



Hydrothermal contamination of public supply wells in Napa and Sonoma Valleys, California



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ARTICLE INFO

Article history:

Received 11 July 2012

Accepted 15 January 2013

Available online 7 February 2013

Editorial handling by Peter Birkle

ABSTRACT

Groundwater chemistry and isotope data from 44 public supply wells in the Napa and Sonoma Valleys, California were determined to investigate mixing of relatively shallow groundwater with deeper hydrothermal fluids. Multivariate analyses including Cluster Analyses, Multidimensional Scaling (MDS), Principal Components Analyses (PCA), Analysis of Similarities (ANOSIM), and Similarity Percentage Analyses (SIMPER) were used to elucidate constituent distribution patterns, determine which constituents are significantly associated with these hydrothermal systems, and investigate hydrothermal contamination of local groundwater used for drinking water. Multivariate statistical analyses were essential to this study because traditional methods, such as mixing tests involving single species (e.g. Cl or SiO₂) were incapable of quantifying component proportions due to mixing of multiple water types. Based on these analyses, water samples collected from the wells were broadly classified as fresh groundwater, saline waters, hydrothermal fluids, or mixed hydrothermal fluids/meteoric water wells. The Multivariate Mixing and Mass-balance (M3) model was applied in order to determine the proportion of hydrothermal fluids, saline water, and fresh groundwater in each sample. Major ions, isotopes, and physical parameters of the waters were used to characterize the hydrothermal fluids as Na–Cl type, with significant enrichment in the trace elements As, B, F and Li. Five of the wells from this study were classified as hydrothermal, 28 as fresh groundwater, two as saline water, and nine as mixed hydrothermal fluids/meteoric water wells. The M3 mixing-model results indicated that the nine mixed wells contained between 14% and 30% hydrothermal fluids. Further, the chemical analyses show that several of these mixed-water wells have concentrations of As, F and B that exceed drinking-water standards or notification levels due to contamination by hydrothermal fluids.

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1. Introduction

Groundwater quality in the ~2600 km² North San Francisco (NSF) Bay study unit (Fig. 1) was investigated from August to November, 2004 and again in November 2007 as part of the Priority Basin Project of the California State Water Board's Groundwater Ambient Monitoring and Assessment (GAMA) Program (Belitz et al., 2003; <http://ca.water.usgs.gov/gama/>). Details of sample collection, analyses and quality-assurance procedures are described by Kulongoski et al. (2006). Here, the data from 44 wells in Napa, Sonoma and Marin Counties were used to identify the primary constituents associated with deep hydrothermal fluids.

Multivariate analyses were applied in order to elucidate constituent distribution patterns, determine which constituents are significantly associated with hydrothermal systems, and quantify the contribution of the hydrothermal system to groundwater used

for drinking-water supply. Multivariate statistical methods can help elucidate groundwater flow in complex aquifer systems, particularly when integrated with information regarding geological and hydrological settings (e.g. Farnham et al., 2000; Stetzenbach et al., 2001; Cloutier et al., 2008). Principal Components Analyses (PCA) have been applied to several large and complex water quality datasets obtained from groundwater monitoring studies (e.g. Cruz and Franca, 2006; Kouras et al., 2007). Multi-sample graphical techniques such as Piper plots, used in tandem with PCA and Cluster Analyses, can also facilitate the classification of large numbers of water samples into major groups, help determine the factors affecting groundwater quality, and assist with the identification of water–rock interaction and groundwater redox conditions (Melloul and Collin, 1992; Schot and van der Wal, 1992; Güler et al., 2002).

Relatively few studies have attempted to quantify mixing between deep hydrothermal systems and public supply aquifers. Near the geothermal field of Los Azufres in Mexico, Birkle and Merkel (2000) investigated the lateral extent and distribution of constituents

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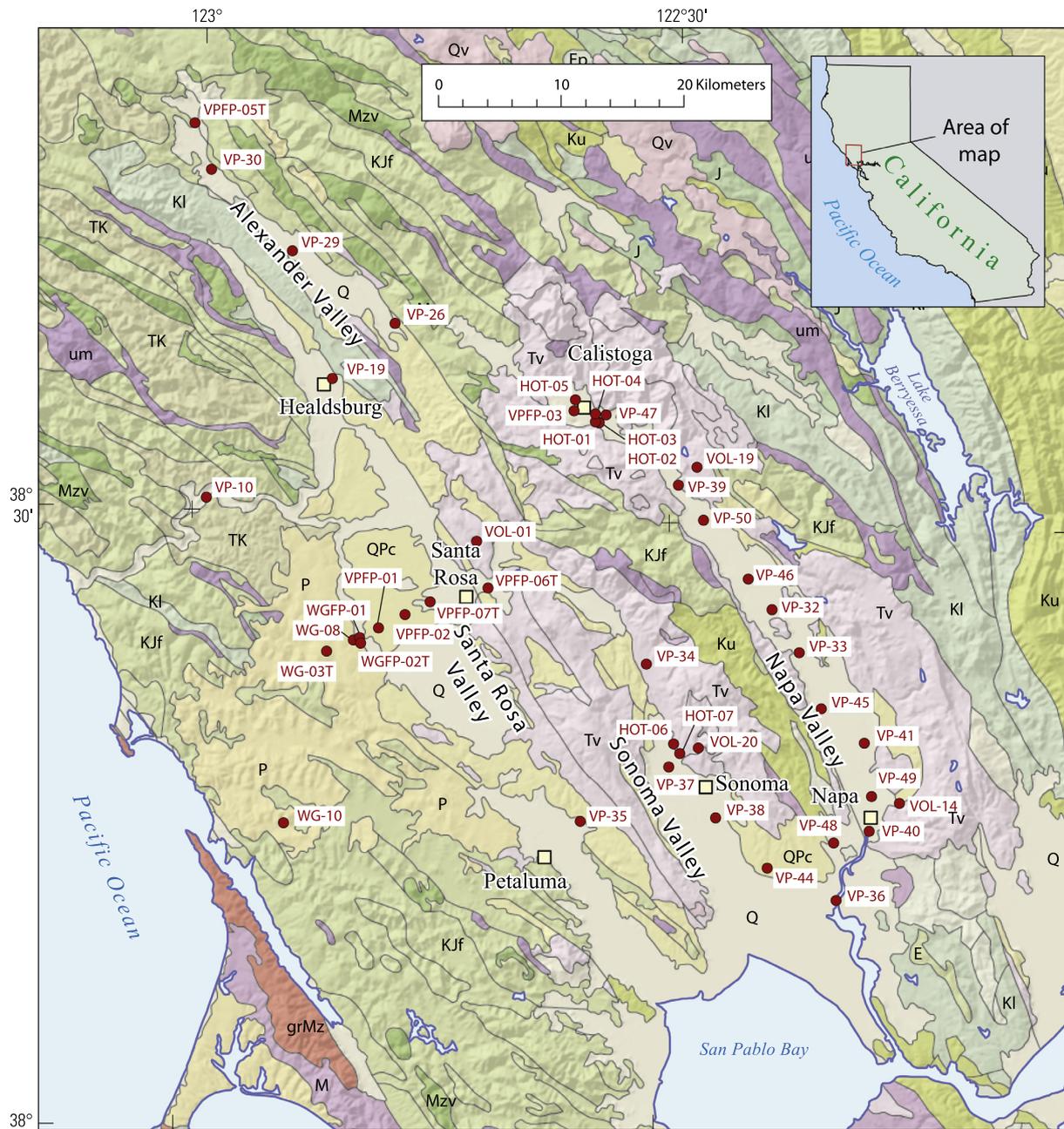


Fig. 1. Geologic map of the North San Francisco Bay study unit with locations of sampled wells (from Kulongoski et al., 2010).

associated with the hydrothermal system, finding that W, Li, Cs, Mo, As and B are suitable tracers of hydrothermal contamination, and that rivers discharge these elements as far as 10 km away. In Ethiopia's central Rift Valley Region, Reimann et al. (2003) documented that the deepest drinking water wells have elevated concentrations of As, B, F, Ge, I, Li, Mo, Na, Rb, Sb, Ta, U and W due to a hydrothermal component in the groundwater. Aksoy et al. (2009) investigated shallow groundwater contamination in the Balcova Geothermal system in Izmir, Turkey, and found that the cold groundwater in the alluvial aquifer mixes with hydrothermal fluids, resulting in elevated concentrations of As, Sb and B. Near the Akarcay Basin in Turkey, Dogdu and Bayari (2005) investigated the impact of thermal water on ground and surface waters, and found that mixing with hydrothermal fluids results in higher electrical conductivity, warmer temperatures, and elevated concentrations of Na, Cl, Fe, Li, B, Br, Mn, Al, I and As.

