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**Analytical Data for Waters of the Harvard Open Pit,
Jamestown Mine, Tuolumne County, California,
March, 1998–September, 1999**

by

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INTRODUCTION

The Jamestown mine is located in the Jamestown mining district in western Tuolumne County, California (Fig. 1). This district is one of many located on or near the Melones fault zone, a major regional suture in the Sierra Nevada foothills. The districts along the Melones fault comprise the Mother Lode gold belt (Clark, 1970).

The Harvard pit is the largest of several open pits mined at the Jamestown site by Sonora Mining Corporation between 1986 and 1994 (Fig. 2; Algood, 1990). It is at the site of an historical mine named the Harvard that produced about 100,000 troy ounces of gold, mainly between 1906 and 1916 (Julihn and Horton, 1940).

Sonora Mining mined and processed about 17,000,000 short tons of ore, with an overall stripping ratio of about 4.5:1, yielding about 660,000 troy ounces of gold (Nelson and Leicht, 1994). Most of this material came from the Harvard pit, which attained dimensions of about 2700 ft (830 m) in length, 1500 ft (460 m) in width, and 600 ft (185 m) in depth. The bottom of the pit is at an elevation of 870 ft (265 m). Since mining operations ceased in mid-1994, the open pit has been filling with water. As of November, 2000, lake level had reached an elevation of about 1170 ft (357 m).

Water quality monitoring data gathered after mine closure showed rising levels of arsenic, sulfate, and other components in the lake, with particularly notable increases accompanying a period of rapid filling in 1995 (County of Tuolumne, 1998). The largest potential source for arsenic in the vicinity of the Harvard pit is arsenian pyrite, the most abundant sulfide mineral related to gold mineralization. A previous study of weathering of arsenian pyrite in similarly mineralized rocks at the Clio mine, in the nearby Jacksonville mining district, showed that arsenic released by weathering of arsenian pyrite is effectively attenuated by adsorption on goethite or coprecipitation with jarosite, depending upon the buffering capacity of the pyrite-bearing rock (Savage and others, 2000). Although jarosite would be expected to dissolve in water having the composition of the developing pit lake, iron oxyhydroxide species (ferrihydrite and goethite) would be stable, and strong partitioning of arsenic onto suspended particles or bottom sediments containing these iron phases would be expected. Arsenic release to the lake would not be expected until stratification develops, producing a reducing, non-circulating hypolimnion in which the iron phases would be destroyed by dissolution.

The fact that arsenic concentrations increased rapidly before the pit lake was deep enough to stratify shows that arsenic may not be attenuated in the ways that the earlier Clio mine area study indicated, and suggested that our understanding of release and transport of arsenic in this environment is incomplete. Therefore, in 1997 we decided to study the chemical evolution of the Harvard pit lake as part of a project on environmental impacts of gold mining in the Sierra Nevada, and in early 1998 we developed a cooperative

study with several of the investigators in the Stanford University Department of Geological and Environmental Sciences who had done the Clio study. The U.S. Geological Survey portion of the project has been funded by the Mineral Resources Program.

It is anticipated that a better understanding of the release and transport of arsenic into the Harvard pit lake and its accumulation there will contribute to more accurate predictions of arsenic release from weathering of sulfide-bearing rocks exposed by mining or other activities or events, and to better forecasts of pit lake evolution in this and similar environments, leading to more effective monitoring and mitigation strategies.

An accurate predictive model is needed for the Harvard pit lake to forecast trends in metal concentrations, particularly arsenic, and also concentrations of major cations and anions. As the lake approaches pre-mining groundwater levels the lake water could move down the hydrologic gradient to the southeast into domestic wells, and could also affect the surface water of Woods Creek (Figures 1-3).

This report presents data for water samples collected from March, 1998 through September, 1999. Selected preliminary data for the pit lake for the 1998 calendar year have been reported (Savage and others, 2000).

