chance MacDonald[d], Ron Weyand[c], Anne Liston[c], Brian Cohn[a,b], Ken McElroy[a,b], Peggie King[a,b]

[a] Department of Wildlife, Fish and Conservation Biology
[b] U.C. Davis - Clear Lake Environmental Research Center
[c] Department of Environmental Science and Policy
[d] Section of Microbiology, Division of Biological Sciences

University of California, One Shields Ave., Davis, CA 95616

The major goals of this project are (1) to identify mercury (Hg) minerals and precipitate-associations from upstream mining regions 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.

Summary of Task Objectives

• 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 is being accomplished via laboratory experiments (see below for methods).

• Using selected mining-related and natural inorganic Hg source materials from the mining regions above Cache Creek, evaluate these source materials as potential substrates for elevated Hg methylation in downstream Sacramento-San Joaquin Delta sediments.

Summary of Hypotheses

• Abandoned mining (primarily mercury and/or gold mine) sites contribute significant inorganic 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.

Approaches / Methods

Collaborations/Integration:
Task 5A is being conducted in close coordination with:
(1) R. Churchill *et al*. (CA Div. Mines & Geology - Task 5C1, 2) 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 sediments from the Sacramento-San Joaquin Delta to simulate 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:
Figure 1 shows the location of the mining regions in relation to the Upper Cache Creek Watershed Region. The primary sites where intensive investigations are ongoing are:
(1) Sulphur Bank Mercury Mine at Clear Lake [feeds directly into Cache Creek];
(2) Abbott/Turkey Run Mercury Mine Complex [feeds through Harley Gulch into Cache Creek];
(3) Sulfur Creek Mining Complex (mercury and gold mines) [feeds through Sulfur Creek and Bear Creek into Cache Creek].

Figure 2 gives a more detailed view of the landscape topography in the region of the two mining site regions under consideration for possible remediation.

Figures 3a and 3b provide more detailed relationships between the location of each mine and small tributaries and geothermal springs for the Harley Gulch and Sulfur Creek region respectively.

Quantifying Hg Loading:
Water samples are collected from key tributary locations where previous mining activities were documented and from natural geothermal spring inputs to tributaries that flow into Cache Creek. It is anticipated that the greatest transport of particulate material containing Hg-laden particles from the mining sites occurs during winter storm runoff. Thus, samples are collected during high flow periods that maximize the probability of quantifying maximum loading. Figures 4a and 4b show hydrographs for the USGS Sulfur Creek and Harley Gulch gauging stations for calendar year 2000, indicating that the annual storm samples were collected from Harley Gulch and Sulfur Creek mining regions during peak flow regimes. Additional sampling of integrated export flows from these two primary potential remedial zones is conducted during a range of flow conditions as part of Task 5B. These data, when combined with aqueous Hg concentrations sampled during winter (maximal erosional period) and summer (minimal erosional period) will provide an upper and lower bound, respectively, to the range of loading values predicted from these specific mining zones. At each site water is collected (using standard ultra-clean techniques) 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) are analyzed on all samples. At a selected subset of these sites additional samples are collected for USGS analysis, for both unfiltered and filtered (0.45 µm pore size) water, of (an extensive suite of cations/anions and metals potentially useful in linking loading to specific sources).At each site ancillary data on temperature, pH, conductivity, specific conductivity, oxidation/reduction potential and oxygen concentration is also collected using a YSI 6000 multiprobe meter.

Water samples are shipped overnight FedEx and analyzed for Hg by Battelle Marine Sciences Laboratory, Sequim, WA and for sulfate and TSS by Columbia Analytical (Kelso, WA). Stream flow rates are measured directly by USGS gauging stations at the Clear Lake dam outflow, on Harley Gulch (Abbott/Turkey Run Mining Region) and Sulfur Creek (Sulfur Creek Mining Region). At all sites, including the gauged sites, we also calculate independent field estimates of flow to compare with the automated gauges and to estimate flow and loading from each specific mine sub-site or sub-watershed.

Hg Methylation from In-Situ Sediments: (Core-Tube Microcosm Experiments)

These laboratory trials are being conducted under the direction of Professor Doug Nelson, Microbiology, UC Davis. Earlier comparable experiments have been conducted at Clear Lake, indicating significant differences in sediment methyl Hg production between different regions within the lake. Results obtained for the methylation of Sulfur Creek Hg source materials will be compared with those obtained from Clear Lake. The first experiment that was conducted for this CALFED project utilized Hg-rich flocculent material from Sulfur Creek, immediately below the input from a geothermal spring with extremely high total Hg concentrations (> 24,000 ng/L unfiltered total Hg and > 8,500 ng/L filtered total Hg). Hg source material is collected in teflon core tubes from the site. Each core tube is plugged with a rubber stopper on the bottom (beneath the sediment/floc) and one on the top (Figure 5). The test material (in this case floc from Sulfur Creek) 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 and analyzed for methyl Hg concentrations. Cumulative methyl Hg production and production rates for each treatment and time interval were quantified.

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

The focus of these laboratory trials (intended for summer 2001) is to differentiate the relative potential of selected mine-derived, inorganic Hg source materials to produce toxic methyl Hg. Based on data compiled by our group and the mining geology team (Task 5C1), representative samples of relatively homogeneous, erodeable materials are being collected for additional Hg analysis and laboratory trials. Our current plan is for these upstream mine-derived source materials to be added to downstream sediments from the Sacramento-San Joaquin Delta and/or Yolo Bypass, 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 is key to this work, we have chosen a slurry experimental design, as opposed to more natural intact core approaches, and will be analyzing the homogeneous slurry mixture over time for methyl Hg production. The intent for these trials is 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 lower Cache Creek region. Currently the plan for this experiment will involve Source and Receiving sediments. Below are listed some of the potential source and receiving materials that might be used.

Potential Source Sediments:
1) Abbott Mine tailings pile fine grained sieved particulate material from the main waste pile.
2) Floc precipitate material from below geothermal spring on Sulfur Creek
3) possible local soils that are expected to erode during large winter storm events
4) soils from the Turkey Run mining site which likely become transported into Harley Gulch
5) Sulfur Creek stream bed sediments
6) soils from the bottom of pools in Harley Gulch

Potential Receiving Sediments:
1) Yolo Bypass sediments
2) sediments from the Cache Creek Settling Basin
3) Cache Creek sediments near Capay
4) sediments from Bear Creek above Sulfur Creek confluence
5) sediments from Bear Creek below Sulfur Creek confluence
6) sediments from the North Fork of Cache Creek

The design of these laboratory trials are under development at this time and will be discussed with the Scientific Review Committee before any final decisions are made on the specific protocols to be used during the summer of 2001.

Discussion of Progress To Date / Results / Preliminary Conclusions

Loading and Site-Specific Variability:

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 8 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 months. Hg loading estimates from the Clear Lake dam outlet are being conducted in Task 5B.

At the other mine sites (e.g. Harley Gulch and Sulfur Creek mines), inorganic particulate Hg loading occurs during winter storm seasons. Inorganic Hg export from the Turkey Run/Abbott mine complex clearly derive from the large tailings piles at Abbott Mine, with a large, hot geothermal spring at the Turkey Run Mine having extremely low concentrations of Hg. Water samples were collected in February 2000 and February 2001.

