Application of environmental groundwater tracers at the Sulphur Bank Mercury Mine, California, USA

Mark A. Engle · Fraser Goff · David G. Jewett · Gregory J. Reller · Joel B. Bauman

Abstract Boron, chloride, sulfate, δD, $\delta^{18}O$, and ^{3}H concentrations in surface water and groundwater samples from the Sulphur Bank Mercury Mine (SBMM), California, USA were used to examine geochemical processes and provide constraints on evaporation and groundwater flow. SBMM is an abandoned sulfur and mercury mine with an underlying hydrothermal system, adjacent to Clear Lake, California. Results for non-^{3}H tracers (i.e., boron, chloride, sulfate, δD, and $\delta^{18}O$) identify contributions from six water types at SBMM. Processes including evaporation, mixing, hydrothermal water input and possible isotopic exchange with hydrothermal gases are also discerned. Tritium data indicate that hydrothermal waters and other deep groundwaters are likely pre-bomb (before ~1952) in age while most other waters were recharged after ~1990. A boron-based steady-state reservoir model of the Herman Impoundment pit lake indicates that 71–79% of its input is from meteoric water with the remainder from hydrothermal contributions. Results for groundwater samples from six shallow wells over a 6–month period for δD and $\delta^{18}O$ suggests that water from Herman Impoundment is diluted another 3% to more than 40% by infiltrating meteoric water, as it leaves the site. Results for this investigation show that environmental tracers are an effective tool to understand the SBMM hydrogeologic regime.

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M. A. Engle · G. J. Reller · J. B. Bauman
Tetra Tech EM Inc.,
10860 Gold Center Drive, Suite 200,
Rancho Cordova,
California 95670, USA

F. Goff
Geology/Geochemistry Group,
Los Alamos National Lab, Los Alamos,
New Mexico 87545, USA

D. G. Jewett
US Environmental Protection Agency Office of Research and Development, Ada, Oklahoma 74820, USA

Present Address:
M. A. Engle (✉)
US Geological Survey,
956 National Center, Reston, Virginia 20192, USA
e-mail: engle@usgs.gov

Present Address:
F. Goff
Earth and Planetary Sciences Department,
University of New Mexico, Albuquerque,
New Mexico 87131, USA

Résumé Les concentrations en bore, chlorure, sulfate, δD, $\delta^{18}O$, et ^{3}H d'échantillons d'eaux de surface et souterraine prélevés dans le banc de soufre de la mine de mercure (SBMM en anglais) en Californie, USA, ont été utilisées pour étudier les processus géochimiques et pour fournir des contraintes à l'évaporation et à l'écoulement des eaux souterraines. La SBMM est une mine de soufre et de mercure abandonnée, adjacente au lac Clear en Californie et sous laquelle se trouve un système hydrothermal.Les résultats des traceurs autres que le tritium (bore, chlorure, sulfate, δD, et $\delta^{18}O$) ont permis d'identifier des contributions de six types d'eaux à SBMM. Des processus tels que l'évaporation, le mélange, l'entrée d'eau hydrothermale et de possibles échanges isotopiques avec des gaz hydrothermaux ont également été identifiés. Les données de tritium montrent que les eaux hydrothermales et d'autres eaux profondes sont probablement d'âge antérieure à la bombe (avant ~1952), alors que la plupart des autres eaux sont issues de la recharge après ~1990. Un modèle de réservoir représentant le lac situé dans la partie Herman Impoundment de l'ancienne mine, en régime permanent et basé sur le bore, montre que 71–79% de l'eau provient des précipitations, le reste provenant de contributions hydrothermales. Les résultats de δD et $\delta^{18}O$ pour des échantillons d'eau souterraine de six puits peu profonds sur une période de 6 mois suggèrent que l'eau de Hermann Impoundment est encore diluée entre 3% jusqu'à plus de 40% lorsqu'elle quitte le site du fait de l'infiltration d'eau météorique. Les résultats de cette étude montrent que les traceurs environnementaux constituent un outil efficace pour comprendre le régime hydrogéologique de la SBMM.

Resumen Se han utilizado datos de concentraciones de boro, cloruros, sulfatos, δD, $\delta^{18}O$, y ^{3}H en muestras de aguas superficiales y subterráneas procedentes de la Mina de Mercurio Sulphur Bank (SBMM), California, USA,

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para estudiar los procesos geoquímicos y caracterizar la evaporación y el flujo del agua subterránea. SBMM es una mina abandonada de azufre y mercurio con un sistema hidrotermal subyacente, cercano al Lago Clear, California. Los resultados de los trazadores que no son ^{3}H (por ejemplo, boro, cloruros, sulfatos δD, y $\delta^{18}O$) identifican las contribuciones de seis tipos de agua en la SBMM. Se han identificado diversos procesos, como evaporación, mezcla, entrada de agua hidrotermal y la posibilidad de intercambios isotópicos con gases hidrotermales. Los datos de tritio indican que las aguas hidrotermales y otras aguas subterráneas profundas son probablemente pre-bombas (previas a ~1952) en edad mientras que la mayoría de las otras aguas se han recargado después de ~1990. Un modelo estacionario basado en el boro de la fosa del lago Herman Impoundment indica que el 71–79% de su entrada procede de agua meteórica con restos de contribución hidrotermal. Los resultados para las muestras de aguas subterráneas procedentes de seis pozos superficiales en un periodo de 6 meses para δD y $\delta^{18}O$ sugieren que el agua procedente de Herman Impoundment se diluye en otro 3% hasta más del 40% debido a la infiltración de agua meteórica., que sale del sitio. Los resultados de esta investigación muestran que los trazadores ambientales son una herramienta efectiva para entender el régimen hidrogeológico de la SBMM.

Keywords Groundwater flow · Stable isotopes · Water budget · USA · Hydrochemistry

Introduction

Maximum dissolved groundwater mercury (Hg) concentrations at the Sulphur Bank Mercury Mine (SBMM) Superfund Site, California, currently exceed the US Environmental Protection Agency (EPA) maximum contaminant level (2.0 μg/L) by more than two orders of magnitude (Jewett et al. 2000a). These groundwaters flow into adjacent Clear Lake, where Hg can be potentially converted to more bioavailable species such as methylmercury via biologically mediated reactions in the near-surface sediments or on 'floc', an alumino-silicate precipitate that forms from the neutralization of acidic SBMM-derived waters in the lake (Suchanek et al. 2000; Batten and Scow 2003). Methylmercury can be bioaccumulated and biomagnified and is a neurotoxin to humans. Concern due to elevated levels of Hg in Clear Lake fish and other biota, thought to be a result of input from SBMM, led to placing the site on the EPA Superfund List in 1990. Since then, the EPA and other researchers have conducted a variety of studies on the site, investigating the source and transport of Hg from SBMM and its impact on Clear Lake and the surrounding ecosystem (Goff and Bergfeld 1997; Jewett et al. 2000a, b; Suchanek et al. 2000; Batten and Scow 2003; Hammack et al. 2003; Lowry et al. 2004; Randall and Chattopadhyay 2004).

Despite characterization and classification of samples from 50+ wells and 14 surface water sites, sources of SBMM waters are not well constrained, or in some cases are disputed (Shipp and Zierenberg 2001). In addition, estimates of groundwater flow rates, generated using various methods, vary more than an order of magnitude (1.40×10^{4} to 2.17×10^{5} m^3/yr; Jewett et al. 2000b). To better constrain and understand Hg and trace element transport in SBMM waters, a realistic model of groundwater flow needs to be developed. This report details the analyses of several hydrogeochemical tracers including boron (B), chloride (Cl), sulfate (SO_4), tritium (^{3}H), and stable isotopic ratios of oxygen ($\delta^{18}O$) and hydrogen (δD) from 63 groundwater and surface water samples, used in conjunction with data from previous studies, to examine sources of SBMM waters and to provide information on groundwater flow and mixing.

Metals and acid released from the oxidation of sulfide minerals during water–rock interaction in the mine waste and hydrothermally altered rocks impact surface water and groundwater quality at the site (Suchanek et al. 2000; Jewett 2000b). In addition, a small Hg-emitting geothermal reservoir, located beneath SBMM, produces surface manifestations such as fumaroles exhausting acid- and Hg-bearing gas and upwelling of hydrothermal waters which further exacerbate water quality (White and Roberson 1962). On account of the potential for both meteoric and hydrothermal waters to impact water quality, and because the site is host to a complex geologic setting, a multi-tracer approach was taken as it allows for distinguishing input and mixing of different sources. Typically conservative environmental tracers (δD, $\delta^{18}O$, B, and Cl) were chosen for this study because they are effective in discriminating between various water sources and allow for application of chemical mass balance methods to determine input of end-member waters during mixing.