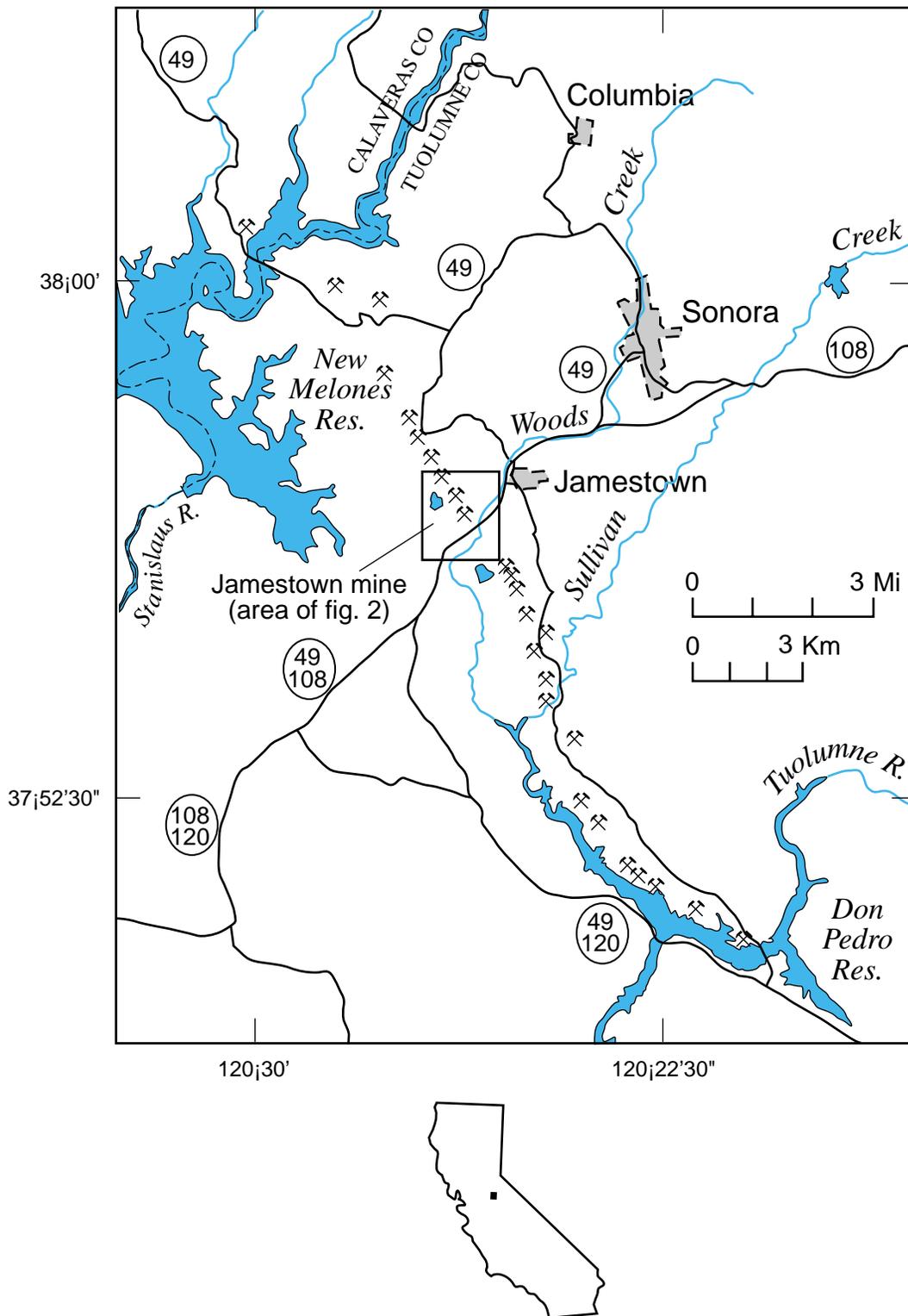


Figure 1. Map showing location of the Jamestown mine site. Symbols show locations of mines of the Mother Lode belt.