Data from the Harley Gulch mining region (Abbott/Turkey Run Mines) from February 2000 are presented in Figure 6 and Table 1. Hg concentrations are typically quite elevated (1,000-2,000 ng/L = parts per trillion) in most of the 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. An exceptionally high Hg concentration (ca. 6,400 ng/L) was recorded in water from the Turkey Run Mine run-off (ATM-704), and an exceptionally low concentration of Hg was recorded from the geothermal spring at the Turkey Run Mine (ATM-709). These values compare with water from Clear Lake, under the influence of the Sulphur Bank Mercury Mine, which average about 1-2 ng/L total (unfiltered) Hg concentrations. Nearly all Hg (typically > 95%) from terrestrial mine run-off was in particulate form. However, 61% of the Hg in the Turkey Run geothermal spring was in dissolved form. The single, integrated export 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. Calculations of total Hg loading were derived from daily flow rates (provided by a USGS gauging station on Harley Gulch) and Hg concentrations from each of the individual sub-sites from the Harley Gulch Mining Region. Figure 7 provides an example of an estimated and projected 'upper bound' on monthly minimum, maximum and mean total Hg loading from the Harley Gulch Mining Region that can be produced from these data. This dataset indicates that the greatest Hg loading occurs in January through March. These 'upper bound' values reflect the assumed maximal erosional mobilization of particulate and/or dissolved Hg derived from upstream mining sources. The minimum, maximum and mean estimates are based on the corresponding minimum, maximum and mean daily flow data from the USGS gauging station at Harley Gulch. Figure 8 provides a comparable cumulative 'upper bound' estimate of minimum, maximum and mean annual total Hg loading from this region (based on minimum, maximum and mean monthly flow data) with estimates ranging from 0.1-35 kg/yr. Nearly all of this loading is believed to be derived from mining wastes. NOTE: these very preliminary data must be interpreted in the context of a single sampling date during a single year. There are other time periods when erosion of Hg-laden surface particles may be eroded, or when dissolved Hg may be transported into streams, at both a lesser and a greater rate. Periods of lower loading could be experienced during comparable flows, but later in the season when most of the initially mobile materials were already stripped from the soil surface. Periods of higher loading might occur during the first flush of the season, or during larger storm events either in the same year or during different years. In fact, it is quite possible that the majority of Hg loading occurs during catastrophic storm events, which were not sampled in this study.

Sulfur Creek mining region Hg data from February 2000 are presented in Figure 9 and Table 1. Here, several sites exhibited elevated (1,000-2,500 ng/L) Hg concentrations. The particulate fraction of aqueous Hg was typically lower (at 35-85%) than at the Harley Gulch sites. Even water above the primary Sulfur Creek mining region, with only the upstream Elgin Hg Mine influence, had 340 ng/L Hg. The three most elevated samples were (1) a sulfurous creek with likely geothermal spring origin above the Cherry Hill Gold Mine (1,110 ng/L), (2) the run-off tributary from the Wide Awake Hg Mine (2,450 ng/.L) and (3) the "Jones Fountain of Life" geothermal spring (with significantly elevated total Hg at 24,300 ng/L). The downstream Sulfur Creek Index Station (also sampled in Task 5B), was 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). Figure 10 provides an estimated ‘upper bound’ for monthly minimum, maximum and mean total Hg loading from the Sulfur Creek Mining Region, indicating (and similar to the Harley Gulch system) that the greatest Hg loading occurs in January through March. As above, these ‘upper bound’ values reflect the assumed maximal erosional mobilization of particulate and/or dissolved Hg derived from upstream mining sources. The minimum, maximum and mean estimates are based on the minimum, maximum and mean daily flow data from the USGS gauging station at Sulfur Creek. Figure 11 provides a cumulative ‘upper bound’ estimate of minimum, maximum and mean annual total Hg loading from this region (based on minimum, maximum and mean monthly flow data), with estimates ranging from 0.5-160 kg/yr. This loading is likely derived from a combination of mining wastes and geothermal spring activity.

Hg Methylation from In-Situ Sediments: (Core-Tube Microcosm Experiments)

Preliminary (non-QCed) results for the floc core-tube microcosm experiment indicates that there was non-detectable methyl Hg production from any of the floc treatments (oxic and anoxic) that were incubated over 2.5 days and 5 days. This is in sharp contrast to the results obtained from a comparable experiment conducted on Clear Lake sediments under the influence of the Sulphur Bank Mercury Mine in which a relatively high production of methyl Hg was documented.

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

A preliminary slurry experiment was conducted in January 2001, but the complete data from that experiment have not been fully analyzed yet and we are reevaluating the approach to any further slurry experiments at this time.

Potential for Future Research / Recommended Changes in Existing Research Program

• Flow rate estimates obtained in Feb 2001 will be compared with those from Feb 2000 and comparable loading estimates will be calculated to evaluate inter-annual variability.

• Laboratory trials for methylation potential experiments are still under development.

• Dry season sampling of Hg loading will be conducted during summer 2001 to obtain a ‘lower bound’ for annual loading estimates, and determine whether there are any differences in total Hg versus methyl Hg production/transport during the summer season in comparison with winter values.

Table 1. Cache Creek aqueous Hg concentrations from Mining Region tributaries

MINE SITE WATER COLLECTIONS, February 14, 2000
(Peak runoff conditions)

(underlined values are means of laboratory or field replicates)

Site Code	Site Description	TSS (mg/L = ppm)	flow rates (cfs)	total Hg unfiltered (ng/L = pptr)	total Hg filtered (ng/L = pptr)	percent in filtered fraction	total Hg on particles (µg/g=ppm)	methyl Hg unfiltered (ng/L = pptr)	methyl Hg filtered (ng/L = pptr)	percent in filtered fraction	methyl Hg on particles (µg/g=ppm)
Harley Gulch Mining Region											
530 HAR	Harley Gulch combined flow	111.40		493.00	42.20	8.6%	4.05	0.354	0.298	84.2%	0.503
701 ATM	S. Side (non-mine) trib.	93.60	22.75	135.00	20.50	15.2%	1.22				
702 ATM	Mine-side trib. at confluence	165.70	3.78	2,070.00	128.00	6.2%	11.72				
703 ATM	Mine-side trib. W of Hwy 20	184.80	4.58	1,930.00	85.70	4.4%	9.98				
704 ATM	Turkey Run S Fk: from piles	206.80	0.05	6,350.00	73.70	1.2%	30.35				
705 ATM	Turkey Run N Fk: from spring etc.	28.60	0.15	404.00	43.60	10.8%	12.60				
709 ATM	Turkey Run spring to 705	3.43	0.05	4.32	2.64	61.1%	0.49				
706 ATM	Mine-side trib. above TR Mine input	201.00	2.54	1,650.00	89.20	5.4%	7.77				
707 ATM	Mine-side trib. btw main Abbott piles	361.00	2.94	1,911.00	78.80	4.1%	5.08				
707 ATM	Mine-side trib. btw main Abbott piles-DUP	232.50		1,528.00	84.50	5.5%	6.21				
708 ATM	Mine-side trib. above all main Abbott piles	178.00	2.04	181.00	29.80	16.5%	0.85				
Sulfur Creek Mining Region											
540 SUL	Sulfur Creek combined flow at Index	114.70		974.00	100.00	10.3%	7.62	0.481	0.453	94.2%	0.244
601 SCM	Sulfur Ck above Wilbur Springs	97.70		620.00	83.20	13.4%	5.49				
601 SCM	Sulfur Ck above Wilbur Springs-DUP	99.70		673.00	87.60	13.0%	5.87				
602 SCM	First south side Ck (clean?)	87.00	2.19	229.00	35.80	15.6%	2.22				
603 SCM	"Old Faithful" geyser spring	1.58		24,300.00	8,120.00	33.4%	10,200.00				
604 SCM	Sulfur Ck above "Old Faithful"	82.30		351.00	80.70	23.0%	3.28				
605 SCM	Creek from Wide Awake mine	103.00	1.85	2,450.00	1,420.00	58.0%	10.00				
606 SCM	(Non-mine?) sulfurous creek by Cherry Hill	222.30	0.24	1,110.00	224.00	20.2%	3.99				
607 SCM	Sulfur Ck above 605/606 input	81.30		230.00	64.20	27.9%	2.04				
608 SCM	Sulfur Ck above all mines except Elgin	101.00		340.00	226.00	66.5%	1.13				

Fig. 1. Cache Creek Watershed: Regional View of Mining Site Regions Under Intensive Study Box represents area in Figure 2.