Tritium (^{3}H), the radioactive isotope of hydrogen (λ=12.4 yrs), was released during nuclear testing, peaking in atmospheric concentration in 1962 (Michel 1989). Since then, ^{3}H concentrations in precipitation have decreased significantly and reached near background levels by 1990 (Clark and Fritz 1997). Atmospheric ^{3}H is removed through precipitation and subsequent infiltration into groundwater. This process creates a strong correlation between groundwater and atmospheric ^{3}H concentrations, taking into account loss from radioactive decay. This makes it ideal for qualitatively dating young groundwaters (<50 yrs; Fontes 1980), although ^{3}H concentrations associated with peak testing have decayed to near background levels making interpretation more difficult.

Goff et al. (1993) presented tritium-based residence times for Clear Lake region groundwaters using two end-member reservoir types, well-mixed and piston-flow (Pearson and Truesdell 1978). These models allow for the evaluation of mean residence times of groundwaters based on the ^{3}H activity in the water. Using an updated version of this work, taking into account additional radioactive decay and atmospheric input, qualitative ages can be generated for groundwaters at SBMM. In general,

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waters with ^{3}H concentrations below 2.5 TU were generally recharged prior to ~1952, while those with ^{3}H concentrations greater than approximately 4.5 TU were likely recharged between 1952 and 1990 years old. Finally, waters with ^{3}H activities between 2.5 and 4.5 TU are modern (younger than 1990) waters and tend to get older with decreasing ^{3}H contents. These guidelines are only applicable to pure end-member waters because mixed waters do not have a definite age.

Although not typically conservative, SO_4 was selected to identify chemical processes thought to occur within the SBMM hydrologic system. The dominant chemical reactions controlling SO_4 concentrations at SBMM include oxidation of Fe-sulfide minerals (e.g., pyrrhotite and pyrite), oxidation of H_2S, and dissolution of sulfate minerals. Thus, elevated SO_4 in groundwater at SBMM was used as an indicator of acid generating water-rock and/or water–gas interactions.

Site description

The Sulphur Bank Mercury Mine is an abandoned mine and pit lake that lies on a 0.65 km^2 site on the eastern shore of the Oaks Arm of Clear Lake, California, USA (Fig. 1). The mine property is bound on the west by Clear Lake, and to the north by a wetland adjacent to Clear Lake (Fig. 2); both are potential receptors for contamination.

The mine is centered over a zone of hydrothermal alteration and activity at the intersection of three faults and a shear zone. Upwelling hydrothermal fluids, rising along faults over the last ~10,000 yrs (Varekamp and Waibel 1987), have altered the rock units and deposited various mercury and sulfur ore and alteration minerals. The fluids are continuing to deposit sulfur-bearing and mercury-bearing minerals at the surface (White and Roberson 1962; White 1981). Hydrothermal waters, with temperatures as high as 200°C (at a depth of 637 m below ground surface) have been encountered during geothermal exploration at the site (Beall 1985). Deep-seated thermal and pressure gradients still exist in the geothermal system.

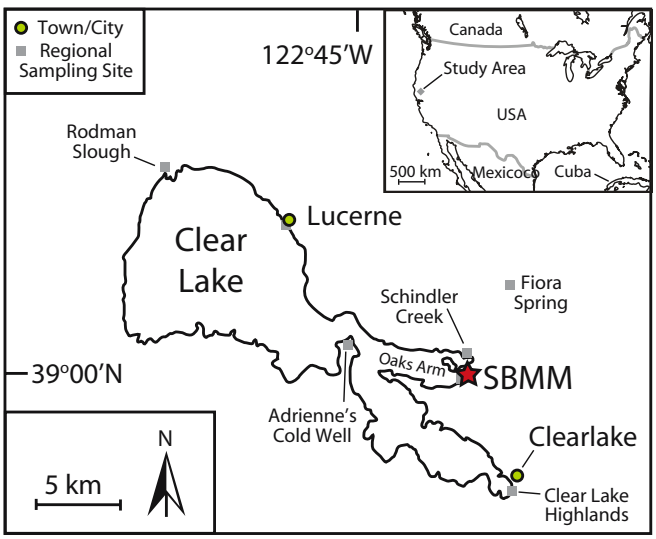

Fig. 1 Map of the Clear Lake region showing location of the Sulphur Bank Mercury Mine (*SBMM*), nearby cities and towns, and regional water sampling sites

Hot vapors, sulfurous fumes, and hydrothermal gases escape from cracks and fissures and are observed bubbling through Herman Impoundment, pond waters, and in monitoring wells. Bergfeld (2000) also demonstrated that significant quantities of hydrothermal gas are emitted through soils and fumaroles throughout the site, with the largest emissions on the north and east sides of Herman Impoundment. Gases emanating from the site typically contain 88–93% CO_2, 5–10% CH_4, 1.5–2.5% N_2, and 0.1–0.4% H_2S (Nehring 1981; Goff et al. 2002).

Between 1864 and 1957, SBMM was the site of underground and open-pit mining and processing operations for sulfur, and then mercury, located along faults at hydrothermal vents. After mining ceased in 1954, the open pits filled with water derived from hydrothermal fluids, meteoric groundwater, and surface water runoff (White and Roberson 1962). The largest open pit, Herman Impoundment, currently covers 0.093 km^2 and is filled with water to a depth of 30 m. Mining disturbed most of the SBMM area and generated ore, tailings, and waste-rock piles across the mine site. Of significance is the waste-rock dam, which was built in the 1950s to minimize surface water flow from Herman Impoundment to adjacent Clear Lake (Fig. 2).

The site hydrogeology can be characterized by four significant water-bearing units, including, from deepest to shallowest, (1) muddy sandstones and black shales of Franciscan Complex sediments, (2) lake sediments consisting of conglomerates, sands, silts, and clays, (3) the andesite flow of Sulphur Bank, and (4) the waste-rock dam and lake sediments that mantle the andesite on the western edge of Herman Impoundment (Fig. 2). This last water-bearing unit acts as a significant groundwater pathway between Herman Impoundment and Clear Lake, and contains groundwaters with the highest concentrations of dissolved Hg at the site (Jewett et al. 2000a, b). The unique chemical and physical properties of these units greatly affect groundwater flow mechanics and solute transport at the site.

Based on groundwater equipotentials, the direction of flow in each of the water-bearing units is generally toward Herman Impoundment from the north, east, and south (Fig. 2). However, directions and rates of groundwater flow are thought to be complicated by potential structures (e.g., faults), identified via geological mapping and airborne geophysical surveys of the site, that may act as potential groundwater conduits (White and Roberson 1962; Hammack et al. 2003). Many of the wells installed at SBMM were intentionally placed and screened to intercept these structures; results for pump tests, geochemical analyses, and mass balance constraints indicate that most of these structures do not appear to be significant groundwater conduits (Jewett et al. 2000b). The water level in Herman Impoundment is roughly 2.96–4.31 m higher than in Clear Lake, resulting in year-round groundwater flow through the waste-rock dam to the lake. Significantly less flow occurs through the underlying

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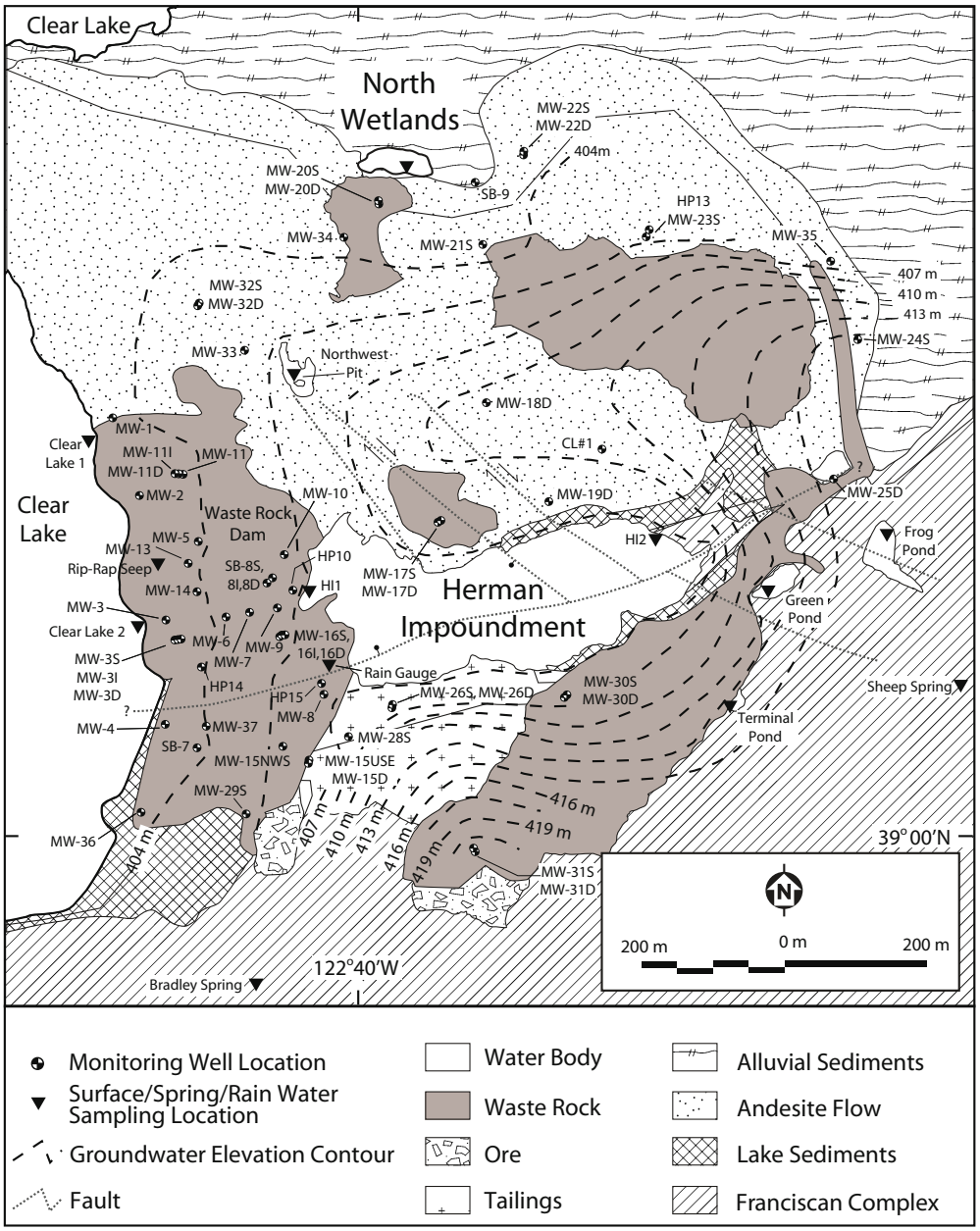