The elements F and As are often useful in determining whether hydrothermal contamination is occurring, despite the fact that

they may be affected by water–rock interaction (Mahon, 1970; Aiuppa et al., 2003). Fluoride is often highly enriched in hydrothermal fluids (Ellis and Mahon, 1967; Dissanayake, 1991; Reimann et al., 2003; Shitumbanuma et al., 2007), commonly exceeding the US EPA Maximum Contamination Level (MCL) for drinking water of 4.0 mg/L. Water at high temperatures can also leach As from rock, which explains the high concentrations of As in many hydrothermal fluids – often exceeding the MCL for drinking water of 10 µg/L. Angelone et al. (2009) found that the occurrence of As in groundwater of the Cimino-Vico volcanic area in central Italy is mainly connected with upflowing fluids from deep hydrothermal systems, with the highest As concentrations in thermal springs and wells.

Hydrothermal contamination of public supply aquifers may have serious ramifications because As has been linked to cancer of the bladder, lungs, skin, kidney, nasal passages, liver and prostate, and elevated F in drinking water may lead to increased

likelihood of bone fractures in adults and mottling and pitting in tooth enamel in children (US EPA, 2006). Boron has also been classified as a pollutant of drinking water in national and international drinking water legislation (WHO, 1998 Guidelines: 2.4 mg/L, EU Directive, 1998 98/83/EC: 1 mg/L). The California Department of Public Health Drinking Water Program Notification Level for B is 1.0 mg/L. Boron also affects the health and production of certain plants (Nable et al., 1997), and becomes toxic for sensitive crops (e.g. avocado, citrus fruits) at concentrations >1 mg/L in irrigation water (Kloppmann et al., 2005).

1.1. Hydrogeologic setting

The NSF study unit (Fig. 1) extends from Alexander Valley in the north to the San Francisco Bay (San Pablo Bay) in the south, and includes most of the alluvium-filled basins that result from a series of NW-trending structural depressions in the southern part of the Coast Ranges of northern California (Bailey et al., 1964; Fox, 1983). Mountain ranges 300–1200 m in altitude bound the study area to the north and east, and separate the Napa Valley, Sonoma Valley and the Santa Rosa Plain. The San Francisco Bay bounds the study area to the south, and the Wilson Grove Formation Highlands bounds the study area to the west. The valleys consist of a relatively thin cover of Quaternary alluvium overlying a thick section of Neogene volcanics and sedimentary rocks, Cretaceous sedimentary rocks, Franciscan Complex sedimentary and metamorphic rocks, and Jurassic serpentinite (Bailey et al., 1964; Fox, 1983). In these valleys, the main water-bearing unit is the alluvium and underlying Neogene sedimentary and volcanic rocks. The thickness of alluvium increases from north to south and from the margin of the valleys towards the rivers. In most valleys, the thickness of the alluvium ranges from less than 3 m to more than 90 m. Water in the alluvium is generally unconfined and moves under a natural hydraulic gradient, reflecting the surface topography (Faye, 1973). Groundwater recharge to the alluvial aquifers occurs by stream-channel infiltration beneath the major rivers and their tributaries, and by direct infiltration of precipitation on alluvial fans.

The climate in the study area is characterized by warm, dry summers and cool, moist winters. The National Climate Data Center station in Sonoma reports the average annual temperature of 15 °C, and the average annual precipitation of 0.76 m, occurring as rain during the winter and early spring. However, the distribution of precipitation across the study area depends on the topography, as precipitation increases with altitude.

1.2. Napa Valley-Calistoga hydrothermal system

The hydrothermal system near Calistoga is thought to be two or more hydrothermal convection systems (Youngs et al., 1980) that are associated with faulting along the axis of the upper Napa Valley at Calistoga (Fig. 1). In this system it appears that heated meteoric water ascends along fault or fracture zones to near surface depths. Measured temperatures of wells and springs range from 20 to 130 °C (Murray, 1996). Drilling and well tests by Taylor et al. (1981) support this hypothesis, and show the highest temperature surficial waters coinciding with projected traces of faults. Detailed gravity surveys identified two negative gravity anomalies in the upper Napa Valley, the larger of which is located approximately 1 km SW of Calistoga (Chapman et al., 1982). According to Murray (1986), the gravity anomaly near Calistoga may represent partially molten silicic volcanic rock intruded into the higher density rock of the Franciscan Formation at a depth of 1–2 km. Murray et al. (1985) also suggested that these gravity anomalies may represent shallow magma chambers that were the source of the late Pliocene–Pleistocene volcanic sequences in the Calistoga–Clear Lake region, and that residual heat from these, now-crystallized, shallow intrusive rocks,

may be the heat source for the hydrothermal activity at Calistoga. Murray (1996) found that the upper Napa Valley hydrothermal fluids are distinguished by elevated concentrations of Na (>170 mg/L), Cl (>180 mg/L), B (>8 mg/L), and F (>7 mg/L), while the non-hydrothermal waters of the shallow unconfined aquifer are Ca–Mg–HCO₃ type waters with relatively high concentrations of Mg, Ca, Fe, SO₄ and HCO₃ (Murray, 1996; Kulongoski et al., 2010).

1.3. Sonoma Valley hydrothermal system

In Sonoma Valley, hydrothermal fluids with temperatures ≥20 °C, have been identified in wells and thermal springs across an area that extends north from Sonoma (Fig. 1), and includes Fetter's Hot Springs, Boyes Hot Springs, and Agua Caliente (Waring, 1915; California Division of Mines and Geology, 1984). The north Sonoma hydrothermal system was constrained to depths from 15.2 to 167.6 m (50–550 ft) below land surface based on temperature gradient data from wells (Farrar et al., 2006). Hydrothermal fluids in the southern part of Sonoma Valley may be separate from the northern Sonoma hydrothermal system, and could be related to upflow along fractures in the Rodgers Creek Fault Zone (Farrar et al., 2006). The Eastside fault is thought to form the western boundary for the hydrothermal systems (California Division of Mines and Geology, 1984).

Hydrothermal fluids in the Sonoma area generally are Na–Cl type waters and often contain As, B, F and Li in concentrations that exceed drinking-water standards (California Division of Mines and Geology, 1984; Farrar et al., 2006; Kulongoski et al., 2010). Hydrothermal fluids are significant components in some wells in the Sonoma Valley, particularly in the area between Fetter's Hot Springs and the city of Sonoma (Farrar et al., 2006). The source and movement of hydrothermal fluids in the Sonoma Valley may be similar to those in the upper Napa Valley, where hot mineralized waters upwell along faults or fractures extending from depth to near land surface (Murray, 1996). The most mineralized hydrothermal fluids in the Sonoma Valley, characterized by the composition of samples from wells HOT-07 and HOT-06 from this study, may coincide with the topographic axis of the valley, as in the upper Napa Valley.

2. Methods

Water samples were collected from 96 wells in 2004 using standard USGS protocols (Kulongoski et al., 2006), and 21 of these wells were resampled in November of 2007 using the same protocols. Samples were analyzed for major and minor ions, trace elements, TDS, isotopes (³He/⁴He, δ¹⁸O, δD), pH, DO, SC and water temperature. Complete data were available for 44 wells used in this study, except for the well VP-44, which was missing data for ³He/⁴He. Seven wells identified as hydrothermal wells by Kulongoski et al. (2010) were sampled, four in northern Napa Valley near the city of Calistoga (HOT-01, HOT-02, HOT-03, HOT-04 and HOT-05) and two in Sonoma Valley near Agua Caliente (HOT-06 and HOT-07) (Fig. 1). The hydrothermal well samples ranged in temperature from 29.5 °C to 97.5 °C, the hottest from a well near the active geyser 'Old Faithful' in Calistoga (HOT-05).