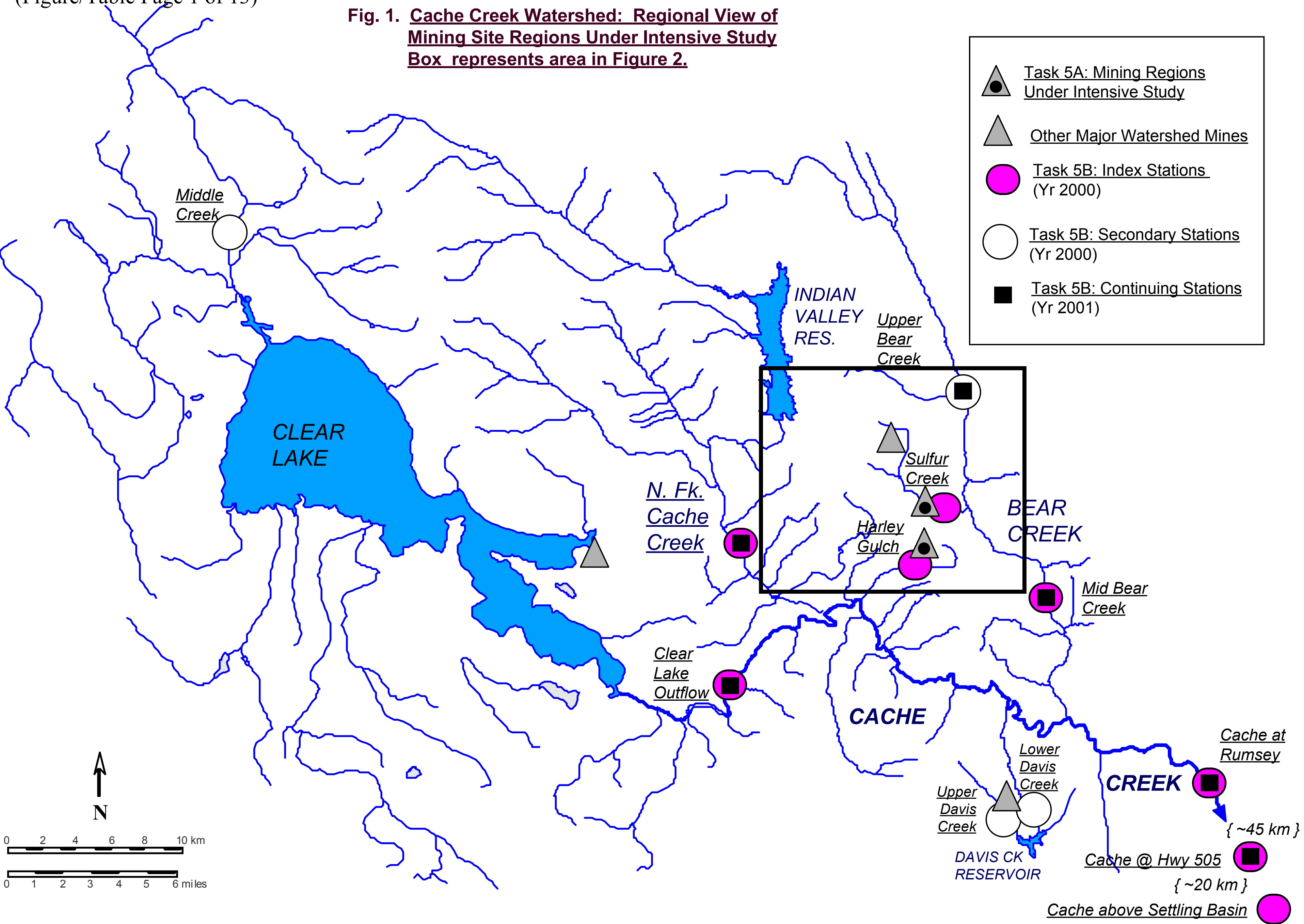

Figure 2: Topographic landscape view of mining regions under intensive study.

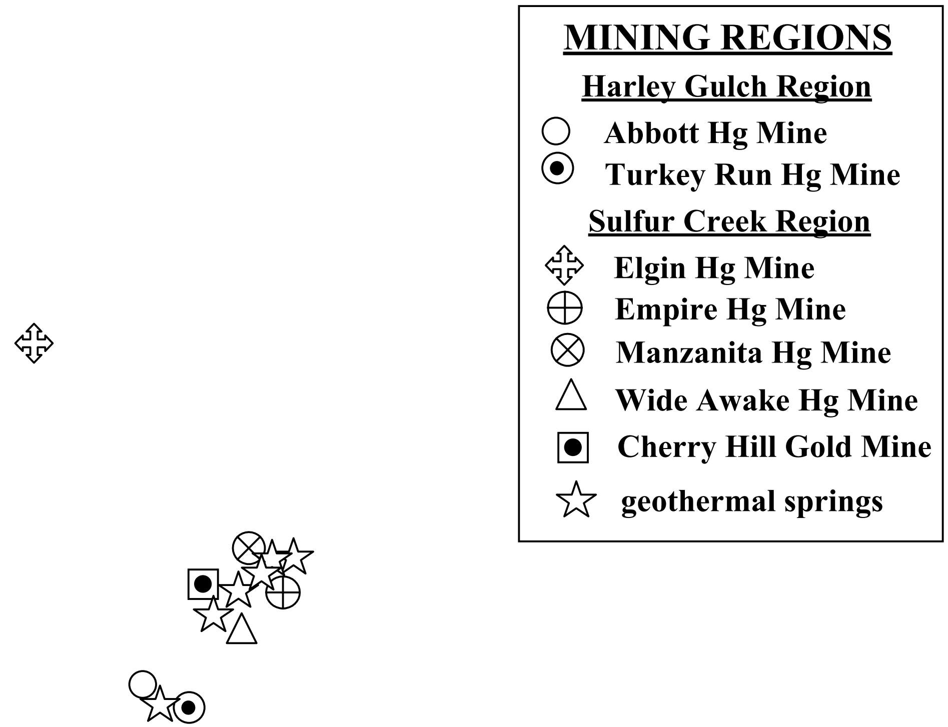

Figure 3a. Local features of the Harley Gulch Mining Region.