Fig. 2 Geologic and hydrologic map of the Sulphur Bank Mercury Mine showing sampling locations, groundwater contours, and fault locations. Groundwater contours were generated from the uppermost water-bearing units using groundwater elevation data collected in January 2002

alluvial sediments and andesite water-bearing units (Jewett et al. 2000a).

Methods

Water samples were collected from 42 monitoring wells (MW) and hydropunch (HP) peizometers, 13 surface waters sites, and 1 rain gauge at SBMM and around Clear Lake in December 2000. In the summer of 2001, seven new monitoring wells were installed at SBMM and developed. Surface water and groundwater samples were collected from each of these newly installed wells in January of 2002 for a total of 63 samples. Water samples were collected using either low-flow purge methods (Puls and Barcelona 1996) or, in the case of the HP peizometers and surface water samples, a peristaltic pump.

All samples were analyzed for B, Cl, SO_4, $\delta^{18}O$, and δD unless the volume was insufficient (in which case only $\delta^{18}O$ and δD were analyzed). In addition, splits were collected from 23 of the samples for tritium analysis. Field parameters (pH, Eh, specific conductance, and temperature) were also measured using a calibrated YSI multiparameter water quality meter and recorded during sampling. Samples for B analysis were filtered to 0.45 μm and acidified using 10% HNO_3. All other samples were neither filtered nor acidified. Analyses of B, Cl, and SO_4 were completed by STL Laboratory in West Sacramento,

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California using ICP-AES and ion chromatography. Analyses for $\delta^{18}O$ and δD were performed by the stable isotope laboratory at the University of Arizona. Tritium enrichments and analyses were obtained at the University of Miami Tritium Laboratory. Enrichment of the tritium samples allowed for a detection limit of 0.1 TU. All samples were collected and analyzed using strict EPA QA/QC methodologies.

Data from previous workers were also used in this study. Sources include data from White and Roberson (1962), White et al. (1973), Thompson et al. (1981), Donnelly-Nolan et al. (1993), Shipp and Zierenberg (2001), Goff et al. (2002), and one of the authors (F. Goff, Los Alamos National Lab, personal communication, 2002). In total, data from 106 water samples are incorporated in this study.

Results and discussion

Chemical characterization of SBMM Waters

Analytical results for this and previous studies are provided in the section Electronic supplementary material. Using a geochemical classification from previous work for SBMM (Jewett et al. 2000b), the data were separated into six different water types as described in the following sections.

Clear Lake and other off-site meteoric waters. These waters include cool (<25°C), meteoric, nonevaporated background surface waters and groundwaters, as well as evaporated meteoric waters such as Clear Lake. The unevaporated meteoric waters (e.g., Sheep Spring, Bradley Spring, Schindler Creek, Fiora Spring; see section Electronic supplement material) are characterized by low TDS and a low (typically <0.1) B/Cl value (weight ratio). Isotopic compositions for these waters plot on the Global Meteoric Water Line (GMWL) of Craig (1961) and show the range of nonevaporated meteoric water near SBMM (Fig. 3). This range falls within the typical distribution of unevaporated meteoric waters for the greater Geysers–Clear Lake area (Donnelly-Nolan et al. 1993).

Water samples collected from Clear Lake (adjacent to the waste-rock dam and at Lucerne), Rodman Slough, and Adrienne's cold well (all Clear Lake Water or inputs to Clear Lake) exhibit a fairly low TDS, circum neutral pH (usually 5.5 to 8.0), and a B/Cl value typically between 0.05 and 0.20. Isotopic results from these waters plot along a linear evaporation trend to the upper right of the unevaporated meteoric waters (Fig. 3) in which both $\delta^{18}O$ and δD are enriched in the heavier isotope relative to unevaporated waters (Gonfiantini 1986). More evaporated waters are enriched in ^{18}O and ^{2}H and lie further along (up and to the right) the evaporation trend, while less evaporated waters lie closer to the meteoric water on the evaporation trend line. However, two of the three Clear Lake samples collected in 1997 by Goff et al. (2002) are depleted in ^{18}O relative to the rest of the samples from the lake and plot on the GMWL (Fig. 3). These findings suggest that the isotopic composition of Clear Lake varies with time and likely exhibits seasonal and annual differ-

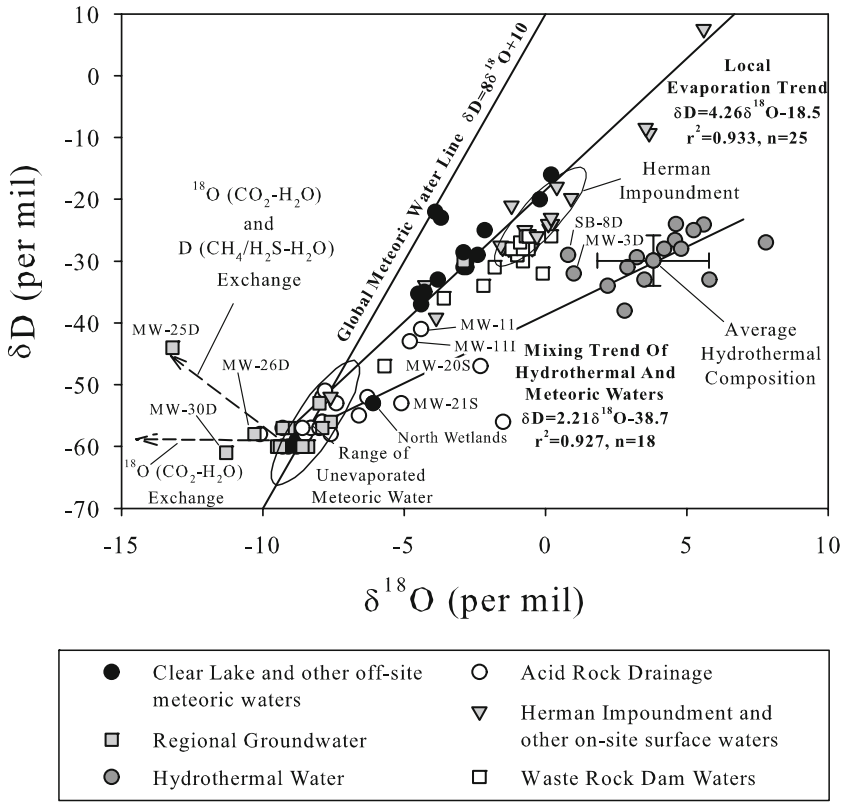

Fig. 3 $\delta^{18}O$ vs. δD diagram for SBMM surface water, groundwater, and precipitation samples

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ences due to evaporation and precipitation. Using a Rayleigh distillation model for the evolution of $\delta^{18}O$ and δD in Clear Lake (assuming an average humidity of 40% and an average temperature of 25°C), including both kinetic and equilibrium effects (Clark and Fritz 1997), approximately 32–35% of the meteoric water in the Lake has been removed via evaporation. Applying this loss due to evaporation to the total water volume and residence time of Clear Lake (1.43×10^9 m^3 and 2.8 yrs, respectively; Richerson et al. 1994), an average evaporation rate of 1.63×10^8 to 1.78×10^8 m^3/yr (0.92 to 1.01 m/yr) is calculated.