2.1. Statistical methods

Non-parametric statistical methods were used to test the significance of correlations between water temperature, constituent concentrations, isotopes and well type (i.e. hydrothermal, groundwater, saline water). Correlations were investigated using Spearman's method to calculate the rank-order correlation coefficient (ρ) between continuous variables. The values of ρ can range from

+1.0 (perfect positive correlation) to 0.0 (no correlation) to –1.0 (perfect negative correlation). The significance level (p) used to test hypotheses for this report was compared to a threshold value (α) of 5% ($\alpha = 0.05$) to evaluate whether the relation was statistically significant ($p < \alpha$).

2.1.1. Multivariate statistical analyses

PRIMER (v. 6.0) software (Clarke and Warwick, 2001) was used for multivariate statistical analyses of the measured constituents. Prior to analyses, data were 4th-root transformed and normalized to eliminate inappropriate weighting of some measurements. In the multivariate analyses of environmental data, normalization is usually essential because environmental data have different measurement scales or units (e.g. concentrations in $\mu\text{g/L}$, mg/L , temperatures in $^{\circ}\text{C}$, etc.) (Clarke and Warwick, 2001). After normalization, the data are dimensionless, and can be compared by examining and interpreting relationships based on Euclidean distances (distance measure between vectors where squared differences between corresponding elements are summed, followed by taking the square root of this sum). These transformed and normalized data were then used to generate a resemblance matrix based on Euclidean distances between site pairs for subsequent multivariate statistical analyses.

Cluster Analyses take a similarity matrix as their starting point and successively fuse samples into groups, and the groups into larger clusters starting with the highest mutual similarities; then gradually decrease the similarity levels at which the groups are formed (Clarke and Warwick, 2001). The results of the hierarchical clustering are represented by a dendrogram, with the samples on the x -axis, and the y -axis defining the similarity levels (in Euclidean distances) at which samples or groups are considered to have fused.

The purpose of Multidimensional Scaling (MDS) is to construct a visual representation of a complex set of relationships using a “map” or ordination of the samples in a specified number of dimensions, which attempts to satisfy all of the conditions imposed by the rank similarity matrix (Clarke and Warwick, 2001). An MDS map represents an optimal configuration of the sample points in two-dimensional space, where proximity indicates similarity.

Principal components analysis (PCA) is a recognition technique used to explain the variance of a large set of intercorrelated variables with a smaller set of independent variables, or principal components. PCA is the longest-established method of approximating high-dimensional information in low-dimensional plots, and is particularly useful for multivariate analyses of environmental data (Clarke and Warwick, 2001). PCA is an ordination in which samples are regarded as points in high-dimensional variable space, and are projected onto a best fitting plane, or other low dimensional solution. The principal components (PC) are simply a rotation of the original axis, and thus a linear combination of the input variables. The purpose of the principal components is to capture as much of the variability in the original space as possible, and the extent to which the first few PC's allow an accurate representation of the true relationship between the samples in the original dataset is summarized by the % variation explained.

Analysis of Similarities (ANOSIM) tests operate on a resemblance matrix, and carry out an approximate analog of the standard 1- and 2-way ANOVA (Analysis of Variance) tests. ANOSIM provides a test of the null hypothesis that there are no assemblage differences between groups of samples (Clarke and Gorley, 2006).

Similarity Percentage Analyses (SIMPER) are useful in interpreting differences between groups of samples when they have been shown to exist. SIMPER examines the roles of individual constituents contributing to the separation between two groups of samples or the “closeness” of samples within a group. SIMPER operates on

the dissimilarities in their high-dimensional relationships, and not on the approximations represented by a 2-D ordination (MDS) (Clarke and Gorley, 2006).

2.2. Multivariate Mixing and Mass-balance model (M3)

The M3 method uses multivariate analyses to aid in understanding groundwater compositions by assuming that the groundwater chemistry is a result of mixing between reference waters and water/rock interaction (Laaksoharju et al., 1999). In evaluating the chemical evolution of groundwater, the M3 model differs from many geochemical models which are based primarily on water-rock interaction, rather than groundwater mixing. M3 modeling of groundwater mixing involves (1) a standard Principal Component Analysis (PCA) of the data, (2) a mixing evaluation, and (3) a mass-balance calculation. M3 modeling uses the PCA method to analyze similarities in groundwater compositions in order to identify components that can be used to investigate mixing and chemical reactions within the groundwater, and to quantify component proportions. The method quantifies hydrochemical variations in δD , $\delta^{18}\text{O}$, and chemical species due to mixing of groundwater masses by comparing groundwater compositions to reference waters. The mixing calculations (i.e., mixing portions as a percentage of a selected reference water) determine how much of the observed groundwater composition is due to mixing between the selected reference waters (Laaksoharju et al., 1999).

The following wells were selected as reference waters for M3 analyses: HOT-05, the hottest well (97.5°C) as the reference hydrothermal fluids from Calistoga (HC); WG-03T as the reference well for groundwater (GW); and VP-36 as the reference well for saline water (SW) (Kulongoski et al., 2010). While none of these wells should be regarded as “pure end-members”, they are considered to be the most representative of each of the water types relevant to this study. Well VP-44 was not used in the M3 modeling because $^3\text{He}/^4\text{He}$ data were not available for this well, and the constituents Zn, Cu, Al, Fe, Pb, Ni, V, and Co were not used in the PCA analyses within the M3 model because they provided insignificant contributions to variance in the principal components.

3. Results

Concentrations of trace elements (in $\mu\text{g/L}$) are presented in Table 1. Values for temperature, pH, isotope ratios, concentrations of major and minor elements, and Total Dissolved Solids (TDS) are presented in Table 2. Table 3 presents mean and median values for some important constituents: water temperature, $^3\text{He}/^4\text{He}$, B, Cl, F, Mg, As, Li, δD , and $\delta^{18}\text{O}$, and the ratios of Cl/B arranged according to water types.

3.1. Statistical results

3.1.1. Spearman's correlations

The constituents with significant ($p \leq 0.05$) positive correlation to water temperature were Li, W, Si, F, K, Na, Mo, Hg, Be, B, $^3\text{He}/^4\text{He}$, pH and As. The constituents with significant negative correlation to water temperature were Sr, Mg, Ca, δD , Ni, $\delta^{18}\text{O}$ and Co. The constituents significantly positively correlated to $^3\text{He}/^4\text{He}$ were Hg, Al, Li, Be, W, water temperature, Si, pH and B; while Co and Mg were significantly negatively correlated with $^3\text{He}/^4\text{He}$ (Table 4).

Initial classifications of the wells in terms of water types were based on Spearman's Correlation results, which identified constituents significantly correlated with water temperature and high $^3\text{He}/^4\text{He}$ ratios, known indicators of hydrothermal fluids (Murray, 1996; California Division of Mines and Geology, 1984; Farrar

Table 1
Trace elements for all 44 wells used in statistical analyses (in µg/L). Well type classifications are defined as follows: HC: hydrothermal fluids from Sonoma; MW: mixed hydrothermal/meteoric water; SW: saline water; GW: non-hydrothermal groundwater.