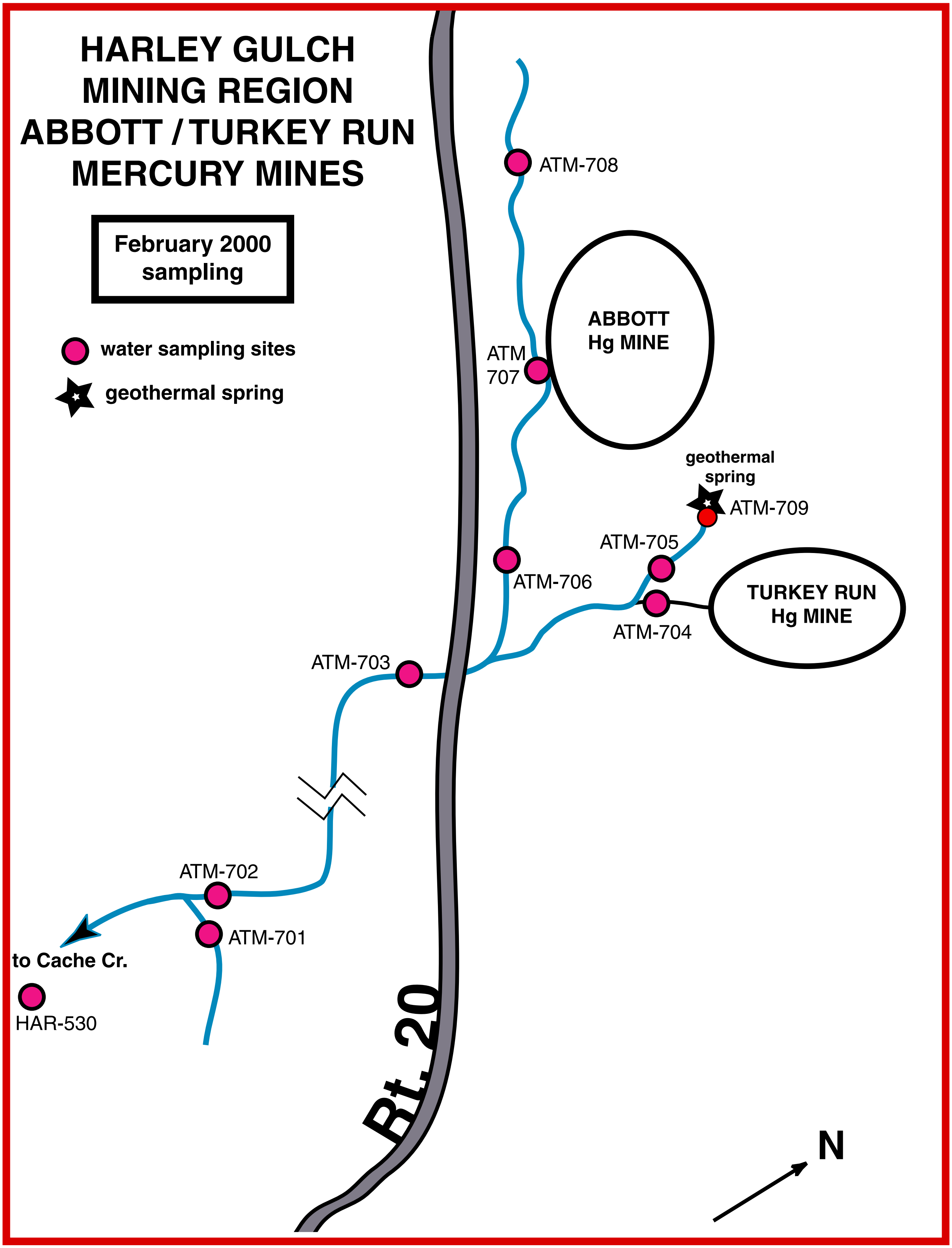

Figure 3b. Local features of the Sulfur Creek Mining Region.