The isotopic composition of Clear Lake samples for this study, collected adjacent to the waste-rock dam and at Lucerne, and a sample from Rodman Slough during the January 2002 sampling event (locations shown in Fig. 1) are nearly identical. These data suggest that the isotopic composition of Clear Lake is more or less uniform at a given time and that the flow of water from Herman Impoundment, through the waste-rock dam, is too small to significantly change the isotopic composition of adjacent Clear Lake waters.

One sample of Clear Lake water was collected for ^3H analysis (Fig. 4). It exhibits a relatively high ^3H activity (2.75 TU), indicating it is a mixture of young precipitation and older groundwaters. Three cold, unevaporated, meteoric waters were analyzed for ^3H: Fiora Spring, Bradley Spring, and an average sample of precipitation from several rain events (2001 rainwater). The rainwater sample, which represented average current precipitation, contains the highest ^3H activity (3.18 TU) of the three. The sample from Fiora Spring exhibits the lowest ^3H of the meteoric waters (1.13 TU) and thus, was probably recharged prior to ~1952. A water sample from Bradley Spring (2.46 TU), is either fairly recent (younger than circa 1992) or is older than the large ^3H peak from 1963. Samples from Clear Lake exhibit relatively high ^3H activity (2.75–3.25 TU) indicating the lake water is a mixture of young precipitation and older groundwaters.

Regional groundwater. Uncontaminated groundwaters from the Franciscan Complex water-bearing unit are chemically similar to other groundwater samples from throughout the Clear Lake region (Donnelly-Nolan et al. 1993). The water samples are characterized by neutral to slightly acidic pH (5.15–6.43), low B and Cl concentrations (<25 and <60 mg/L, respectively), a low B/Cl value (typically <0.15), and a large range in SO_4 concentrations (1–7,800 mg/L). Elevated B concentrations (up to 105 mg/L) were measured in samples from MW-1, MW-30D, and MW-37 suggesting a local source. Terrestrial plants at SBMM show signs of B toxicity, indicating that high concentrations of B may be present in soils, rocks, and/or mine wastes. A possible source of elevated B in these samples is water–rock interaction with locally B-enriched rocks.

Stable isotopic compositions of the background groundwaters, in most cases, are very similar to unevaporated meteoric waters indicating they are of meteoric origin. However, several samples of regional groundwater from wells on the east and south margins of Herman Impoundment (e.g., MW-26D, MW-30D) were depleted in ^{18}O relative to the unevaporated meteoric waters; water from MW-25D exhibited depletion in ^{18}O and enrichment in ^2H. Vuataz and Goff (1986) observed a similar ^{18}O shift in CO_2-charged pools in the Valles Caldera, New Mexico. They attributed the shift to uptake of ^{18}O by CO_2 from liquid water via low temperature isotopic fractionation ($\alpha^{18}O_{CO2(g)\text{-}water}$=1.04 at 25°C; Bottinga 1968) and suggested this may be typical in low temperature pools (<90°C) having little discharge of water but high CO_2 flow. Although these reactions are quite slow at normal

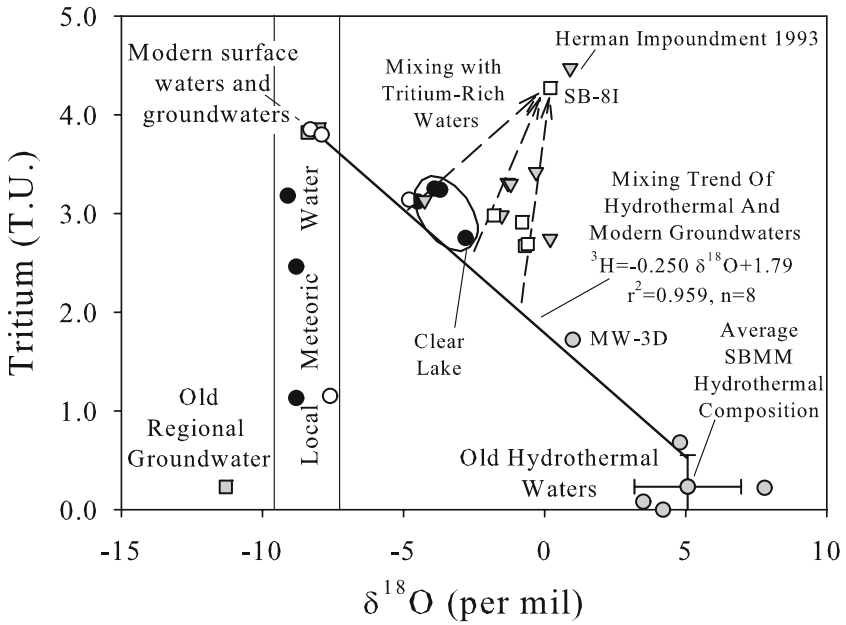

Fig. 4 $\delta^{18}O$ vs. ^3H diagram for SBMM surface water, groundwater, and precipitation samples. Definition of symbols provided in Fig. 3

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groundwater temperatures and rarely observed in most groundwater systems (Clark and Fritz 1997), the waters most depleted in ^{18}O relative to the rest of the background waters (MW-25D, MW-30D, and MW-26D) are generally cool (27–32°C) and slow-moving and were collected from wells that emit CO_2-rich (~90%) hydrothermal gases. These findings suggest that the observed shift in ^{18}O of these waters may be attributed to water-CO_2 isotopic exchange.

A similar isotopic increase in ^{2}H in waters can occur from H_2O_{Liquid} -H_2S and H_2O_{Liquid} -CH_4 hydrogen exchange because the lighter isotopes are sequestered into the gases ($\alpha D_{water\text{-}H2S}$=2.36 at 25°C; Galley et al. 1972; $\alpha D_{water\text{-}CH4}$=2.36 at 25°C; Clark and Fritz 1997). The only sample that exhibits an apparent ^{2}H enrichment was collected from a well (MW-25D) that contains approximately 400 kPa of hydrothermal gases. Although not as abundant in the hydrothermal gases as CO_2, high pressures of CH_4 and H_2S may have produced ^{2}H enrichment in MW-25D waters through water-CH_4 and water-H_2S isotopic exchange.

Three regional groundwater samples were collected for ^{3}H analysis (MW-24S, MW-30D, and MW-31D; Fig. 4). The ^{3}H concentrations (~3.8 TU) in MW-24S and MW-31D suggest they are modern. This is likely because both wells were installed on ridges or high slopes and are likely near recharge areas. The lower ^{3}H concentration from the water in MW-30D (0.23 TU) indicates that this water is significantly older (pre-1952). The lower ^{3}H concentration in MW-30D relative to the other regional groundwater samples is likely due to radioactive decay during groundwater flow from upland recharge areas.

Hydrothermal water. Early geochemical characterization of SBMM waters was completed by LeConte and Rising (1882) and White and colleagues (White 1957; White et al. 1973). This work demonstrated that SBMM hydrothermal waters plot along a trend of enriched ^{18}O and ^{2}H, relative to the cold, nonevaporated meteoric waters and contain a unique almost 1:1 ratio of B to Cl. Samples of these waters are slightly acidic to moderately basic (pH=6.19–8.56), range greatly in temperature (13.6–186°C), and contain fairly low concentrations of SO_4 (<1,000 mg/L except for three samples). Similar isotopic and elemental chemistry of hydrothermal samples collected between 1955 and 2000 demonstrate that the composition of the SBMM hydrothermal fluids has remained nearly constant over that period. In addition, samples of hydrothermal waters collected at depth from previously operational geothermal wells (Hawaiian S.B., No. 1 sampled at 425 m; Magma S.B., No. 1 sampled at 460 m; White et al. 1973) are chemically similar to those collected in this study from shallower wells or springs (see Figs. 3, 5, and 6), indicating that dilution of the hydrothermal waters near the surface by meteoric waters is minimal. The hydrothermal waters at SBMM, which are enriched in ^{18}O and ^{2}H relative to meteoric surface water and regional groundwater, have been classified as having a connate, metamorphic, or magmatic origin by previous authors (White 1957; White et al. 1973; D'Amore and Bolognesi 1994; and Goff et al. 1995).