| GAMA identification no. | Well type | Water temperature (°C) | Aluminium dissolved (µg/L) | Arsenic dissolved (µg/L) | Boron dissolved (µg/L) | Barium (µg/L) | Cobalt dissolved (µg/L) | Copper dissolved (µg/L) | Iron dissolved (µg/L) | Lithium dissolved (µg/L) | Molybdenum dissolved (µg/L) | Manganese dissolved (µg/L) | Nickel dissolved (µg/L) | Lead dissolved (µg/L) | Selenium dissolved (µg/L) | Strontium dissolved (µg/L) | Vanadium dissolved (µg/L) | Tungsten dissolved (µg/L) | Zinc dissolved (µg/L) |
|-------------------------|-----------|------------------------|----------------------------|--------------------------|------------------------|---------------|-------------------------|-------------------------|-----------------------|--------------------------|-----------------------------|----------------------------|-------------------------|-----------------------|---------------------------|----------------------------|---------------------------|---------------------------|-----------------------|
| VP-10 | GW | 16.5 | 0.01 | 0.3 | 323 | 100 | 0.141 | 0.4 | 117 | 3.5 | 0.5 | 203 | 3.02 | 0.05 | 0.01 | 195 | 0.9 | 0.01 | 2.5 |
| VP-19 | GW | 22.9 | 0.01 | 0.4 | 331 | 100 | 0.072 | 1.8 | 10 | 3.4 | 0.6 | 42.2 | 1.76 | 2.07 | 0.01 | 214 | 1.2 | 0.01 | 9.2 |
| VP-26 | GW | 22 | 0.01 | 1.5 | 124 | 247 | 0.113 | 1 | 21 | 14.6 | 4.5 | 241 | 0.39 | 0.09 | 0.01 | 264 | 2.7 | 0.01 | 5 |
| VP-29 | GW | 16.7 | 0.01 | 0.1 | 258 | 172 | 0.127 | 2.3 | 0.1 | 6.5 | 0.2 | 0.1 | 2.48 | 1.02 | 0.01 | 352 | 1.4 | 0.01 | 49.7 |
| VP-30 | GW | 18 | 1.4 | 0.5 | 1350 | 203 | 0.155 | 0.6 | 13 | 18.8 | 0.7 | 36.8 | 2.23 | 0.32 | 0.7 | 379 | 1.9 | 0.01 | 6.3 |
| VP-33 | GW | 21.2 | 0.01 | 3.8 | 29 | 31 | 0.139 | 0.01 | 1090 | 14.1 | 0.5 | 139 | 1.03 | 0.79 | 0.01 | 127 | 0.001 | 0.01 | 19 |
| VP-34 | GW | 19.4 | 0.01 | 7.1 | 120 | 35 | 0.072 | 0.4 | 989 | 4.7 | 1.8 | 434 | 0.26 | 0.001 | 0.01 | 30.9 | 1.3 | 0.01 | 20.1 |
| VP-35 | GW | 19.3 | 1.4 | 8 | 171 | 35 | 0.067 | 0.7 | 17 | 27.5 | 5.1 | 3.6 | 0.69 | 0.38 | 1.6 | 384 | 7.4 | 0.01 | 10.1 |
| VP-37 | GW | 19.3 | 0.01 | 3.4 | 73 | 64 | 0.056 | 3.4 | 6 | 25.6 | 0.6 | 6.4 | 1.49 | 0.37 | 0.7 | 134 | 11.2 | 0.01 | 5.6 |
| VP-39 | GW | 20 | 0.8 | 6 | 293 | 27 | 0.096 | 0.3 | 43 | 68.9 | 1.8 | 78.1 | 0.34 | 2.68 | 0.01 | 39.8 | 3.7 | 0.9 | 9.4 |
| VP-41 | GW | 20.4 | 0.01 | 2.6 | 52 | 148 | 0.331 | 13.1 | 0.1 | 33.5 | 1.6 | 928 | 0.62 | 1.77 | 0.01 | 262 | 3.1 | 0.01 | 5.8 |
| VP-46 | GW | 18.1 | 0.9 | 0.01 | 70 | 106 | 0.079 | 0.5 | 22 | 6.2 | 0.6 | 1.6 | 2 | 0.35 | 1 | 278 | 1.4 | 0.01 | 18.8 |
| VP-47 | GW | 18.1 | 3.7 | 0.2 | 627 | 19 | 0.052 | 14.8 | 0.1 | 12.3 | 0.4 | 0.4 | 0.4 | 15.3 | 0.01 | 98.9 | 0.6 | 0.01 | 34.3 |
| VP-48 | GW | 19.8 | 1 | 4.9 | 380 | 194 | 0.061 | 0.3 | 714 | 17.2 | 0.7 | 181 | 5.21 | 0.08 | 0.7 | 213 | 0.7 | 0.8 | 0.7 |
| VP-50 | GW | 18.6 | 0.01 | 7.7 | 109 | 71 | 0.205 | 0.01 | 57 | 2.9 | 5.7 | 687 | 0.62 | 0.07 | 0.01 | 131 | 6.4 | 0.01 | 8.9 |
| VFPF-01 | GW | 28 | 1 | 1 | 53 | 9 | 0.08 | 0.4 | 36 | 20.5 | 1.1 | 66.4 | 0.05 | 0.58 | 0.01 | 86.2 | 0.001 | 0.01 | 0.6 |
| VFPF-02 | GW | 18 | 0.01 | 2.2 | 93 | 223 | 0.138 | 0.5 | 0.1 | 10.8 | 1.1 | 355 | 0.3 | 0.27 | 0.01 | 276 | 10 | 0.01 | 1.9 |
| VFPF-03 | GW | 18.2 | 0.01 | 1.3 | 825 | 70 | 0.509 | 2.5 | 4 | 4.8 | 1.3 | 938 | 5.58 | 0.29 | 1.7 | 167 | 1.4 | 0.01 | 2.2 |