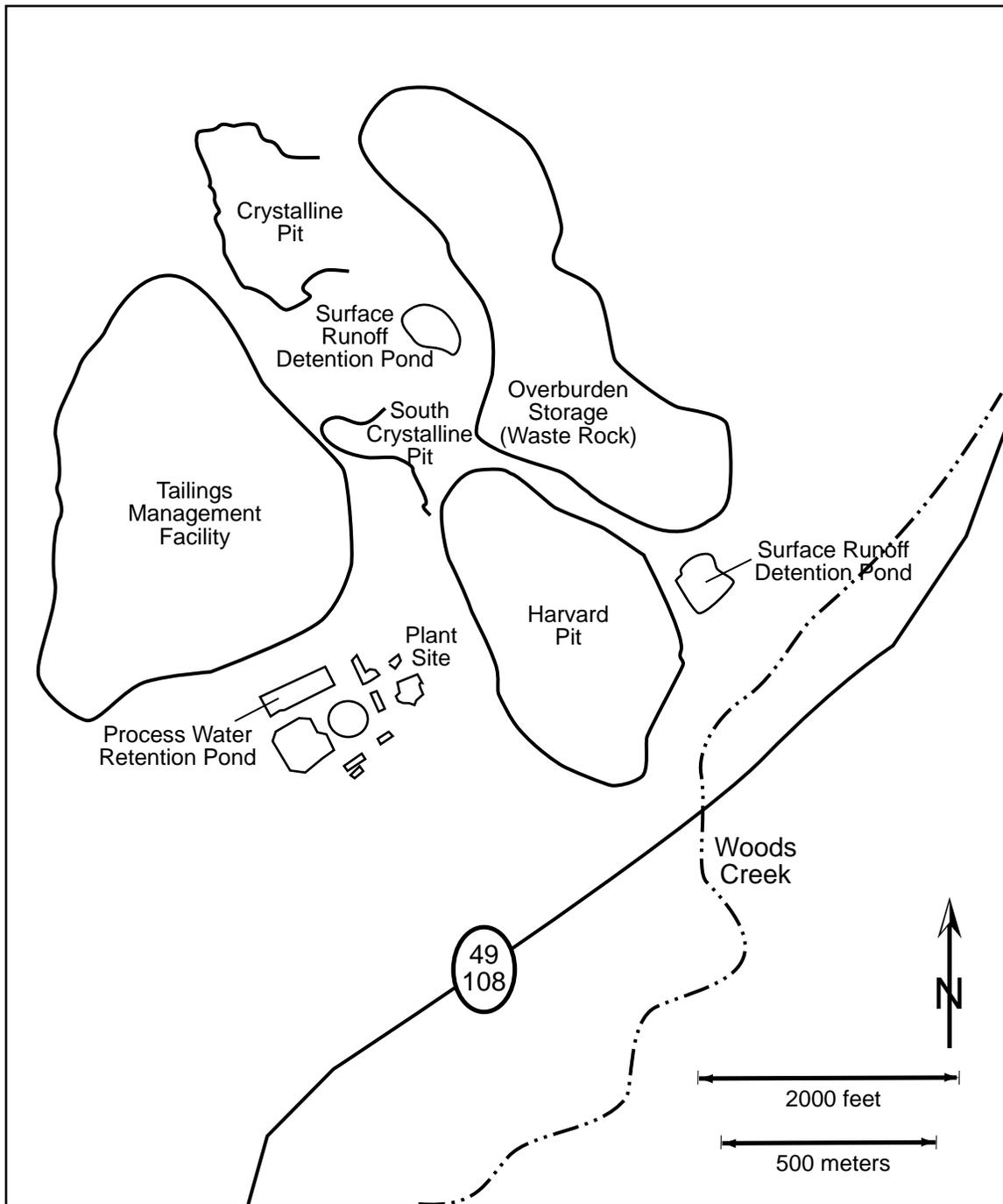


Figure 2. Map showing main features of the Jamestown mine site.