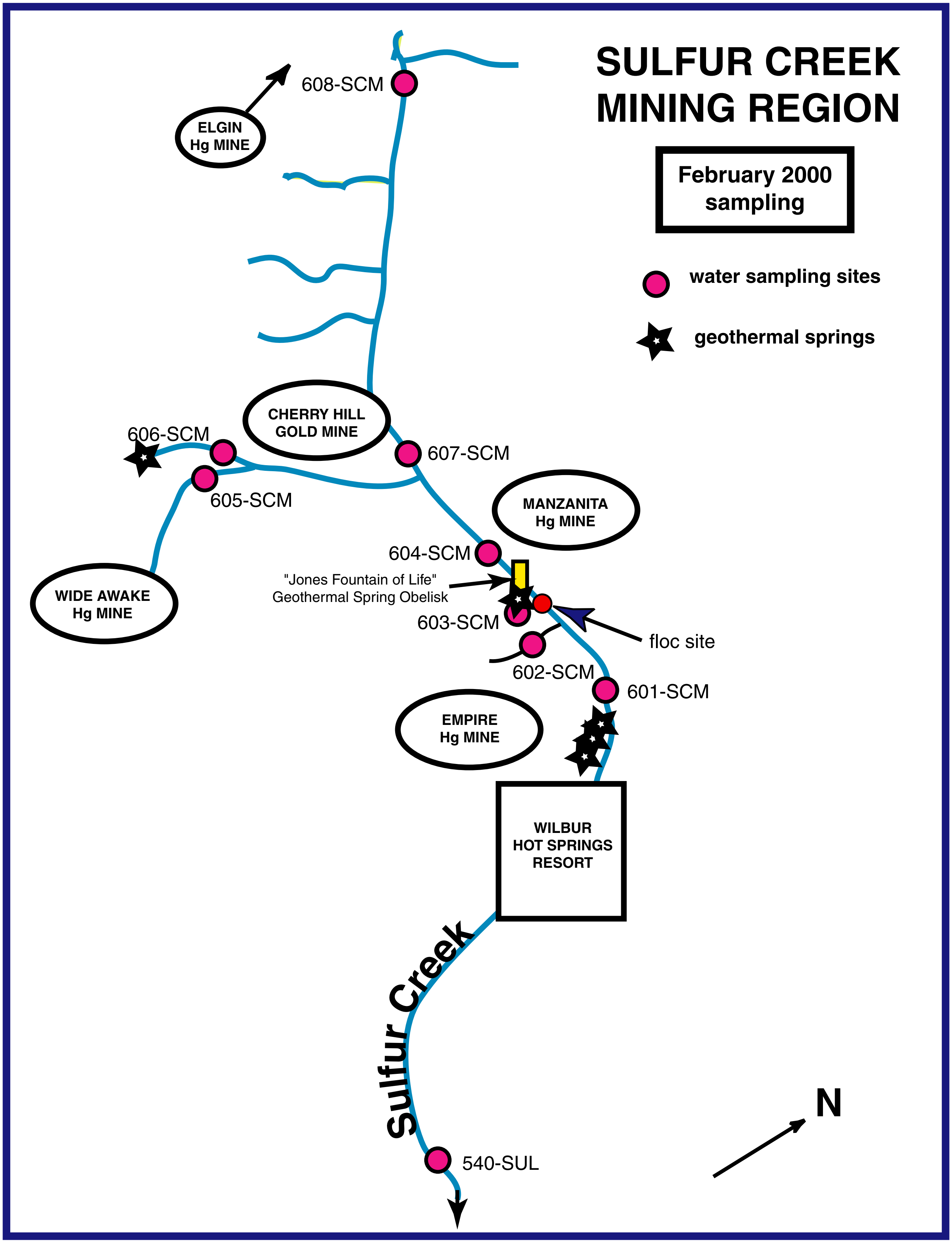

Figure 4a. Stream flow hydrograph for Harley Gulch

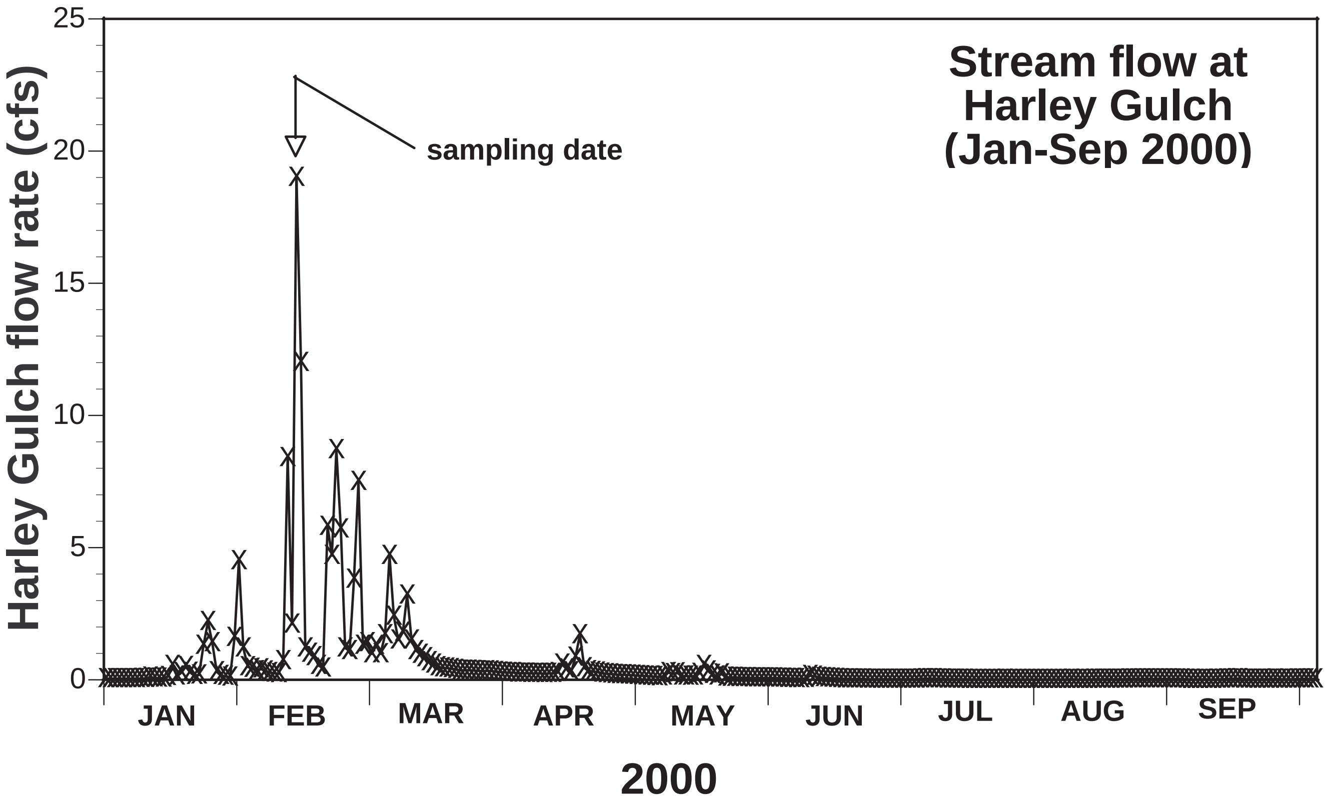

Figure 4b. Stream flow hydrograph for Sulfur Creek

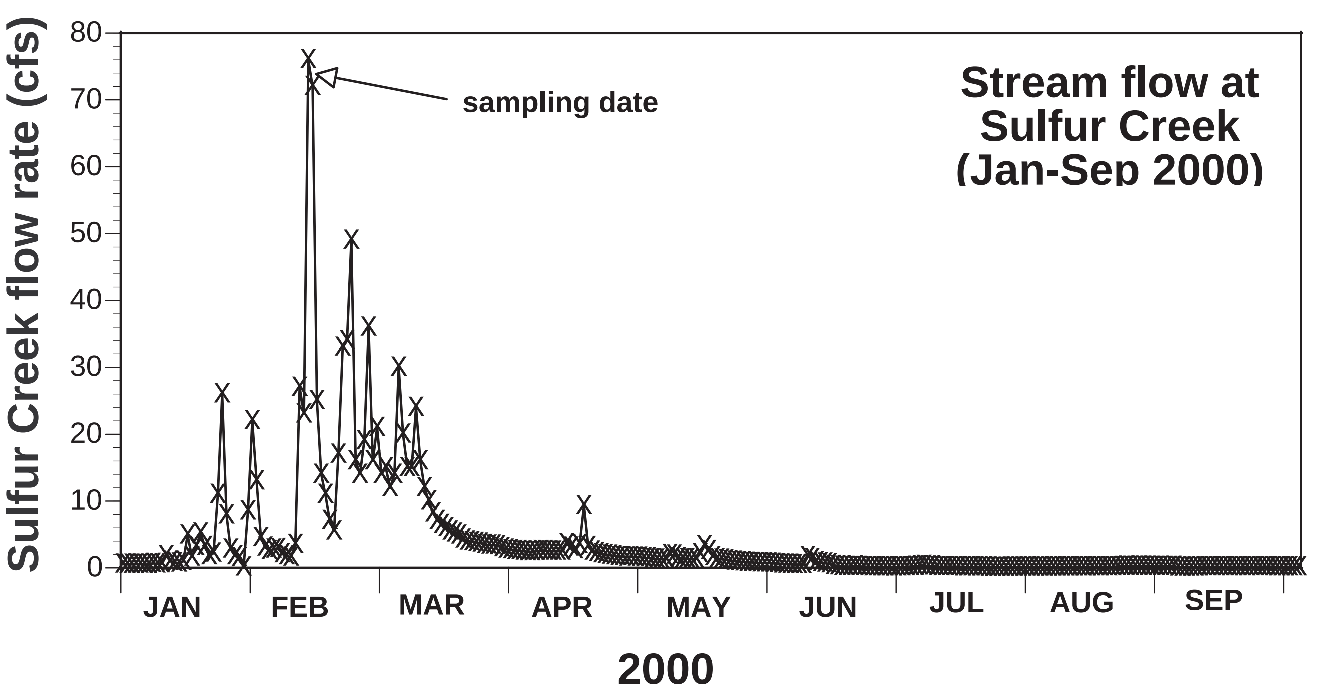