| VFPF-05T | GW | 20 | 1.1 | 0.38 | 345 | 108 | 0.03 | 3.6 | 4 | 3 | 0.4 | 0.4 | 0.72 | 2.19 | 0.05 | 241 | 0.01 | 0.01 | 0.86 |
| VFPF-07T | GW | 18.5 | 5.3 | 1.4 | 80 | 121 | 0.03 | 1.4 | 0.1 | 10 | 0.9 | 2.2 | 0.39 | 0.37 | 0.33 | 214 | 6.6 | 0.01 | 4 |
| VOL-01 | GW | 23.5 | 0.01 | 1.4 | 28 | 8 | 0.048 | 2.8 | 80 | 10.3 | 0.2 | 4.8 | 0.46 | 0.73 | 0.01 | 61.9 | 19.6 | 0.01 | 3.5 |
| VOL-14 | GW | 21.5 | 0.9 | 7.1 | 18 | 6 | 0.132 | 3.5 | 0.1 | 11.2 | 1.5 | 10.7 | 0.76 | 2.79 | 0.01 | 38 | 15.4 | 0.01 | 8.2 |
| VOL-19 | GW | 24.8 | 1 | 1.3 | 42 | 49 | 0.436 | 0.6 | 235 | 23.2 | 0.6 | 127 | 3.72 | 0.35 | 0.01 | 33.5 | 1.5 | 0.01 | 63.8 |
| VOL-20 | GW | 25.2 | 0.01 | 5.6 | 71 | 9 | 0.019 | 0.4 | 4 | 42.3 | 1.9 | 0.3 | 0.25 | 0.63 | 0.01 | 29.8 | 11.6 | 0.6 | 15 |
| WG-08 | GW | 17 | 2.2 | 1.6 | 7 | 3 | 0.45 | 0.01 | 2420 | 8.5 | 0.6 | 76 | 8.8 | 0.23 | 0.01 | 176 | 0.06 | 0.01 | 3.9 |
| WG-09T | GW | 19 | 1.1 | 13 | 16 | 1 | 0.17 | 0.9 | 40 | 12.4 | 1.2 | 12.9 | 1.08 | 0.11 | 0.3 | 198 | 1.1 | 0.01 | 1.7 |
| WGFP-01 | GW | 19.5 | 0.01 | 4.8 | 22 | 4 | 0.14 | 0.4 | 29 | 10.6 | 0.7 | 16 | 0.43 | 0.59 | 0.01 | 188 | 1.7 | 0.01 | 4.2 |
| WGFP-02T | GW | 19 | 5.3 | 3.1 | 10 | 5 | 0.001 | 0.61 | 4 | 6 | 0.3 | 1.3 | 0.13 | 0.25 | 0.36 | 178 | 3.6 | 0.01 | 0.68 |
| HOT-01 | HC | 81 | 17.3 | 70.5 | 9590 | 0.78 | 0.017 | 0.6 | 45 | 1920 | 6.5 | 12.4 | 0.27 | 0.06 | 0.8 | 110 | 0.6 | 112 | 0.6 |
| HOT-02 | HC | 60 | 6.2 | 50.2 | 11,000 | 0.594 | 0.012 | 0.5 | 28 | 1450 | 6.2 | 17.2 | 0.17 | 0.001 | 0.01 | 39.6 | 0.001 | 138 | 0.01 |
| HOT-04 | HC | 63 | 5.7 | 64.6 | 11,200 | 0.936 | 0.018 | 1 | 272 | 1440 | 3.4 | 88.8 | 0.57 | 0.04 | 0.7 | 34.5 | 0.1 | 234 | 26.8 |
| HOT-05 | HC | 97.7 | 126 | 128 | 11,100 | 1 | 0.016 | 0.6 | 14 | 1720 | 10.3 | 2.8 | 0.2 | 0.11 | 0.01 | 152 | 0.7 | 152 | 15.7 |
| HOT-07 | HSON | 41.5 | 4.7 | 3 | 15,700 | 20 | 0.023 | 0.3 | 41 | 1650 | 13.2 | 11.9 | 0.21 | 0.19 | 1.4 | 21.8 | 0.001 | 54.2 | 0.01 |
| HOT-06 | MW | 34.3 | 2.4 | 12.4 | 3570 | 14 | 0.094 | 1.2 | 302 | 703 | 2.8 | 373 | 0.5 | 0.04 | 0.4 | 161 | 0.2 | 7.6 | 8.8 |
| HOT-03 | MW | 29.5 | 1 | 30.9 | 2530 | 25 | 0.144 | 1.3 | 4 | 224 | 3.4 | 559 | 1.21 | 0.001 | 0.7 | 102 | 9.3 | 2 | 1.4 |
| VP-32 | MW | 35.4 | 0.8 | 8.8 | 283 | 69 | 0.258 | 4.5 | 5 | 52.5 | 1.5 | 129 | 0.24 | 4.12 | 0.2 | 124 | 1.5 | 0.9 | 4.2 |
| VP-38 | MW | 25.7 | 1.2 | 17.2 | 3830 | 69 | 0.031 | 3.3 | 12 | 61.3 | 13.7 | 14.5 | 0.25 | 0.73 | 0.5 | 83.9 | 1 | 0.01 | 5.9 |
| VP-40 | MW | 33 | 1.2 | 0.01 | 474 | 13 | 0.067 | 0.01 | 331 | 80.9 | 1.8 | 40.1 | 1.23 | 0.001 | 0.01 | 127 | 0.6 | 0.7 | 15.6 |
| VP-45 | MW | 28 | 0.01 | 32.8 | 496 | 56 | 0.033 | 0.2 | 135 | 72 | 8.4 | 50.1 | 0.68 | 0.77 | 0.01 | 84.6 | 2 | 2.3 | 13.2 |
| VP-49 | MW | 19.6 | 1.8 | 24.6 | 316 | 115 | 0.216 | 0.3 | 362 | 72.9 | 20.3 | 43.5 | 0.66 | 0.24 | 0.01 | 142 | 0.9 | 0.01 | 4.3 |
| VFPF-06T | MW | 28 | 1.3 | 1.5 | 482 | 40 | 0.02 | 0.22 | 154 | 67 | 2.2 | 59.7 | 0.12 | 0.34 | 0.01 | 79.2 | 0.04 | 0.74 | 1.1 |
| VOL-18T | MW | 28.5 | 1 | 0.88 | 463 | 112 | 0.05 | 0.01 | 332 | 48.5 | 1.8 | 54.4 | 0.16 | 0.001 | 0.01 | 97.2 | 1 | 0.66 | 2 |
| VP-36 | SW | 18.6 | 0.01 | 5.7 | 136 | 492 | 0.141 | 0.3 | 671 | 33.8 | 1 | 1220 | 0.65 | 1.07 | 2 | 440 | 0.4 | 0.01 | 49.8 |
| VP-44 | SW | 21 | 1.1 | 3.3 | 819 | 121 | 0.092 | 1.4 | 310 | 68.3 | 20 | 135 | 0.63 | 0.001 | 0.3 | 384 | 0.4 | 0.01 | 29.6 |