Regardless of the source of this water, the hydrothermal waters are isotopically and chemically distinct from other waters at the site (see Figs. 3, 5, and 6). The average isotopic composition (calculated using the arithmetic mean) of the hydrothermal end-member is shown in Figs. 3 and 5 ($\delta^{18}O$=4.89±1.71‰, δD=−29.6±4.6‰, Cl=656±154 mg/L, B=660±143 mg/L). This calculation does not include hydrothermal waters collected from the andesite and lake sediment water-bearing units beneath the waste-rock dam (MW-3D, SB-8D, and MW-16D). Samples from wells MW-3D and SB-8D are isotopically shifted toward the

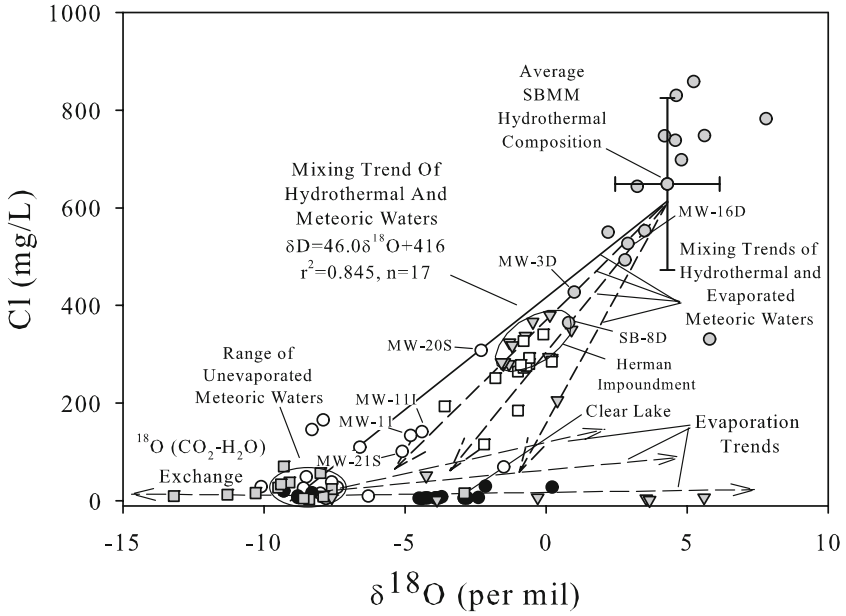

Fig. 5 $\delta^{18}O$ vs. Cl diagram for SBMM surface water, groundwater, and precipitation samples. Definition of symbols provided in Fig. 3

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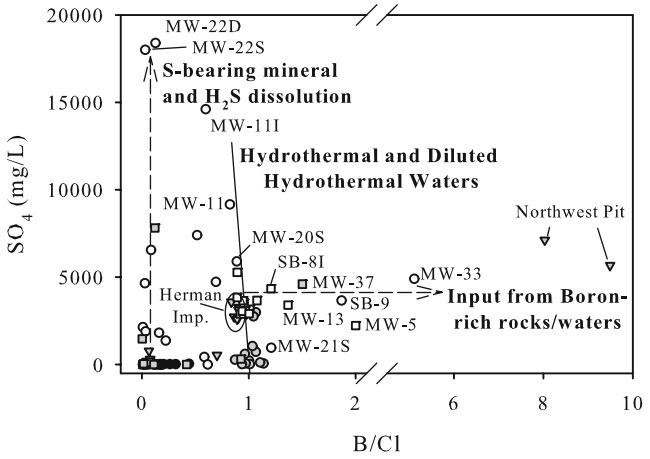

Fig. 6 B/Cl (weight ratio) vs. SO_4 diagram for SBMM surface water, groundwater, and precipitation samples. Note *scale break* on *x*-axis. Definition of symbols provided in Fig. 3

waste-rock dam waters (discussed in the following section) and contain lower B and Cl concentrations than other hydrothermal waters (see Figs. 3, 5). This suggests that water in these wells is a mixture of hydrothermal and waste-rock dam water (Herman Impoundment + meteoric waters). Mixing trends between hydrothermal waters (not including those in the waste-rock dam) and meteoric waters are also shown in Figs. 3 and 5.

Five hydrothermal waters were collected from SBMM and analyzed for ^3H: MW-3D, MW-11D, MW-17D, MW-19D, and Clear Lake 1 Well (Fig. 4). The ^3H concentrations in all of these wells, except for MW-3D (1.72 TU), are less than ~1 TU, indicating they are likely pre-bomb (pre-1952) age, which is typical of hydrothermal waters (Goff and McMurty 2000). The higher ^3H activity in water from MW-3D is consistent with a mixed source of older hydrothermal water and younger waste-rock dam water (discussed in the following section).

Herman Impoundment and other on-site surface waters. These waters include samples from Herman Impoundment and other ponds and impoundments across SBMM. The Herman Impoundment isotopic data plot on a linear $\delta^{18}O$ vs. δD trend (with the exception of one sample from June 1976), between evaporated meteoric water and hydrothermal water, which is roughly parallel to the evaporation trend (Fig. 3). This trend is the evaporation trend for Herman Impoundment and is analogous to the evaporation trend for meteoric waters.

The $\delta^{18}O$ and δD data for the Herman Impoundment samples plot near the local evaporation trend suggesting that meteoric water is its only significant water source. However, comparable average B/Cl values in Herman Impoundment (0.90) and in the hydrothermal water samples (1.02) and elevated B and Cl concentrations (205–380 mg/L and 249–286 mg/L, respectively) suggest that hydrothermal waters are a primary input (Fig. 6). This apparent discrepancy is further examined in section Chemical mass balance and steady-state mixing models for Herman Impoundment and the waste-rock dam.

Temporal trends for $\delta^{18}O$ and Cl from Herman Impoundment and precipitation values from the nearby town of Clearlake (Western Regional Climate Center 2003) from 1954 to 2002 are shown in Fig. 7. This plot demonstrates that the chemistry of Herman Impoundment has remained fairly constant over the last 50 years. However, also noted is a recent trend of decreasing Cl concentration and in ^{18}O (a similar depletion is also noted in D) peaking in 2000, followed by a return to conditions more typically observed at the site by January 2002. The decrease in Cl, ^{18}O, and ^2H occurred after several years of above average precipitation correlated with El Niño events 1994–1995 and 1997–1998. This above-average precipitation produced dilution of Cl, and a shift in $\delta^{18}O$ and δD towards a meteoric end-member. The rapid shift towards higher Cl, ^{18}O, and ^2H in 2001 is correlated with decreased precipitation from 1999 onwards in combination with the installation of a storm-water diversion system in 1999, which reduced the watershed area of Herman Impoundment by ~12%.

The north wetlands may have a minor (~10%) hydrothermal component based on a data point that plots along the mixing trend of hydrothermal and meteoric waters in Fig. 3. Samples from Frog Pond and Green Pond plot along the evaporated meteoric line, generally contain fairly low SO_4 (37–301 mg/L), and exhibit low B/Cl values (0.018–0.076). These waters are likely evaporated meteoric waters with minimal inputs of gas from the hydrothermal system. Lastly, samples from Northwest Pit plot along the local evaporation trend, indicating a meteoric origin, and exhibit a distinct B/Cl (8.031) value suggesting input from a local B-rich source such as interaction with B-rich rocks or mine waste in the area (Fig. 6).

On-site surface waters that were analyzed for ^3H include samples from Herman Impoundment and Frog Pond. Frog Pond has a ^3H concentration similar to that of

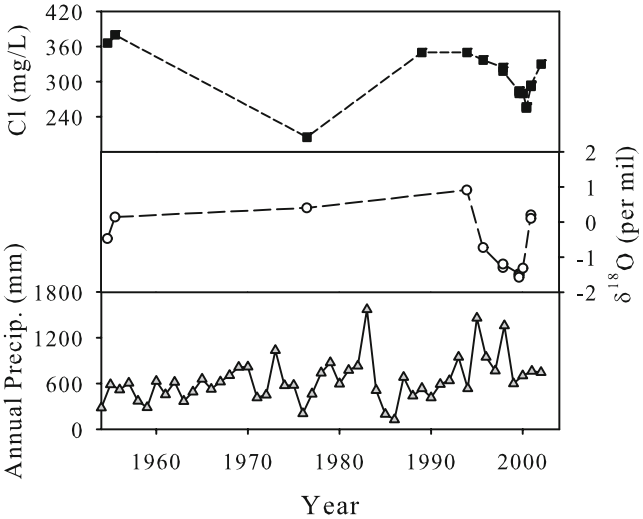

Fig. 7 Temporal trends in $\delta^{18}O$ and Cl in Herman Impoundment and annual precipitation in Clearlake, California from 1954 to 2002

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rainwater, indicating that the residence time for meteoric water in the pond is fairly short relative to the decay rate of ^{3}H. Samples from Herman Impoundment water plot above the mixing line for hydrothermal and meteoric waters suggesting an input of ^{3}H-rich groundwaters (recharged between circa 1952 and 1992) such as the water sampled in SB-8I (Fig. 4).