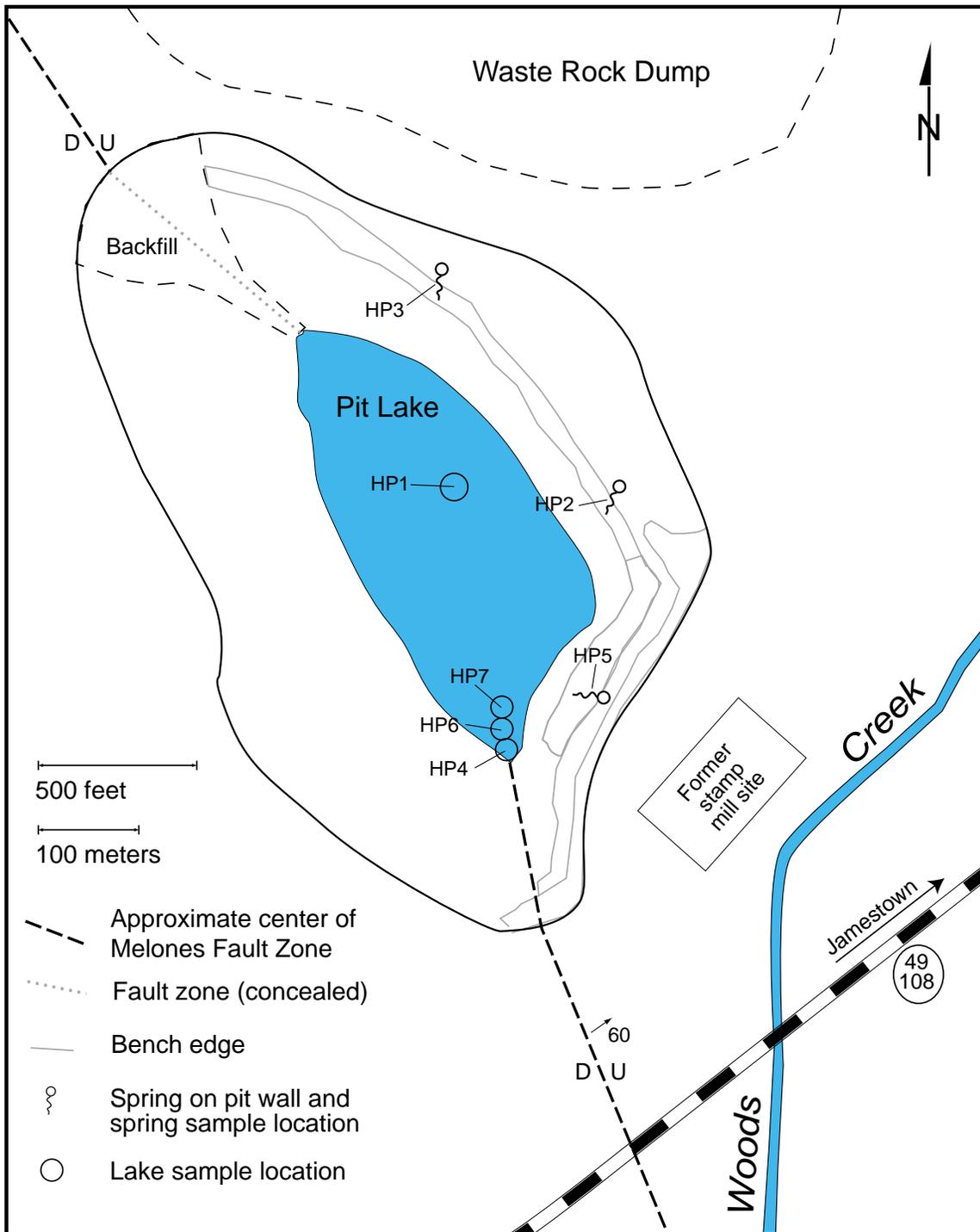


Figure 3. Sketch map of Harvard pit showing water sample locations.

Figure 3. Sketch map of Harvard pit showing water sample locations.

GEOLOGY AND DEPOSIT CHARACTERISTICS

In the vicinity of the Harvard pit the Melones fault trends N25-30°W and dips 60-75°E (Fig. 3). It separates a serpentinite melange on the footwall from slate on the hanging wall (Eric and others, 1955; Nelson and Leicht, 1994). Several other rock types, including greenstone, diorite, metatuff(?), and dikes of intermediate composition, are found locally in the melange and along the fault (R.P. Ashley and D.P. Cox, unpub. data, 1992). Hydrothermal alteration has affected the rocks along the fault in a zone 100-200 m wide. In the alteration zone calcium, magnesium, and iron-bearing silicates are altered to carbonate minerals (mainly ferroan dolomite). Potassium micas, including mariposite, a chromium-bearing mica, albite, and pyrite have been added. Quartz-carbonate veins in many different orientations cut the altered rocks. Locally massive quartz veins, generally parallel to the fault, occur within the altered rocks.