Table 2
 Values for temperature, pH, isotope ratios, concentrations of major and minor elements, and Total Dissolved Solids (TDSs) for all 44 wells used in statistical analyses (in mg/L). Well type classifications are defined as follows: HC: hydrothermal fluids from Calistoga; HSON: hydrothermal fluids from Sonoma; MW: mixed hydrothermal/meteoric water; SW: saline water; GW: non-hydrothermal groundwater.

| GAMA identification no. | Well type | Water temperature (°C) | pH (standard units) | Deuterium/protium (‰) | Oxygen-18/Oxygen-16 (‰) | Helium-3/Heium4 (isotope ratio) × 10 ⁻⁶ | Total dissolved solids (mg/L) | Sodium, dissolved (mg/L) | Chloride, dissolved (mg/L) | Fluoride, dissolved (mg/L) | Silica, dissolved (mg/L) | Sulfate, dissolved (mg/L) | Magnesium, dissolved (mg/L) | Potassium, dissolved (mg/L) | Calcium, dissolved (mg/L) | Bromide, dissolved (mg/L) | Iodide, dissolved (mg/L) |
|-------------------------|-----------|------------------------|---------------------|-----------------------|-------------------------|--|-------------------------------|--------------------------|----------------------------|----------------------------|--------------------------|---------------------------|-----------------------------|-----------------------------|---------------------------|---------------------------|--------------------------|
| VP-10 | GW | 16.5 | 6.5 | -39.90 | -6.28 | 0.83 | 213 | 10.9 | 6.73 | 0.37 | 29.6 | 11.3 | 26.3 | 0.94 | 23.2 | 0.06 | 0.005 |
| VP-19 | GW | 22.9 | 7.4 | -51.00 | -7.41 | 0.96 | 162 | 8.39 | 5.19 | 0.37 | 22.5 | 9.63 | 18.7 | 1.25 | 22.8 | 0.03 | 0.004 |
| VP-26 | GW | 22 | 7.5 | -44.10 | -6.92 | 0.58 | 381 | 76.7 | 13.2 | 0.3 | 38.1 | 21.7 | 19.2 | 1.3 | 34.5 | 0.11 | 0.069 |
| VP-29 | GW | 16.7 | 7.5 | -43.70 | -6.98 | 1.02 | 24.9 | 9.06 | 5.94 | 0.001 | 24.8 | 19.1 | 24.5 | 0.99 | 35.7 | 0.17 | 0.001 |
| VP-30 | GW | 18 | 6.6 | -46.30 | -7.04 | 0.81 | 254 | 13.3 | 8.82 | 0.001 | 24.8 | 19.1 | 24.5 | 0.99 | 38.4 | 0.07 | 0.007 |
| VP-33 | GW | 21.2 | 7.2 | -40.20 | -6.40 | 0.90 | 270 | 19.6 | 9.52 | 0.16 | 94.4 | 19.3 | 15.6 | 3.48 | 26 | 0.14 | 0.011 |
| VP-34 | GW | 19.4 | 7.1 | -46.50 | -7.12 | 2.85 | 185 | 23.4 | 10.6 | 0.34 | 85.3 | 2.58 | 6.26 | 4.7 | 9.14 | 0.07 | 0.02 |
| VP-35 | GW | 19.3 | 7.3 | -39.10 | -5.89 | 1.04 | 318 | 58.8 | 30.8 | 0.22 | 74.6 | 21.2 | 12.6 | 2.2 | 25.1 | 0.07 | 0.003 |
| VP-37 | GW | 19.3 | 7.6 | -39.00 | -6.00 | 1.34 | 255 | 42.5 | 23 | 0.16 | 67.8 | 14.8 | 14.7 | 1.32 | 25.1 | 0.12 | 0.002 |
| VP-39 | GW | 20 | 7.6 | -46.80 | -7.11 | 1.17 | 267 | 28.3 | 7 | 0.37 | 105 | 5.46 | 7.88 | 6.79 | 13.9 | 0.09 | 0.077 |
| VP-41 | GW | 20.4 | 7.3 | -40.30 | -5.99 | 0.98 | 313 | 39.2 | 42.4 | 0.24 | 50.2 | 23.6 | 20.9 | 2.09 | 33 | 0.19 | 0.015 |
| VP-46 | GW | 18.1 | 7.2 | -42.60 | -6.43 | 2.95 | 249 | 21.5 | 9.88 | 0.13 | 29.7 | 43.7 | 22.4 | 0.59 | 32.7 | 0.71 | 0.003 |
| VP-47 | GW | 18.1 | 7.3 | -39.70 | -6.06 | 1.22 | 194 | 25.4 | 21.3 | 0.56 | 33.1 | 37.9 | 7.47 | 0.55 | 22.9 | 0.14 | 0.005 |
| VP-48 | GW | 19.8 | 7.7 | -40.90 | -6.35 | 0.39 | 464 | 113 | 62.9 | 0.16 | 47.6 | 14.9 | 16.2 | 13.2 | 18.6 | 0.11 | 0.179 |
| VP-50 | GW | 18.6 | 7 | -48.50 | -7.15 | 0.63 | 261 | 27.1 | 5.1 | 0.26 | 69.5 | 3.84 | 22.7 | 8.19 | 18.9 | 0.07 | 0.038 |
| VPPF-01 | GW | 28 | 8.1 | -38.90 | -6.25 | 1.01 | 179 | 30.2 | 13.2 | 0.21 | 54.4 | 4.7 | 3.64 | 1.52 | 17.5 | 0.05 | 0.006 |
| VPPF-02 | GW | 18 | 6.9 | -38.70 | -5.93 | 0.97 | 364 | 40 | 47.2 | 0.001 | 38 | 15.4 | 29.4 | 1.89 | 44.2 | 0.13 | 0.024 |
| VPPF-03 | GW | 18.2 | 7.2 | -41.20 | -6.33 | 0.38 | 346 | 31 | 41.7 | 0.26 | 52.9 | 32.7 | 40.1 | 2.67 | 28.4 | 0.25 | 0.011 |
| VPPF-05T | GW | 20 | 7 | -49.50 | -7.33 | 1.01 | 155 | 8.3 | 4.72 | 0.09 | 15.2 | 10.1 | 12 | 1.03 | 23.8 | 0.02 | 0.002 |
| VPPF-07T | GW | 18.5 | 7.3 | -38.70 | -5.94 | 1.06 | 315 | 28.6 | 23.8 | 0.17 | 38.7 | 14.7 | 30.2 | 1.79 | 37.2 | 0.14 | 0.005 |
| VOL-01 | GW | 23.5 | 7 | -41.00 | -6.46 | 0.91 | 214 | 12.9 | 5.55 | 0.35 | 98.5 | 1.42 | 10.8 | 1.74 | 19.2 | 0.03 | 0.001 |
| VOL-14 | GW | 21.5 | 7.2 | -39.90 | -6.12 | 1.03 | 185 | 13.4 | 7.79 | 0.15 | 87 | 7.4 | 7.57 | 2.18 | 12.8 | 0.03 | 0.004 |
| VOL-19 | GW | 24.8 | 6.8 | -47.00 | -7.39 | 0.90 | 184 | 15.9 | 5.34 | 0.27 | 97.9 | 5.94 | 8.1 | 4.41 | 7.34 | 0.04 | 0.002 |
| VOL-20 | GW | 25.2 | 7.7 | -45.00 | -6.98 | 0.86 | 197 | 31.3 | 4.62 | 0.34 | 87 | 4.56 | 4.09 | 4.34 | 8.96 | 0.03 | 0.001 |
| WG-03T | GW | 17 | 6.5 | -37.20 | -6.06 | 0.96 | 202 | 22.5 | 27.2 | 0.08 | 62.3 | 32.9 | 6.11 | 1.65 | 13.5 | 0.11 | 0.009 |
| WG-08 | GW | 19 | 7.2 | -37.70 | -6.12 | 1.01 | 263 | 18.2 | 13.2 | 0.07 | 42.2 | 20.3 | 6.38 | 1.24 | 53.6 | 0.06 | 0.004 |
| WGFP-01 | GW | 19.5 | 7.8 | -37.70 | -6.14 | 0.99 | 242 | 22 | 15.4 | 0.1 | 37.9 | 14 | 3.77 | 1.33 | 50 | 0.08 | 0.007 |
| WGFP-02T | GW | 19 | 7.8 | -38.30 | -6.14 | 1.06 | 237 | 18.4 | 16.1 | 0.001 | 45.5 | 7.79 | 2.94 | 1.13 | 44.6 | 0.08 | 0.002 |
| HOT-01 | HC | 81 | 7.8 | -50.90 | -7.84 | 4.93 | 646 | 186 | 183 | 10.2 | 108 | 30.8 | 0.134 | 7.54 | 7.63 | 0.8 | 0.299 |
| HOT-02 | HC | 60 | 7.7 | -53.20 | -8.28 | 4.95 | 685 | 185 | 190 | 9.56 | 165 | 0.97 | 0.274 | 8.37 | 5.04 | 0.73 | 0.334 |
| HOT-04 | HC | 63 | 7.5 | -53.90 | -8.18 | 4.90 | 670 | 174 | 194 | 10.6 | 164 | 27.4 | 0.883 | 7.9 | 4.31 | 0.9 | 0.351 |
| HOT-05 | HC | 97.7 | 8.1 | -53.00 | -8.25 | 5.01 | 648 | 173 | 187 | 11.3 | 151 | 10.8 | 0.015 | 7.91 | 6.32 | 0.75 | 0.226 |
| HOT-07 | HSON | 41.5 | 8.3 | -52.00 | -7.64 | 2.53 | 1230 | 381 | 578 | 8.47 | 99.5 | 40.5 | 0.078 | 20.2 | 9.01 | 2.44 | 1.61 |
| HOT-06 | MW | 34.3 | 7.3 | -41.70 | -6.09 | 2.69 | 673 | 208 | 255 | 2.01 | 85.6 | 14 | 6.33 | 17.5 | 39.7 | 0.37 | 0.19 |
| HOT-03 | MW | 29.5 | 7.2 | -40.70 | -6.23 | 1.68 | 539 | 138 | 51.4 | 1.9 | 84.1 | 58.3 | 12.9 | 8.93 | 22.3 | 0.16 | 0.01 |
| VP-32 | MW | 35.4 | 7.5 | -44.20 | -6.80 | 1.57 | 321 | 40.2 | 9.34 | 0.27 | 134 | 32.1 | 14.7 | 9.93 | 29.6 | 0.1 | 0.012 |
| VP-38 | MW | 25.7 | 8.2 | -50.40 | -7.75 | 1.15 | 503 | 177 | 25.5 | 0.42 | 52.9 | 1.72 | 1.51 | 2.29 | 6.26 | 0.1 | 0.138 |
| VP-40 | MW | 33 | 7.7 | -47.10 | -6.98 | 3.58 | 428 | 57.8 | 99.1 | 0.38 | 110 | 3.17 | 21 | 5.68 | 34.5 | 0.37 | 0.047 |
| VP-45 | MW | 28 | 6.7 | -42.30 | -7.82 | 0.21 | 399 | 77.9 | 6.83 | 0.68 | 126 | 19.9 | 5.95 | 19.7 | 15.5 | 0.06 | 0.009 |
| VP-49 | MW | 19.6 | 7.3 | -50.60 | -7.48 | 4.62 | 417 | 104 | 42.5 | 0.24 | 64.3 | 7.12 | 11 | 9.02 | 20 | 0.16 | 0.077 |
| VPPF-06T | MW | 28 | 7.7 | -42.10 | -6.61 | 3.40 | 336 | 49.6 | 17.2 | 0.26 | 86.8 | 0.11 | 17.3 | 7.3 | 27.3 | 0.07 | 0.057 |
| VOL-18T | MW | 28.5 | 7.2 | -48.60 | -7.22 | 1.23 | 321 | 42.5 | 12.6 | 0.35 | 120 | 3.76 | 17.9 | 6.48 | 14.5 | 0.06 | 0.024 |
| VP-36 | SW | 18.6 | 7.6 | -52.90 | -7.72 | 0.32 | 685 | 148 | 250 | 0.16 | 46.8 | 12.4 | 50.8 | 7.14 | 51.6 | 1.44 | 0.261 |
| VP-44 | SW | 21 | 7.9 | -47.80 | -7.18 | | 1000 | 270 | 191 | 0.1 | 27.9 | 239 | 21.6 | 3.03 | 36.5 | 0.99 | 1.14 |

Table 3
Mean (first row) and median (second row in bold text) values of constituents important to the classifications of the wells from this study. Well type classifications are defined as follows: HC: hydrothermal fluids from Calistoga; HSON: hydrothermal fluids from Sonoma; MW: mixed hydrothermal/meteoric water; SW: saline water; GW: non-hydrothermal groundwater.