Figure 5. Microcosm laboratory trial core tube design

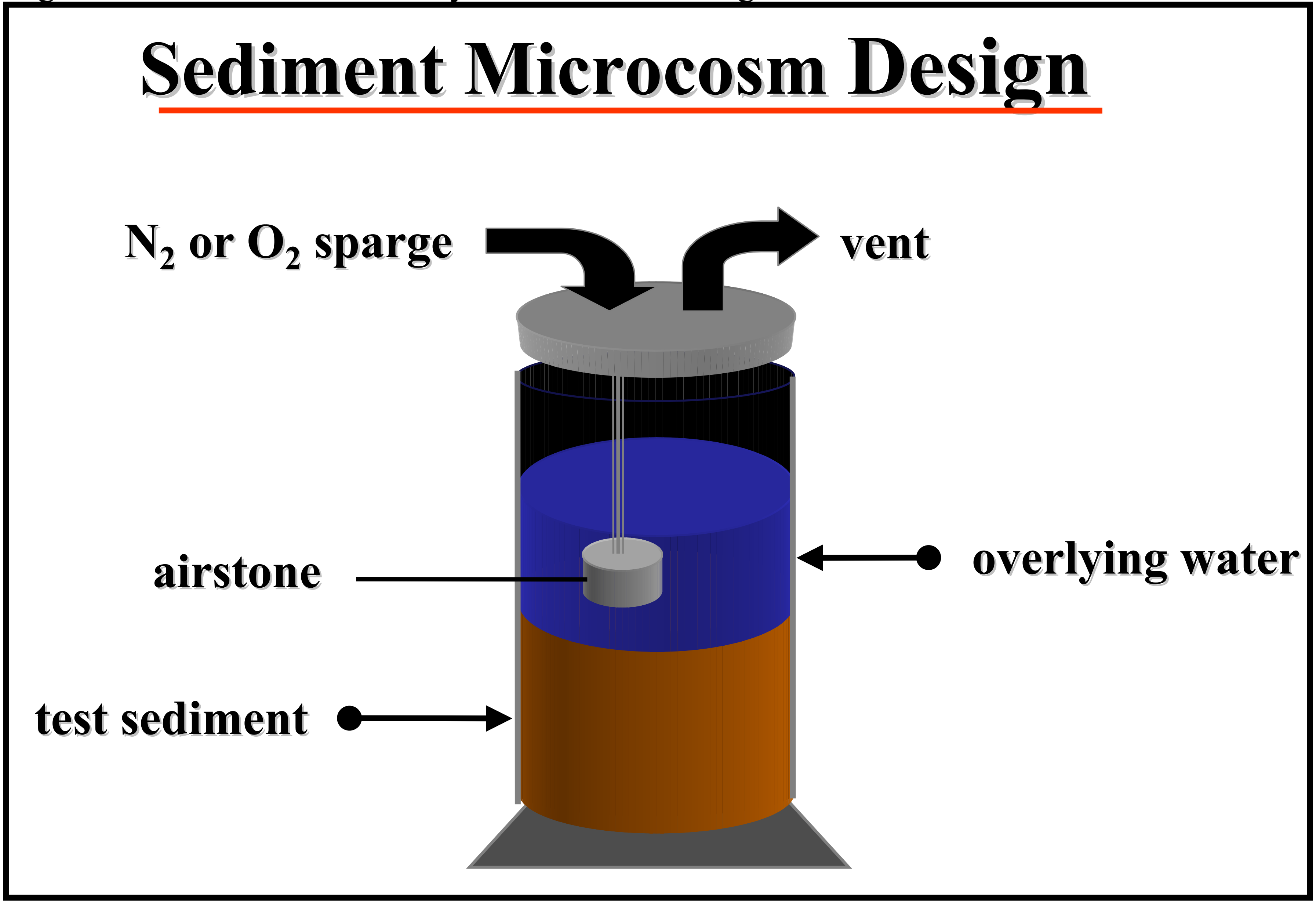

Figure 6. Hg in water from the Harley Gulch Mining Region Sites

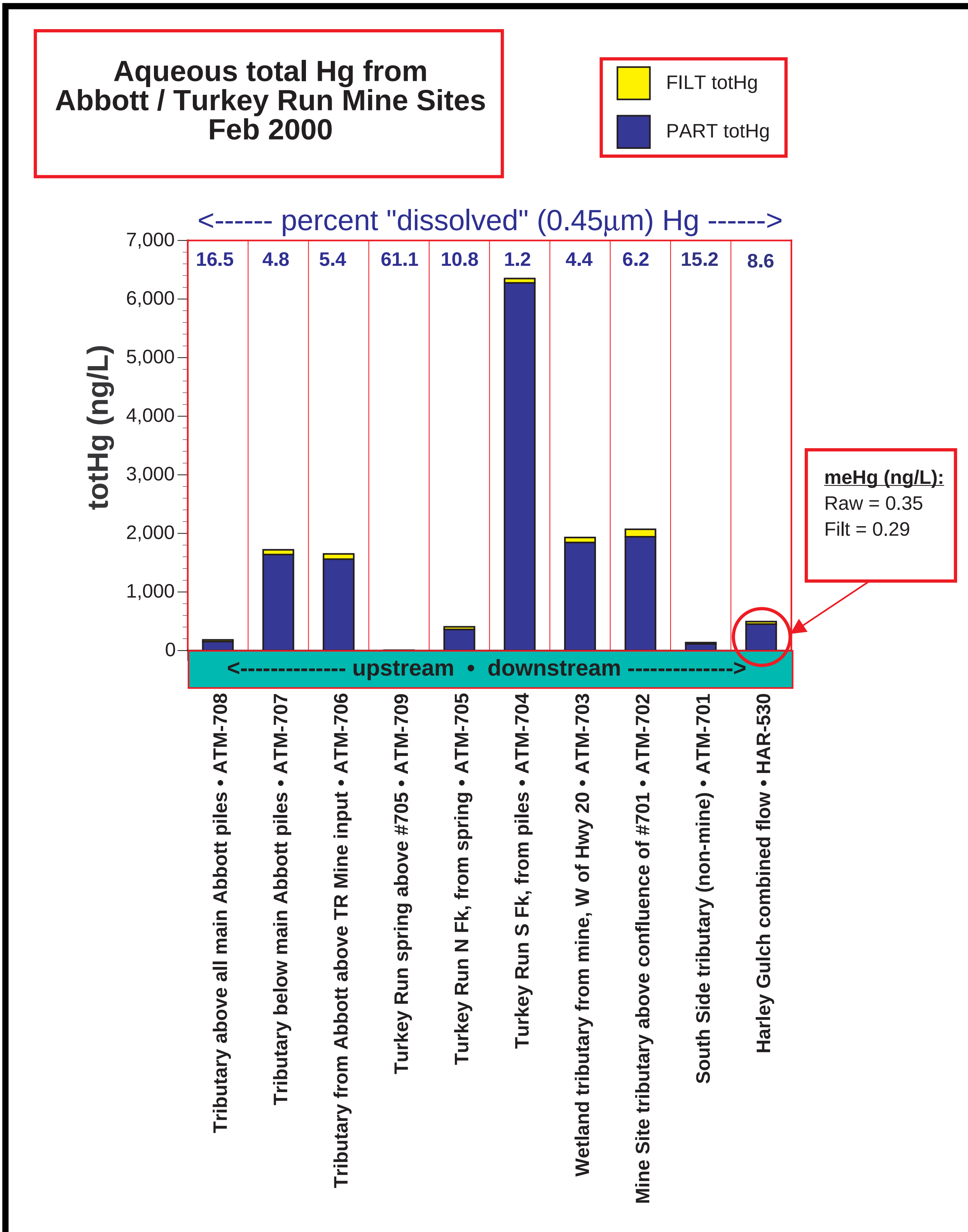

Figure 7. Estimated monthly loading of total Hg (kg/month) from Harley Gulch