The ore bodies consist of gold disseminated in the altered rocks. In many Sierran gold districts the ore bodies are found in quartz veins, but here the larger quartz veins are low grade. Most of the gold is associated with pyrite, but some is free-milling (Algood, 1990; Nelson and Leicht, 1994). Less-abundant sulfide minerals observed and reported include chalcopyrite, pyrrhotite, sphalerite, galena, tetrahedrite, gersdorffite, niccolite, millerite, cobaltite, cubanite, linneite, bornite, covellite, melonite, and several gold-silver tellurides.

The host rocks at the Harvard mine are Jurassic in age (Bowen and Crippen, 1997), and the Melones fault was active from late Jurassic to early Cretaceous time (Landefeld, 1990). Serpentinite and associated mafic intrusive rocks were tectonically emplaced in the Melones fault zone. Radiometric ages for alteration minerals associated with the Sierran gold deposits are mostly between 108 and 127 Ma (Böhlke, 1999).

The deposits of the Mother Lode gold belt are classified as low-sulfide gold-quartz veins (Berger, 1986). Other names for this deposit type include mesothermal, orogenic, metamorphic rock-hosted, shear-zone hosted, greenstone-hosted, turbidite-hosted, and slate-belt gold (Groves and others, 1998).

FIELD METHODS

We have taken samples at seven sites in the pit (Fig. 3). We located springs and seeps (sites HP2, HP3, and HP5) initially by inspection using a 1994 map of the pit, and later obtained geographic coordinates using a hand-held Global Positioning System (GPS) unit. Lake sites HP4, HP6, and HP7, all near the south end of the lake, were similarly located by inspection. The lake site (HP1) was originally selected using an acoustic depth finder to locate the deepest spot in the lake, and its position relative to landmarks around the pit was determined with a laser range finder. Through 1999 this site was

recovered mainly by using the depth finder, but subsequently its coordinates have been obtained and recovered by GPS.

Water sampling protocols used here, including bottle preparation and sample preservation, generally follow those of Water Resources Division of the U.S. Geological Survey for trace metals (Horowitz and others, 1994). Table 1 lists the usual subsamples and summarizes procedures applied to each. Field filtrations were generally done with disposable 25 mm-diameter sterile cellulose acetate filters (0.45 μm opening) and disposable syringes.

Chemical parameters and temperature were measured at 25-foot intervals through the water column of the pit lake at HP1 with a Hydrolab Minisonde. Samples were taken through this profile at spacings of 40 to 75 feet. For the sampling period covered in this report, a 2-liter Kemmerer-type bottle was used to recover samples at various depths. During every sampling event, a field blank was collected by processing de-ionized water through the Kemmerer bottle and collecting the same subsamples (except for alkalinity) by the same procedures as used for the field samples (Table 1). In addition to calibrating the Hydrolab before each profile run, pH and redox potential were spot-checked in the field on water withdrawn from the Kemmerer bottle, using a battery-powered meter and appropriate probes, and dissolved oxygen concentration was similarly confirmed with a Chemets colorimetric field kit.

For the spring waters, parameters were measured in the field with a battery-powered meter with pH and redox probes, and a specific conductivity meter. Dissolved oxygen concentrations were determined with a Chemets colorimetric field kit. At times alkalinity, pH, nitrite, and nitrate were checked in the field with Hach indicator strips. Spring waters were collected in 1-liter HDPE bottles; at each sampling event all subsamples for analysis of metals and anions were removed from the same 1-liter bottle.

Laboratory blanks and acid blanks were processed periodically to determine whether our equipment, containers, reagents, and procedures introduced significant contamination.