Waste-rock dam water. Waste-rock dam waters were fairly homogenous chemically, exhibiting a chemical composition similar to Herman Impoundment water—low pH (2.63–6.24), high SO_4 (2,220–5,280 mg/L), B/Cl near 1. Previous workers (Goff and Bergfeld 1997; Jewett et al. 2000b) argued that the groundwater in the waste-rock dam is a mixture of Herman Impoundment water (evaporated meteoric water + hydrothermal water) and shallow groundwater (unevaporated meteoric water). The $\delta^{18}O$-δD and Cl- $\delta^{18}O$ data for waste-rock dam waters plot on a trend between Herman Impoundment and meteoric water (see Figs. 3 and 5) and exhibit a B/Cl value (0.890-2.000) similar to Herman Impoundment (0.861–0.979; Fig. 6), which supports this previous interpretation. The composition of waste-rock dam waters appears to be dominated primarily by Herman Impoundment water, with an increasing meteoric influence in certain areas, especially on the northern and southern ends of the waste-rock dam (e.g., SB-8S, MW-4, MW-5, and HP14), indicating a mix of waste-rock dam waters with upland meteoric and background groundwaters.

Five waters were sampled for ^{3}H in the waste-rock dam: MW-3S, MW-6, MW-9, HP14, and SB-8I (Fig. 4). The first four of these samples were collected from wells screened in the waste-rock dam water-bearing unit and exhibit nearly identical ^{3}H concentrations (2.67–2.91 TU) and chemistries. This suggests that the water in these wells is derived from a common source (Herman Impoundment + meteoric water) and the travel time between these wells is relatively short (e.g., a couple of years). Monitoring well SB-8I is screened in the underlying andesite water-bearing unit; the sample collected from SB-8I exhibits a ^{3}H concentration (4.27 TU) that is markedly larger than the other waste-rock dam water samples (2.67–2.91 TU). These results suggest that the waste-rock dam water-bearing unit exhibits limited, if any, hydrogeologic connection with the underlying andesite water-bearing unit.

Acid-rock drainage. The acidic surface waters and groundwaters that are found in mine wastes at SBMM are very distinct from waters in the waste-rock dam (see Figs. 3, 5, and 6). The acid-rock drainage waters are characterized by neutral to strongly acidic pH (3.02–6.46), a large range in SO_4 concentrations (2–18,400 mg/L) and low B concentrations (<3.70 mg/L). Most of these waters plot with the unevaporated meteoric waters, indicating they are meteoric in origin (Fig. 3). The source of the SO_4 and low pH in some of the samples is likely a result of reaction with sulfide and sulfate minerals. Water samples from wells MW-21S and MW-20S plot along mixing trends of hydrothermal and meteoric waters (Figs. 3 and 5) and have B/Cl values similar to hydrothermal fluids (Fig. 6) suggesting significant input of hydrothermal waters. Simple mixing calculations indicate that these samples may contain up to ~40% hydrothermal water (Figs. 3 and 5). Results for $\delta^{18}O$-δD data from MW-17S fall below this mixing line, indicating that this water sample contains a significant component of hydrothermal waters depleted with respect to ^{2}H. However, the B/Cl value of water from this well (0.516) is too low to support a large hydrothermal input. Samples from wells MW-11 and MW-11I, located on the northern end of the waste-rock dam, exhibit $\delta^{18}O$-δD concentrations that plot on the same trend as the waste-rock dam groundwater. This suggests that these waters are a mixture of Herman Impoundment water (43–49%) and unevaporated, meteoric water (51–57%). Additional evidence for input from Herman Impoundment is the similarity in B/Cl values between these samples and Herman Impoundment waters (Fig. 6). A sample collected from MW-33 exhibits a B/Cl value (5.110) similar to that of Northwest Pit (8.031), which is located just upgradient of the well, suggesting that the pit is the dominant source for water to this well, or that there is a source of elevated B proximal to both locations.

Samples of four acid-rock drainage waters were analyzed for ^{3}H (MW-11I, MW-22S, MW-22D, and MW-23S). The ^{3}H level in MW-11I (3.14 TU) is slightly lower than the composite rainfall sample (Fig. 4). This is consistent with a water source of a mixture of waste-rock dam and young acid-rock drainage waters. The ^{3}H concentrations in samples from MW-22S and MW-22D are slightly higher than the rainwater (~3.9 TU). Tritium concentrations vary seasonally (Goff et al. 1993) and these waters may have been recharged within the last few years when ^{3}H concentrations in rain were slightly higher. If the ^{3}H level in these waters was not from recent precipitation, the waters were probably recharged prior to ~1985. The water in MW-23S contains only 1.15 TU of ^{3}H, indicating that it was recharged prior to ~1952. The old age of this water relative to its proximity to the waste-rock pile on the northeast portion of the site indicates that groundwater flow in this area is slow.

Seasonal variation in water sources

Water elevation, $\delta^{18}O$, and δD data for six wells (HP14, MW-5, MW-9, MW-19D, MW-22S, and MW-29S) were collected monthly from December 2000 to May 2001 to assess the contribution of meteoric infiltration to groundwater near these wells (Fig. 8, Table 1). Acid-rock drainage water samples from MW-29S and MW-22S plot on the meteoric water line and exhibited little variation in $\delta^{18}O$ and δD values over the study period, indicating that meteoric water is the dominant water source to these wells. In these two wells, water-level elevation increases of greater than 1.5 m were observed through the course of the study suggesting that rapid groundwater recharge via infiltration of meteoric waters occurred. Waters from a waste-rock dam well adjacent to Herman Impoundment

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(MW-9) and a hydrothermal well (MW-19D) show very little shift in isotopic composition towards meteoric waters and relatively small increases in water elevation (0.9 and 0.3 m, respectively). These findings suggest that despite roughly 500 mm of precipitation during the study, only minimal meteoric infiltration occurred at these two locations. Samples from HP14 and MW-5, both waste-rock dam waters collected on the west side of the waste-rock dam, show a dramatic shift in isotopic composition towards meteoric water, peaking in March, and declining in April and May. This finding agrees well with water-elevation data which identified a ~1 m increase between February and March as a result of local meteoric recharge, followed by a stabilization in April and decline in May.

These results suggest that seasonal precipitation events do affect the amount of meteoric input in the acid-rock drainage samples and the waste-rock dam waters distal to Herman Impoundment. These findings also indicate that waste-rock dam waters, adjacent to and dominated by Herman Impoundment water, are not dominated by meteoric infiltration, and that hydrothermal waters are not significantly diluted by meteoric waters during recharge.

Chemical mass balance and steady-state mixing models for Herman Impoundment and the waste-rock dam

Simple mass balance estimates using B and Cl suggest that the composition of Herman Impoundment is a mixture of 42–45% hydrothermal water and 55–58% evaporated meteoric water (Table 2). These calculations agree well with previous estimates using similar methods (White and Roberson 1962; Goff et al. 1993). Identical calculations using the δD and $\delta^{18}O$ data are more difficult to interpret (Table 2); the isotopic composition of Herman Impoundment may be affected by evaporation and isotopic exchange with hydrothermal gases (e.g., CO_2, CH_4).

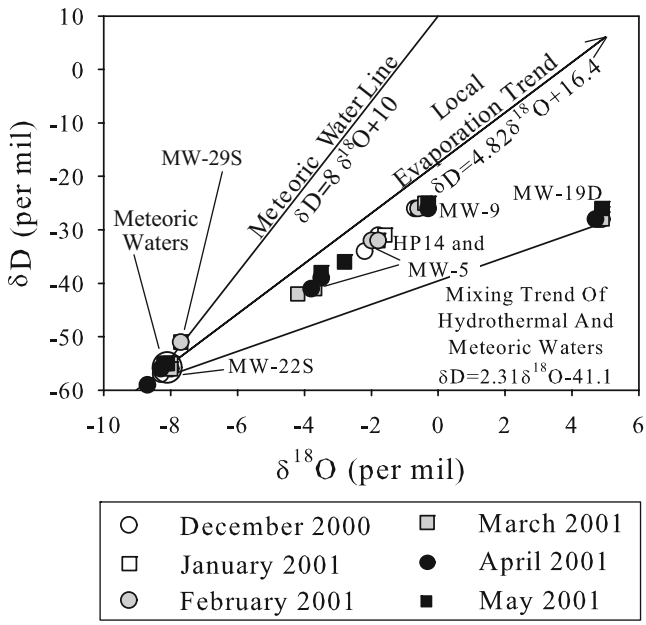

Fig. 8 $\delta^{18}O$ vs. δD diagram for monthly groundwater samples collected from six wells during December 2000 to May 2001

However, assuming that isotopic exchange with hydrothermal gases has a negligible isotopic influence, the proximity of the δD and $\delta^{18}O$ data to the local evaporated meteoric water line in Fig. 3 indicates that the composition of Herman Impoundment is dominated (>90%) by input of meteoric sources that have been evaporated, with minimal input of hydrothermal system water. In this scenario, the high concentrations of B and Cl in Herman Impoundment would result from evaporation rather than hydrothermal water input.

To evaluate the likeliness of a near-equal input of meteoric water scenario vs. an evaporated meteoric dominated scenario, a reservoir mixing model that determines steady-state concentrations of B in Herman Impoundment was developed. Boron was chosen for this model because it is behaves conservatively in most environments and dissolved concentrations in surface water (using results for Frog Pond, Terminal Pond, and Green pond; mean=0.3 mg/L), precipitation—typically <0.1 mg/L using data from Boyd and Walley (1972) and Demuth and Heumann (1999)—and upgradient meteoric groundwater (mean=1.8 mg/L) are similar relative to concentrations in hydrothermal waters (B=660±143 mg/L for water samples not under the waste-rock dam).