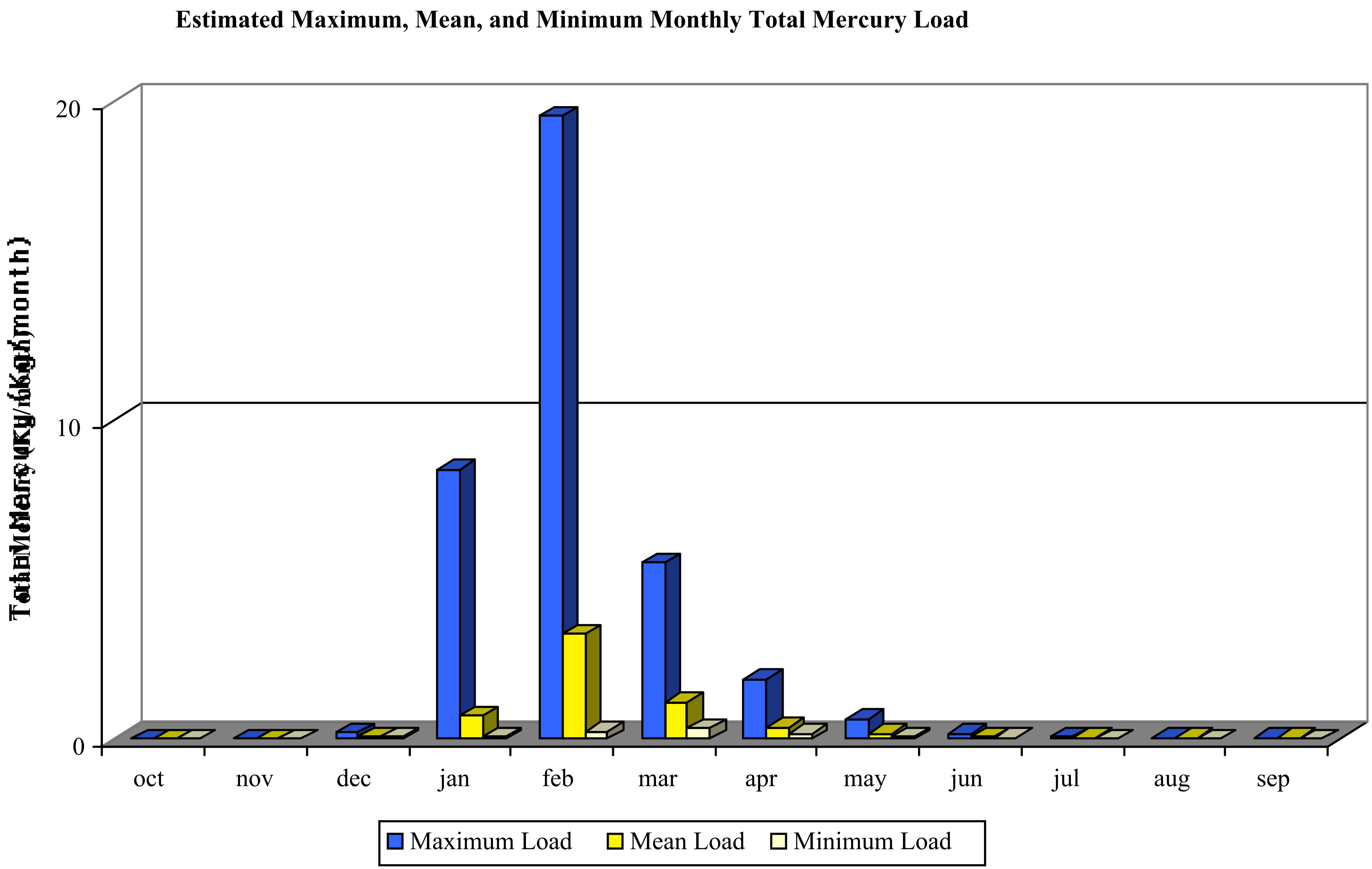

Figure 8. Estimated annual loading of total Hg (kg/yr) from Harley Gulch

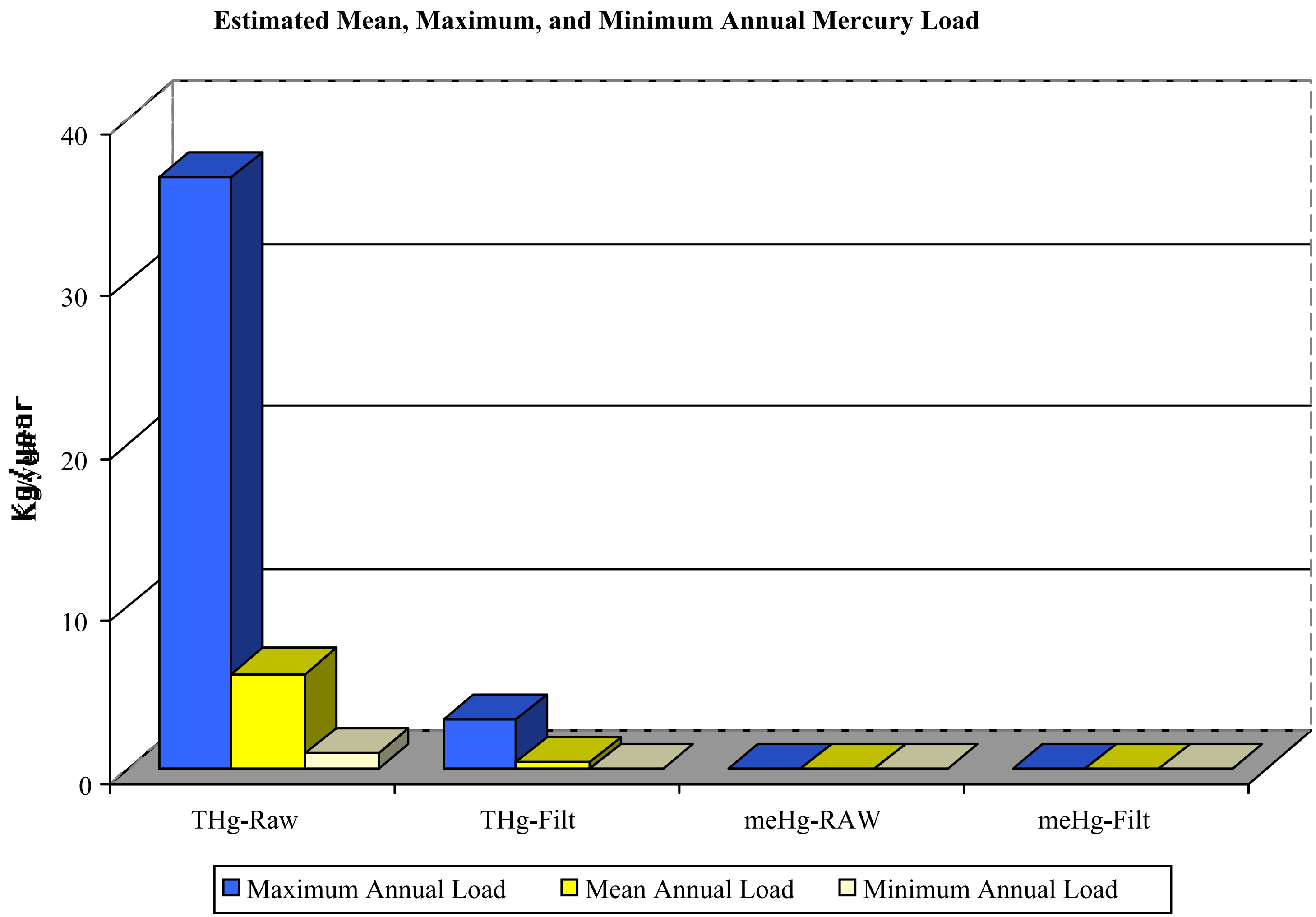

Figure 9. Hg in water from the Sulfur Creek Mining Region Sites