Table 1. Water sampling containers and procedures

Subsample	Abbreviation	Container and preparation	Collection/storage procedures	Purpose
Filtered acidified	FA	HDPE (high-density polyethylene), acid-rinsed, 125-250 ml	Put through sterile cellulose acetate filter, usually 0.45 μm pore size. Preserved with concentrated ultrapure HNO_3 .	Multielement metal scan
Unfiltered (raw) acidified	RA	HDPE, acid-rinsed, 125-250 ml	Preserved with concentrated ultrapure HNO_3 .	Multielement metal scan
Filtered acidified	FA	Amber (opaque) HDPE, 60-250 ml	Put through sterile cellulose acetate filter, usually 0.45 μm pore size. Preserved with concentrated ultrapure HCl . Chilled ($\sim 4^\circ\text{C}$) until analysis.	Arsenic and iron, totals and species
Unfiltered (raw) acidified	RA	Amber (opaque) HDPE, 60-250 ml	Put through sterile cellulose acetate filter, usually 0.45 μm pore size. Preserved with concentrated ultrapure HCl . Chilled ($\sim 4^\circ\text{C}$) until analysis.	Arsenic and iron, totals and species
Filtered unacidified	FU	HDPE, 60-250 ml	Put through sterile cellulose acetate filter, 0.45 μm pore size. Chilled ($\sim 4^\circ\text{C}$) until analysis.	Anions, silica
Filtered unacidified	FU	HDPE, 60-125 ml	Put through sterile cellulose acetate filter, 0.45 μm pore size. Chilled ($\sim 4^\circ\text{C}$) until analysis.	Alkalinity
Unfiltered (raw) unacidified	RU	Glass, 250 ml-1000 ml, excluding top, precleaned	No head space. Chilled ($\sim 4^\circ\text{C}$) until analysis.	Mercury, total and species
Unfiltered (raw) unacidified	RU	HDPE, 250 ml	Stored refrigerated (4°C).	Parameters, archive

ANALYTICAL METHODS

Trace metals and major cations were determined by induction-coupled plasma mass spectrometry (ICP-MS) on both filtered and unfiltered subsamples preserved with Ultrex-grade nitric acid (sample pH reduced to 1-2). The unfiltered subsamples were digested by heating with additional acid before analysis. Bottles for these subsamples were acid-rinsed in the laboratory before use. Most analyses were performed by Chemex Labs (now ALS Chemex) in Vancouver, B.C. Some early analyses were performed by Actlabs (now Actlabs Skyline) in Denver, Colorado.

Anions, including fluoride, chloride, sulfate, and inorganic nitrogen (nitrate plus nitrite), and silica were analyzed by the Water Quality Service Unit of Water Resources Division of U.S. Geological Survey, in Ocala, Florida. Chloride and sulfate were determined by ion exchange chromatography (IC), fluoride by ion-selective electrode, total inorganic nitrogen by a colorimetric method, and silica by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) (Fishman and Friedman, 1989; Fishman, 1993). The subsample used for all these analyses was filtered but not acidified, and kept chilled until analysis.

Frontier Geosciences, Inc., of Seattle, Washington, performed arsenic speciation and iron speciation analyses. Generally only inorganic arsenic species were determined. As(III) and total inorganic arsenic were determined by hydride generation-cryogenic trapping-atomic absorption spectroscopy (HG-CT-AAS), and As(V) by difference. Iron(II) and total iron were both determined by spectrophotometry using the ferrozine method (Stookey, 1970), and iron(III) by difference. The subsamples used for both arsenic and iron analyses, including both filtered and unfiltered subsamples, were acidified with Ultrex-grade hydrochloric acid, and kept chilled until analysis.

Frontier Geosciences also determined total mercury and methyl mercury content. The method for total mercury involves tin chloride reduction, gold amalgamation, and cold vapor atomic fluorescence detection (CVAFS; EPA Method 1631). Methyl mercury was determined by distillation. The distillate was ethylated and purged onto Carbotrap, followed by isothermal gas chromatographic separation and detection by CVAFS (EPA Method 1630). Mercury subsamples were collected in pre-cleaned glass bottles (250 ml to one liter capacity) with no head space, and kept chilled until analysis. Few samples were checked for mercury because it was not used for gold recovery in the modern mining operations, and unusual levels of mercury were not expected.

Alkalinity was determined in our laboratory or in the field, usually within 48 hours of sample collection, by the Gran titration technique (Stumm and Morgan, 1996), using a digital titrator to add 1.6N H₂SO₄. The alkalinity subsample was filtered and kept chilled until analysis. The titration was performed in duplicate and the two readings were averaged; if results did not

agree within about 5 percent, a third titration was performed and the closest two of the three readings were averaged.

WATER CHEMISTRY DATA

We have collected water samples at site HP1, located over the deepest spot in the lake, at almost every sampling event. The final digits of the HP1 sample numbers represent the approximate depth, in feet, at which the sample was taken (Tables 2 and 3). For the other three lake sites (HP4, HP6, and HP7), the last digits also represent depth. Sample numbers that end in ".1" represent subsamples that were put through a 0.1 μm filter (Tables 2 and 3).