| Well type | Water temperature (°C) | Helium-3/Helium-4 (isotope ratio) × 10 ⁻⁶ | Boron, dissolved (µg/L) | Chloride, dissolved (mg/L) | Chloride/Boron | Fluoride, dissolved (mg/L) | Magnesium, dissolved (mg/L) | Arsenic, dissolved (µg/L) | Lithium, dissolved (µg/L) | Deuterium/protium (‰) | Oxygen-18/Oxygen-16 (‰) |
|-----------|------------------------|--|-------------------------|----------------------------|----------------|----------------------------|-----------------------------|---------------------------|---------------------------|-----------------------|-------------------------|
| ALL | 27.4 | 1.68 | 1771 | 63.2 | 317.5 | 1.42 | 13.8 | 12.39 | 229.5 | -44.6 | -6.8 |
| | 20.7 | 1.03 | 293 | 17.2 | 88.3 | 0.26 | 12.3 | 3.40 | 23.2 | -43.9 | -6.9 |
| GW | 20.1 | 1.05 | 211.4 | 17.4 | 401.4 | 0.20 | 15.2 | 3.24 | 15.5 | -42.1 | -6.5 |
| | 19.4 | 0.97 | 86.5 | 11.9 | 153.3 | 0.17 | 13.7 | 1.90 | 11.0 | -40.6 | -6.3 |
| MW | 29.1 | 2.36 | 1383 | 57.7 | 61.3 | 0.72 | 12.1 | 14.34 | 153.6 | -46.4 | -7 |
| | 28.5 | 2.18 | 482 | 25.5 | 33.0 | 0.38 | 12.9 | 12.40 | 72.0 | -47.1 | -7 |
| HC | 75.4 | 4.46 | 10723 | 188.5 | 17.6 | 10.0 | 0.33 | 63.26 | 1633 | -52.8 | -8.1 |
| | 72 | 4.93 | 11050 | 188.5 | 17.3 | 10.2 | 0.2 | 64.60 | 1650 | -53.1 | -8.2 |

et al., 2006; Kulongoski et al., 2010; Kulongoski and Hilton, 2011). Based on the Spearman correlation tests, the following constituents were considered to be the best indicators of hydrothermal fluids: elevated water temperature and ³He/⁴He, along with relatively high concentrations of Li, B, F and As. Using these criteria, samples were initially classified as hydrothermal fluids from Calistoga (HC), which included HON-01, HON-02, HON-04, and HON-05; hydrothermal fluids from Sonoma (HSON): HON-07; mixed hydrothermal/meteoric water (MW): HON-06, HON-03, VP-38, VP-45, VP-49, VP-40, VPFP-06T, VOL18T, and VP-32; saline water (SW): VP-36, VP-44 (Kulongoski et al., 2010); and non-hydrothermal groundwater (GW), which included the remaining samples listed in Tables 1 and 2.

The distributions of isotopes and trace elements in the groundwater samples show several interesting patterns that complicate the analyses and interpretations. Relative to the non-thermal groundwater samples, the hydrothermal fluids from this study are not shifted to heavier δ¹⁸O values, which is generally the case in hydrothermal systems (Panichi and Gonfiantini, 1981). Although the HC wells, and most of the MW wells display higher water temperatures and elevated ³He/⁴He ratios, some cold GW wells, such as VP-46 and VP-34 also have anomalously high ³He/⁴He ratios, approaching 3.0 Ra (Table 2). High ³He/⁴He values are often associated with hydrothermal systems, faulting and volcanism. However, given the sensitivity (and mobility) of He isotope systematics, one can often observe variations in the ³He/⁴He ratios, with no change in groundwater chemistry. Magnesium concentration generally decreases with increasing fluid temperature (Fournier and Potter, 1979), and as a result, Mg is very low in oceanic hydrothermal systems (Scott, 1997). While the HC wells showed Mg depletion (mean [Mg] = 0.33 mg/L), the mean [Mg] in the MW wells (12.1) was more similar to the GW wells (mean = 15.2) (Table 3). Moreover, both SW wells and HC wells have elevated concentrations of Na and Cl, and some GW wells have relatively high SiO₂ (i.e. VP-39, VP-33, VOL-19, VOL-01) (Table 1). Therefore, the division of the samples into types is not straightforward on the basis of any commonly used criterion and multivariate techniques were required for these analyses and classifications.

3.1.2. Cluster Analyses

Fig. 2 is a dendrogram of the results of the hierarchical clustering analyses for the samples. The dendrogram reveals that HC samples cluster together. Interestingly, the higher temperature hydrothermal well from Sonoma (HON-07) forms an isolated branch that clusters with the HC wells at a greater Euclidean distance, suggesting similar composition and/or source. Two wells that had been previously identified as hydrothermal wells (Kulongoski et al., 2010), HON-06 and HON-03 do not cluster closely with the HC or HSON samples. In fact, HON-03 and HON-06 form clusters with the MW wells.

The HON-03 sample was collected from a well located within 50 m of the HON-02 hydrothermal well, however, HON-03 was drilled to only 14 m below land surface (mbls), while HON-02 was drilled to 61 mbls. The lower measured temperature of the HON-03 sample (29.5 °C) compared with the HON-02 sample (60.0 °C) suggests that it contains a greater proportion of groundwater mixed with hydrothermal fluids. Similarly, HON-06 had a lower measured temperature (34.3 °C) than HON-07, the other hydrothermal well from Sonoma (41.5 °C). No information concerning the well depth of HON-06 is available, however HON-07 has a reported depth of 300 mbls. HON-03 and HON-06, lower temperature and relatively shallower wells, are thus more appropriately classified as mixed hydrothermal/meteoric water (MW), with a significant proportion of groundwater diluting the hydrothermal fluids. The fact that these shallow wells cluster with some of the purportedly “non-hydrothermal” wells also suggests that

Table 4
Results of non-parametric Spearman's method analysis of correlations between selected water-quality constituents and groundwater temperature and $^3\text{He}/^4\text{He}$ ratio. *r*: Spearman's correlation statistic; *r* values are shown for tests in which the variables were determined to be significantly correlated on the basis of *p* values (significance level of the Spearman's test) less than threshold value (*a*) of 0.05; ns: Spearman's test indicates no significant correlation between groups; TDS: Total Dissolved Solids.

| Selected water-quality constituent | Groundwater temperature (°C) | | $^3\text{He}/^4\text{He}$ | |
|------------------------------------|------------------------------|---|---------------------------|---|
| | <i>p</i> Value | <i>r</i> : Spearman's correlation statistic | <i>p</i> Value | <i>r</i> : Spearman's correlation statistic |
| Aluminum | 0.024 | 0.340 | 0.000 | 0.616 |
| Arsenic | 0.005 | 0.426 | 0.048 | 0.305 |
| Boron | 0.003 | 0.451 | 0.009 | 0.403 |
| Barium | 0.003 | −0.456 | 0.007 | −0.415 |
| Beryllium | 0.001 | 0.493 | 0.001 | 0.502 |
| Bromide | >0.05 | ns | 0.003 | 0.456 |
| Calcium | 0.001 | −0.503 | >0.05 | ns |
| Chloride | >0.05 | ns | 0.004 | 0.443 |
| Cobalt | 0.003 | −0.451 | 0.005 | −0.432 |
| Copper | >0.05 | ns | >0.05 | ns |
| $\delta^{18}\text{O}$ | 0.002 | −0.472 | >0.05 | ns |
| δD | 0.001 | −0.500 | >0.05 | ns |
| Fluoride | 0.000 | 0.670 | 0.006 | 0.425 |
| Iron | >0.05 | ns | >0.05 | ns |
| Mercury | 0.005 | 0.523 | 0.001 | 0.663 |
| Iodide | 0.004 | 0.438 | 0.027 | 0.341 |
| Potassium | 0.000 | 0.613 | >0.05 | ns |
| Lithium | 0.000 | 0.748 | 0.001 | 0.508 |
| Magnesium | 0.000 | −0.563 | 0.010 | −0.396 |
| Manganese | >0.05 | ns | >0.05 | ns |
| Molybdenum | 0.000 | 0.552 | 0.016 | 0.372 |
| Sodium | 0.000 | 0.580 | 0.010 | 0.395 |
| Nickel | 0.001 | −0.489 | 0.015 | −0.377 |
| Lead | >0.05 | ns | 0.031 | −0.334 |
| pH | 0.004 | 0.437 | 0.009 | 0.405 |
| $^3\text{He}/^4\text{He}$ | 0.004 | 0.447 | – | – |
| Antimony | 0.003 | 0.453 | 0.025 | 0.347 |
| Selenium | >0.05 | ns | >0.05 | ns |
| Silica | 0.000 | 0.699 | 0.007 | 0.418 |
| Sulfate | >0.05 | ns | >0.05 | ns |
| Strontium | 0.000 | −0.617 | 0.023 | −0.351 |
| TDS | 0.003 | 0.456 | 0.022 | 0.354 |
| temperature | – | – | 0.004 | 0.447 |
| well type | 0.000 | 0.581 | >0.05 | ns |
| Uranium | 0.010 | −0.390 | >0.05 | ns |
| Vanadium | 0.048 | −0.299 | >0.05 | ns |
| Tungsten | 0.000 | 0.746 | 0.001 | 0.498 |
| Zinc | >0.05 | ns | >0.05 | ns |

some mixing with hydrothermal fluids is occurring in the following wells: VP-49, VP-45, VP-40, VP-38, VPFP-06T, and VOL-18T. Therefore, in subsequent multivariate analyses, these wells will be considered MW. Although VP-32 does not appear to cluster with the other MW wells, it will be classified with the MW wells due to its very elevated temperature (35.4 °C), $^3\text{He}/^4\text{He}$ (1.57 Ra), and [As] (8.8 $\mu\text{g}/\text{L}$).