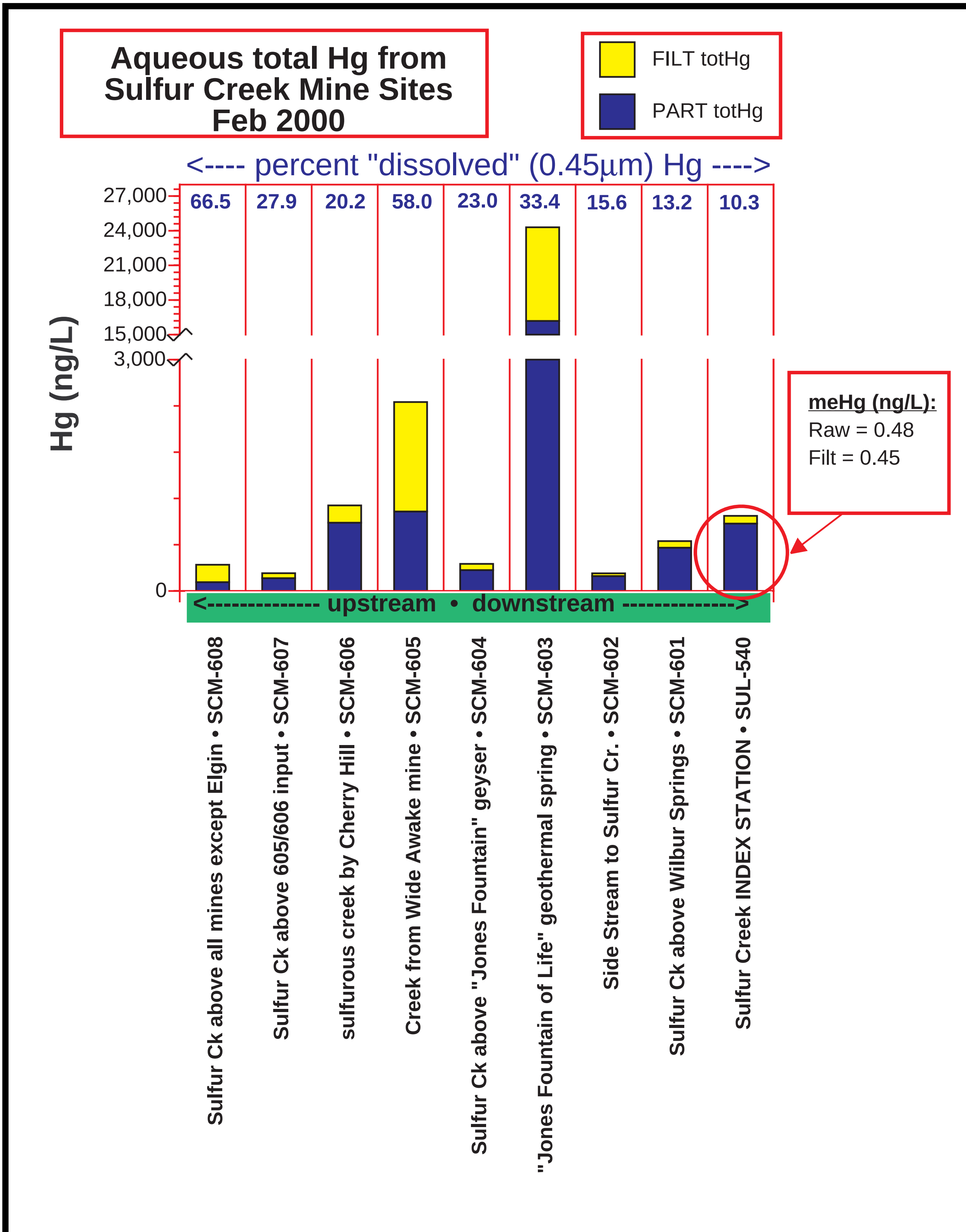

Figure 10. Estimated monthly loading of total Hg (kg/month) from Sulfur Creek

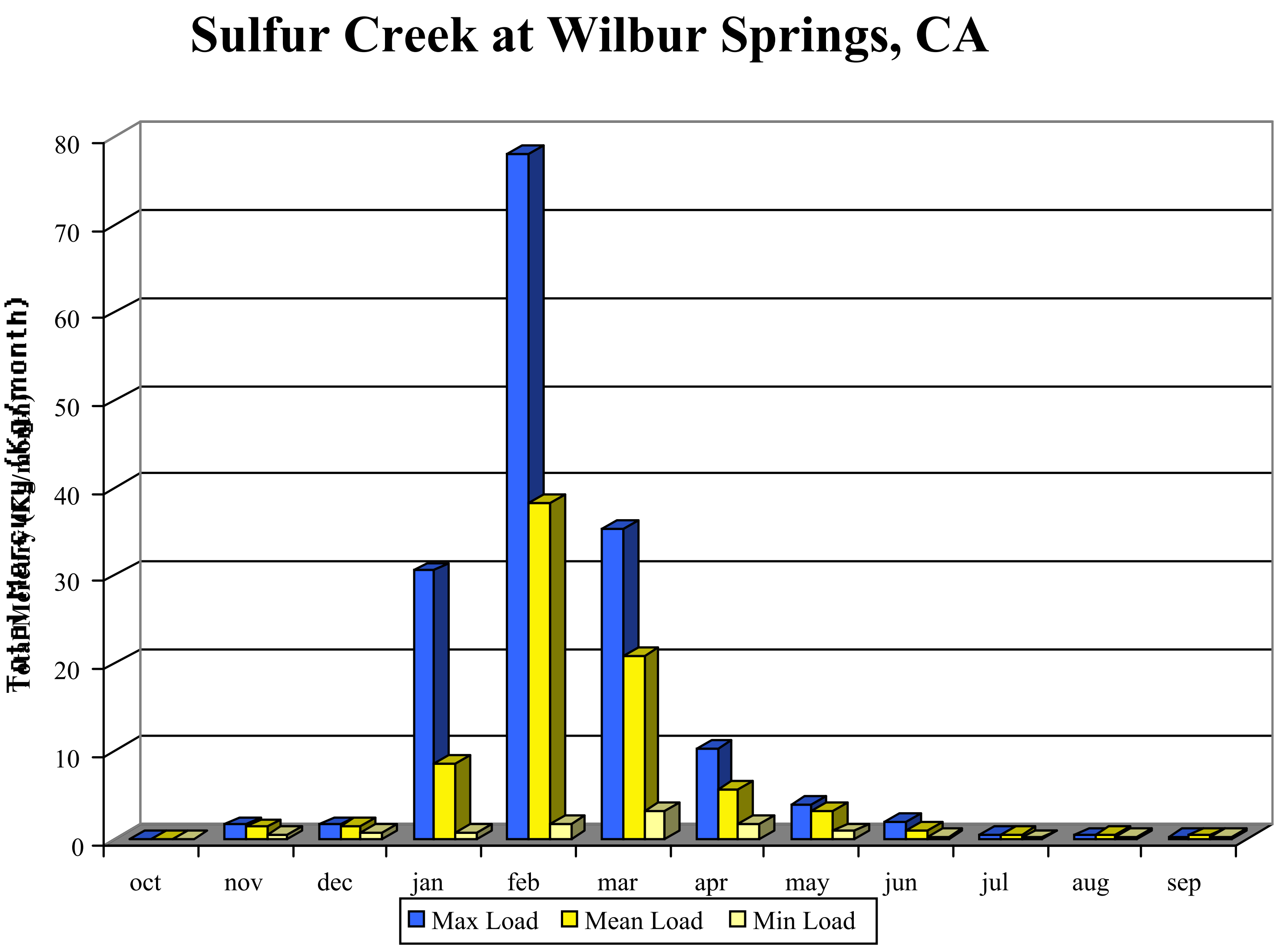

Figure 11. Estimated annual loading of total Hg (kg/yr) from Sulfur Creek