A water mass balance for Herman Impoundment is given by:

$$Q_{GWOUT}+Q_{EVAP}= Q_{HTIN}+Q_{GWIN}+Q_{PPT}+Q_{SWIN}+S \quad (1)$$

where Q_{GWOUT} is the groundwater flow leaving Herman Impoundment through the waste-rock dam (L^3/T), Q_{EVAP} is evaporation rate from Herman Impoundment (L^3/T), Q_{HTIN} is the inflow of hydrothermal water (L^3/T), Q_{GWIN} is the inflow of regional and acid-rock drainage groundwater (L^3/T), Q_{PPT} is the direct average precipitation into Herman Impoundment (L^3/T), Q_{SWIN} the average flow of surface water into Herman Impoundment (L^3/T), and S is change in water storage (volume) of Herman Impoundment (L^3/T). Assuming the volume of Herman Impoundment is constant (S=0) and lumping inputs from waters of meteoric origin, the formula is reduced to

$$Q_{GWOUT}+Q_{EVAP}= Q_{HTIN}+Q_{MET} \quad (2)$$

where Q_{MET} is the input of precipitation, meteoric groundwaters, and meteoric surface waters into Herman Impoundment (L^3/T). This equation can be re-written where the input terms are portions of the total flow:

$$Q_{GWOUT}+Q_{EVAP}= X_{HT}Q_{Total}+X_{MET}Q_{Total} \quad (3)$$

where X_{HT} is the fraction of the total input from hydrothermal waters, X_{MET} is the fraction of the total input from meteoric waters, and Q_{Total} is the total flow into or out

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Table 1 Monthly stable isotope and water elevation data from December 2000 through May 2001

Well	Date	$\delta^{18}O$ per mil	δD per mil	Water elevation (meters)	Change (meters)
HP14	19-Dec-2000	−1.8	−31	402.237	–
	16-Jan-2001	−1.6	−31	402.316	0.079
	13-Feb-2001	−2	−32	402.441	0.125
	12-Mar-2001	−4.2	−42	403.429	0.988
	11-Apr-2001	−3.5	−39	403.450	0.021
	15-May-2001	−3.5	−38	403.377	−0.073
MW-5	12-Dec-2000	−2.2	−34	402.304	–
	16-Jan-2001	−1.8	−32	402.377	0.073
	13-Feb-2001	−1.8	−32	402.518	0.140
	12-Mar-2001	−3.7	−41	403.548	1.030
	11-Apr-2001	−3.8	−39	403.590	0.043
	15-May-2001	−2.8	−36	403.511	−0.079
MW-9	14-Dec-2000	−0.7	−26	403.289	–
	16-Jan-2001	−0.6	−26	403.374	0.085
	13-Feb-2001	−0.6	−26	403.514	0.140
	12-Mar-2001	−0.4	−25	404.163	0.649
	11-Apr-2001	−0.3	−26	404.200	0.037
	15-May-2001	−0.3	−25	404.169	−0.030
MW-19D	18-Dec-2000	4.8	−28	407.876	–
	16-Jan-2001	4.9	−27	407.687	−0.189
	14-Feb-2001	4.9	−28	407.882	0.195
	13-Mar-2001	4.9	−28	408.031	0.149
	12-Apr-2001	4.7	−28	408.165	0.134
	15-May-2001	4.9	−26	408.147	−0.018
MW-22D	22-Dec-2000	−8.3	−57	402.069	–
	16-Jan-2001	−8	−55	402.219	0.149
	14-Feb-2001	−8	−56	402.280	0.061
	12-Mar-2001	−8	−56	403.322	1.042
	11-Apr-2001	−8.3	−56	403.289	−0.034
	15-May-2001	−8.1	−55	404.691	1.402
MW-29S	22-Dec-2000	–	–	402.801	–
	16-Jan-2001	−7.7	−51	402.758	−0.043
	13-Feb-2001	−7.7	−51	402.835	0.076
	13-Mar-2001	–	–	404.685	1.850
	12-Apr-2001	−8.7	−59	404.233	−0.451
	15-May-2001	−8.2	−55	404.270	0.037

of Herman Impoundment (L^3/T). Using average historical evaporation data (1.72 m/yr raw, 1.20 m/yr adjusted) from nearby Class-A pan locations (Berryessa Lake, Lake Solano, Markley Cove, Monticello Dam, and Warm Springs Dam; from the Western Regional Climate Center 2003) and a pan coefficient of 0.7 to adjust for radiation on pan walls and heat exchange with pan material, Q_{EVAP} is estimated at 1.02×10^5 m^3/yr. This evaporation rate compares reasonably well to the range calculated for Clear Lake (0.92–1.0 m/yr) in the previous Chemical characterization of SBMM waters section. Several physical and geochemical methods have previously been used to estimate Q_{GWOUT} at 1.40×10^4 to 2.17×10^5 m^3/yr (Jewett et al. 2000a). Therefore, Q_{Total} is chosen to range from 1.16×10^5 to 3.19×10^5 m^3/yr.

A mass balance to determine annual change in B mass in Herman Impoundment is given by:

$$\begin{aligned} &M_{T=n} + M_{HTIN} + M_{SWIN} + M_{GWIN} + M_{PPT} \\ &\quad - M_{GWOUT} + \Delta M = M_{T=n+1} \end{aligned} \tag{4}$$

where $M_{T=n}$ is the mass of B in Herman Impoundment at the start of year n (M), M_{HTIN}, M_{SWIN}, M_{GWIN}, and M_{PPT} are annual average input of B into Herman Impoundment from hydrothermal waters, meteoric surface waters, meteoric groundwaters, and precipitation (M), M_{GWOUT} is the annual removal of B via groundwater leaving Herman Impoundment through the waste-rock dam (M), ΔM is the gain or loss of B due to chemical reactions (e.g., mineral precipitation, sorption, mineral dissolution, etc.), and $M_{T=n+1}$ is the mass of B in Herman Impoundment at the start of year n+1 (M). This equation is simplified by lumping all meteoric sources and assuming that B is chemically conservative (ΔM=0):

$$M_{T=n} + M_{HTIN} + M_{MET} - M_{GWOUT} = M_{T=n+1} \tag{5}$$

where M_{MET} is the annual input of B from precipitation, meteoric groundwater, and meteoric surface water (M). By substituting concentration and volume terms for mass terms and combining terms from Eq. (3), the model becomes:

$$\begin{aligned} &M_{T=n} + C_{HTIN}X_{HT}Q_{Total} + C_{METIN}X_{MET}Q_{Total} \\ &\quad - Q_{GWOUT}(M_{T=N}/V_{Total}) = M_{T=n+1} \end{aligned} \tag{6}$$

where C_{HTIN} is the average B concentrations in hydrothermal waters (660 mg/L), C_{METIN} is the average B concen-

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Table 2 Results from mixing calculations for Herman Impoundment and waste-rock dam waters

Contributions of hydrothermal and meteoric waters in Herman Impoundment water				
Hydrothermal waters[a]		Meteoric groundwaters[b]		Herman Impoundment
Avg. Cl (mg/L)	% of mixture	Avg. Cl (mg/L)	% of mixture	Avg. Cl (mg/L)
656	44.9	22.4	55.1	307
Avg. B (mg/L)	% of mixture	Avg. B (mg/L)	% of mixture	Avg. B (mg/L)
660	41.9	1.0	58.1	277.1
Avg. $\delta^{18}O$	% of mixture	Avg. $\delta^{18}O$[c]	% of mixture	Avg. $\delta^{18}O$
4.89	60.7	−9.1	39.3	−0.60
Avg. δD	% of mixture	Avg. δD[c]	% of mixture	Avg. δD
−29.6	NA	−60.0	NA	−25.2
Contributions of Herman Impoundment and meteoric waters to waste-rock dam water				
Herman Impoundment		Meteoric recharge[b]		Waste rock dam waters
Avg. Cl (mg/L)	% of mixture	Avg. Cl (mg/L)	% of mixture	Avg. Cl (mg/L)
307	83.9	22.4	16.1	261
Avg. B (mg/L)	% of mixture	Avg. B (mg/L)	% of mixture	Avg. B (mg/L)
277	97.4	1.88	2.6	270
Avg. $\delta^{18}O$	% of mixture	Avg. $\delta^{18}O$[c]	% of mixture	Avg. $\delta^{18}O$
−0.60	94.6	−9.1	5.4	−1.05
Avg. δD	% of mixture	Avg. δD[c]	% of mixture	Avg. δD
−25.2	87.5	−60.0	12.5	−29.1

[a] Average for hydrothermal water samples, excluding those below the waste-rock dam

[b] Average of all meteoric groundwaters that occur along flowpaths toward Herman Impoundment

[c] Isotopic composition of composite sample collected from SBMM rain gauge

trations in meteorically-derived waters (1 mg/L), and V_{Total} is the total volume of water in Herman Impoundment (1.9×10^6 m^3).