In Table 2 (Parameters), the first four columns after the date are parameters we measured in the field, either in place with a Hydrolab, or on water taken from the sampling bottle and usually measured immediately after collection (see table foot notes for method used). Table 3 contains results of multielement scans done by the ICP-MS method. The FB, LB, and AB samples are field blanks, laboratory blanks, and acid blanks, respectively. A few applicable LB and AB samples were batched with samples from other areas, and are not included in Tables 2 and 3.

QUALITY ASSURANCE/QUALITY CONTROL DATA FOR ARSENIC

It is anticipated that the data presented here will be used to develop a predictive model to forecast future changes in chemical composition of the Harvard pit lake. Since arsenic concentrations are of particular concern, we include quality assurance/quality control (QA/QC) data associated with batches of subsamples run by Frontier Geosciences, Inc. for arsenic species (Table 4). QA/QC provided by Frontier included duplicates, laboratory blanks, and matrix spikes for arsenic (III) and total inorganic arsenic. Data for blanks are not included, however, because all samples have concentrations well above detection thresholds for inorganic arsenic species and total arsenic. Data in Table 4 (observed values) are from Frontier Geosciences, Inc.; computed values (e.g. RPD, relative percent difference) are the responsibility of the authors.

COMMENTS ON ANALYTICAL DATA

There are unresolved problems with some alkalinity determinations obtained in March 1998. The numbers in Table 2 are averages of two replicate measurements (see Analytical Methods section, above), but with further evaluation we may reject some measurements, which will change the values.

We had difficulty obtaining consistent redox electrode (Eh) values in the field, which may be the result of problems with instrumentation or lack of strong

redox control in the waters, or both. Consequently, we have little confidence in the Eh numbers.

Results for field blanks (FB samples) show that the Kemmerer-type sample bottle we used for the HP1 profile commonly introduced amounts of tin, zinc, and phosphorus that are significant relative to concentrations encountered in some or all of the associated profile samples. Blanks also occasionally show amounts of aluminum, chromium, copper, or manganese that may be significant relative to amounts in the profile samples.

The spring samples (HP2, HP3, HP5) show much lower levels of some metals than the lake waters. Note, however, that values for the field blanks do not apply to the spring samples, because other sampling equipment was used as described above.

The exceptionally high values for various major cations and trace metals seen in the RA subsample for 98KS1-HP1-250 (Table 3) are the result of incorporating some bottom sediment in the sampler.

Both Tables 2 and 3 have columns for iron (Fe) and arsenic (As). The analytical methods used to obtain the data in Table 2 are different from those in Table 3, and different subsamples were used, as described above. Total iron values obtained for both HCl-preserved filtered subsamples analyzed by the ferrozine method (Table 2) and HNO₃-preserved filtered subsamples analyzed by the ICP-MS method (Table 3) are mostly less than lower detection limits, which range from less than 1 ppb to 2 ppb. However, total iron values determined by ICP-MS during the first half of 1998 are relatively high (as much as 280 ppb in Chemex data, and about 4500 ppb in ACTLABS data), whereas ferrozine iron values are typically low. This discrepancy in results obtained by different laboratories using different methods is unexplained; possibly it reflects an uncorrected analytical interference in the ICP-MS data. We prefer to rely on the data in Table 2 because the ferrozine analyses were monitored with extensive quality assurance/quality control procedures, including analysis of blanks, duplicates, control standards, and spikes.

Total arsenic values obtained for both HCl-preserved filtered subsamples analyzed by the HG-CT-AAS method (Table 2) and HNO₃-preserved filtered subsamples analyzed by the ICP-MS method (Table 3) are similar. Arsenic values for lake waters range from about 720 ppb to about 1100 ppb by both methods. Arsenic values for spring waters range from 1.66 to 6.19 ppb by HG-CT-AAS (total inorganic arsenic, see As Ti-FA column, Table 2), but ICP-MS determinations show a wider range, from 2 ppb to 21 ppb. The stated lower detection limit for arsenic by the ICP-MS method, however, ranges from 1 ppb to 20 ppb, and several determinations are <10 ppb or <20 ppb.

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