This model for estimating steady-state concentration of B (Eq. 6) was run by iteratively calculating $M_{T=n+1}$ for n=0, then using that value for $M_{T=n}$ to calculate a new value for $M_{T=n+1}$ for n=1. This process was repeated for a period of 100 yrs (n=100). Resulting $M_{T=n}$ estimates were converted to average B concentration by dividing by V_{TOTAL}. Different scenarios modeled a range in X_{HT} (and thus X_{MET}) from the B, Cl, δD and $\delta^{18}O$ data of (0.05–0.6) and a range of Q_{GWOUT} estimates from the literature (1.40×10^4, 5.0×10^4, 1.0×10^5, and 2.17×10^5 m^3/yr; as summarized in Jewett et al. 2000a). It was assumed that the starting composition (T=0) of Herman Impoundment is equal to the assumed proportion of X_{HT} and X_{MET} for the modeled conditions.

Output from the model are summarized in Table 3 and an example from one set of model calculations is provided in Fig. 9. Final B concentrations (T=100) for all modeling scenarios using flow rates of 1.40×10^4 and 5.0×10^4 m^3/yr, were non-steady and increased throughout the modeling period as a result evaporation dominating water loss from Herman Impoundment, producing B enrichment. However, the composition of Herman Impoundment has not become increasingly concentrated in conservative constituents over the past 50 yrs (Fig. 7) suggesting that the actual annual average GW_{OUT} from Herman Impoundment is greater than 5.0×10^4 m^3/yr. The modeling scenarios that best fit the data used GW_{OUT} estimates of 1.0×10^5 and 2.17×10^5 m^3/yr (corresponding to a residence time of 6.0–9.4 yrs), achieving steady-state B concentration equal to present levels (286 mg/L) using an X_{HT} of 0.21 and 0.29, respectively. This indicates that hydrologic sources to Herman Impoundment are approximately 71–79% meteoric water and 21–29% hydrothermal water, with evaporation being significant enough to moderately overestimate input of hydrothermal waters using B and Cl mass balance estimates. These findings also suggest that the $\delta^{18}O$ isotopic composition of Herman Impoundment underestimates the contribution of water from the hydrothermal system as a result of ^{18}O depletion in the water during gas-water isotopic exchange.

Because water-gas isotopic exchange and evaporation are negligible for the waste-rock dam waters, which are a mixture of Herman Impoundment and meteoric waters, simple mass balance mixing estimates using B, Cl, δD and $\delta^{18}O$ can be applied. Results for this calculation using the data collected in December of 2000 are shown in Table 2. The four tracers provide similar results; waste-rock dam waters are composed of 84–97% Herman Impoundment water and 3–16% meteoric water. However, as noted in Fig. 8, the input of infiltration on the waste-rock dam waters on the west side (down gradient) of the waste-rock dam and meteoric waters via groundwater flow from the north and south increased during seasonal recharge. Estimates of contributions from Herman Impoundment and meteoric waters in the waste-rock dam from Fig. 8 indicate that the input from meteoric water increased from a few percent in December to >40% in March, then declined in April and May. Given that Herman Impoundment waters are roughly 75% meteoric water and 25% hydrothermal waters, contribution to waste-rock dam waters range from ~23% hydrothermal/~77% meteoric input during the winter to 15% hydrothermal/85% meteoric input in the early spring, with declining meteoric input into late spring and early summer.

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Table 3 Results from Herman Impoundment mixing model for boron

GW_{out} flow rate (m^3/yr)	X_{HT}	Final B concentration[a] (mg/L)
2.17E+05	50	486
	40	389
	30	292
	20	195
	10	98
	5	50
1.00E+05	50	667
	40	534
	30	401
	20	268
	10	135
	5	69
5.00E+04	50	957[b]
	40	766[b]
	30	575[b]
	20	385[b]
	10	194[b]
	5	98[b]
1.40E+04	50	1,576[b]
	40	1,262[b]
	30	948[b]
	20	633[b]
	10	319[b]
	5	162[b]

[a] Concentrations are provided for T=100 yrs

[b] Indicates that boron concentrations did not achieve steady-state by T=100

Summary

This study provides constraints on groundwater flow at SBMM by investigating environmental tracers (B, Cl, SO_4, $\delta^{18}O$, δD, and ^3H) in water samples to examine water sources, mixing calculations, seasonal variations in meteoric input to groundwaters, and relative ages of groundwaters. The data demonstrated that the SBMM hydrologic system is complex; processes including mixing, hydrothermal system input, evaporation, and possibly hydrothermal gas–water isotopic exchange with CO_2 and CH_4 were identified.

The chemical and isotopic composition of hydrothermal and Herman Impoundment waters have remained fairly constant since the mid-1950s, indicating that the hydrology of the site has achieved a relatively stable steady-state condition. However, yearly variances in the meteoric component of Herman Impoundment water were observed, correlating with temporal changes in regional precipitation. Tritium analysis showed mixing and relative ages of SBMM groundwaters. Most waters on site appeared to be fairly modern (recharged after ~1990), except for a few regional and most hydrothermal groundwaters that are likely older than circa 1952.

Six monthly analyses of $\delta^{18}O$ and δD and corresponding water level measurements in six wells across the site showed that infiltrating precipitation produced dramatic increases in water levels and meteoric component in waste-rock dam water on the west side of the waste-rock dam (further along the flow path) and in acid-rock drainage waters. However, samples of waste-rock dam waters adjacent to Herman Impoundment and hydrothermal waters show minimal meteoric influence during recharge.

Results for water-source assessments and simple mixing calculations generally agreed with previous conceptual models, where hydrothermal waters mix with meteoric surface waters and groundwaters in Herman Impoundment, flow through the waste-rock dam, and mix with infiltrating meteoric water—30–45% hydrothermal, 70–55% meteoric; (Jewett et al. 2000a, b). Results from a reservoir mixing model for B in Herman Impoundment suggest that approximately 71–79% of input to Herman Impoundment is from meteoric waters (precipitation, meteorically-derived groundwater, and runoff) and the remainder is from the underlying hydrothermal system (21–29%). Discrepancy between the two estimates can be attributed to evaporative water losses which may moderately overestimate hydrothermal inputs in the simple mixing estimates. The B modeling results also suggest that the annual average groundwater outflow from Herman Impoundment is roughly 1.10×10^5 to 2.17×10^5 m^3/yr (corresponding to a residence time of 6.0–9.4 yrs). Chemical mass balance estimates, indicate that Herman Impoundment waters are diluted by an additional 3% to >40% by meteoric infiltration through the waste-rock dam, increasing along the flow path, prior to flowing into Clear Lake.

Results for this study demonstrate that environmental tracers are an effective tool for providing independent checks and constraints on water sources, mixing, and flow in complex hydrologic systems. Hydrologic, geochemical, and geophysical comparison and characterization of a site is beneficial in developing a reliable hydrologic model. Thus, environmental tracer studies of contaminated hydrologic systems such as this, contribute significant information about several aspects of the site

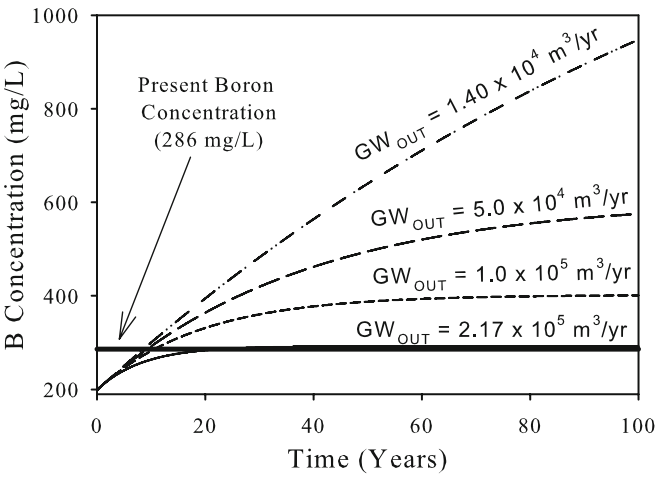

Fig. 9 Modeled concentrations of B in Herman Impoundment for X_{HT}=0.3, X_{MET}=0.7, and Q_{Total}=1.40×10^4 m^3/yr to 2.17×10^5 m^3/yr. This figure demonstrates that when Q_{Total} ≤5.0×10^4 m^3/yr, the model indicates that B concentrations in Herman Impoundment would not achieve a steady-state and would greatly exceed measured concentrations

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and play an essential role in developing a hydrologic model that helps allow for the development of effective remedial strategies and meaningful use of resources dedicated for cleanup.

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