3.1.3. Multidimensional scaling

Fig. 3 is an MDS map of the 44 samples. The 2-D stress result of 0.13 indicates that the MDS is a useful representation of the data, and supports the results from the Cluster Analyses. The HC wells and the HSON well cluster together at a Euclidean distance of <7. All of the MW wells, cluster together with HOT-03 and HOT-06 at a Euclidean distance of <7. However, a subset of these MW wells also cluster together with the GW wells at a Euclidean distance of <7. Wells with known saline water content (SW): VP-44 and VP-36 (Kulongoski et al., 2010) form a separate and distant cluster.

3.1.4. Principal components analysis

The PCA analyses of the constituents from the samples (Fig. 4) show the same groupings that were apparent in the MDS and Cluster Analyses. The HC wells and the HSON well cluster together. The MW wells cluster together, while the non-hydrothermal GW wells also generally group together, and the SW wells form a separate and distant cluster.

The first five principal components account for 72.9% of the variation (Table 5). The first principal component, PC1, accounting for 40.8% of the variance in the entire dataset, was most strongly correlated with Li, W, F, temp, B, Na, TDS, I and Cl, while PC2 accounted for 12.8% of the variance, and was most strongly correlated with Mn, Sr, Ba, Co, SO_4 , Ca, Ni, TDS and Br.

3.1.5. Analysis of similarities

An ANOSIM was performed to test the null hypothesis, that there are no differences between constituents (see Tables 1 and 2) in the hydrothermal wells and the non-hydrothermal public-supply groundwater wells. The results of the ANOSIM test gave an overall (Global R) statistic of 0.728, and a significance level of 0.1% ($p < 0.001$). Therefore, the ANOSIM test indicates that the hydrothermal wells are significantly different from the non-hydrothermal public-supply groundwater wells.

3.1.6. Similarity Percentage Analyses

SIMPER tests were performed to examine the differences between the HC wells and the GW wells. Table 6 lists the average values (after normalization and transformation) of the variables from the GW and HC wells, and the % contributions of each variable to the differences between the two groups. The results indicate that higher values of temp, W, Li, F, B, As, Al, $^3\text{He}/^4\text{He}$ and $\delta^{18}\text{O}$, along with lower values of Mg in the HC wells provide the greatest

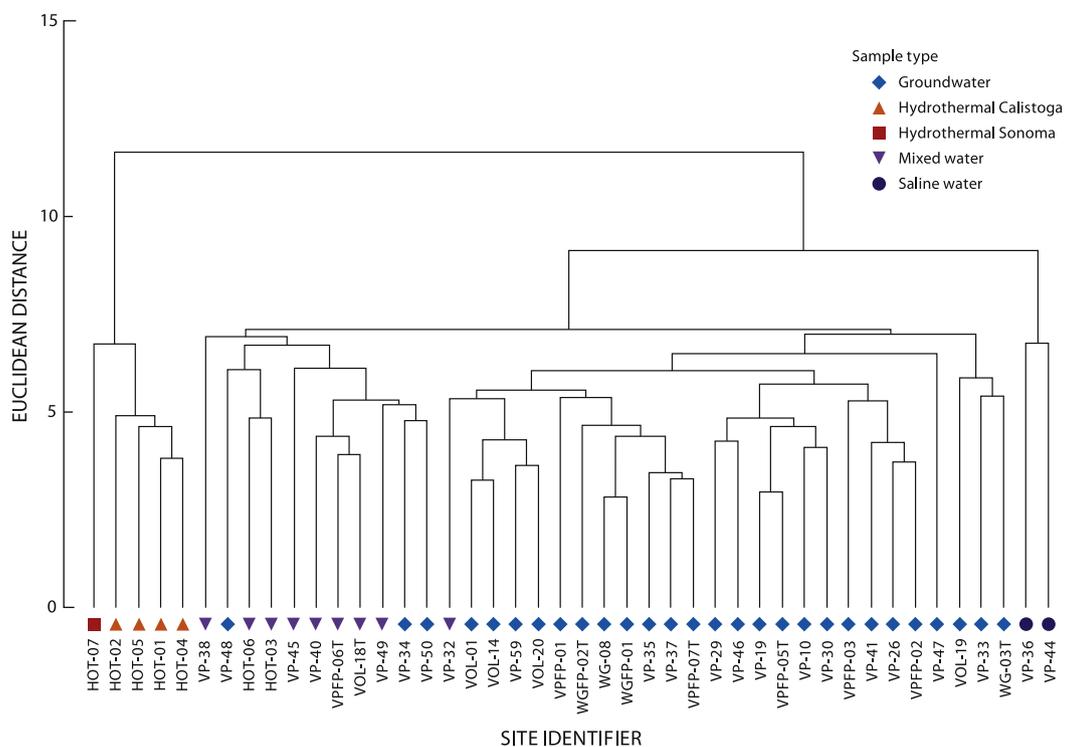


Fig. 2. Dendrogram of the results of hierarchical clustering analyses with the well samples on the x-axis, and the y-axis defining the similarity levels (in Euclidean distances) at which samples or groups are considered to have fused.

contributions to the differences between the HC wells and GW wells, and explains 52.6% of the difference (Table 6).

Table 7 lists the average values (after normalization and transformation) of the variables between GW wells and mixed MW wells, and the % contributions of each variable to the differences between the two groups. The results indicate that lower values of K, Mo, Si, $^3\text{He}/^4\text{He}$, Na, Fe, δD , SO_4 and As; and higher Cu, Pb and Ni in the GW wells provide the greatest contributions to the differences between the GW wells and the MW wells, and explains 50.5% of the difference (Table 7).

Table 8 lists the average values (after normalization and transformation) of the variables from the HC wells and MW wells, and the % contribution of each variable to the differences between the two groups. The results indicate that higher values of W, temp, Al, F, As, Li, B and lower values of Ca and Mg in the HC wells provide the greatest contributions to the differences between the HC wells and MW wells, and explains 51.8% of the difference (Table 8).

Table 9 lists the average values (after normalization and transformation) of the variables from the HC wells and the HSON well and the % contributions of each variable to the differences between the two groups. The results indicate that higher values of As, Zn, Al and temperature and lower values of Se, I and SO_4 in the HC wells, provide the greatest contributions to the differences between the HC wells and the HSON well, and explain 54.7% of the difference (Table 9).

3.2. M3 results

Results from the M3 mixing model, which compares all of the samples to the three reference-water components (HC, GW and SW), indicate that the proportion of hydrothermal fluids within the nine MW wells is between 14% and 30% (Fig. 5; Table 10). These results also corroborate the validity of the initial selections of the MW wells based on the Spearman's Correlation results, multivariate analyses, and trace element data from previous studies of

hydrothermal systems in the area. The proportions derived from M3 for three hydrothermal wells from Calistoga, H07-04, H07-02 and H07-01 indicate that they contain 81%, 77% and 76% mixtures of the reference hydrothermal well H07-05. The lower temperature (29.5 °C) H07-03 well contains only 18% hydrothermal fluids. The higher temperature (41.5 °C) hydrothermal well from Sonoma H07-07 did not plot within the triangle connecting the reference waters (Fig. 5), while the lower temperature (34.3 °C) MW well from Sonoma H07-06 appears to be a mix of groundwater (38%), saline water (33%), and hydrothermal fluids similar to those from Calistoga (29%) (Table 10).

4. Discussion

4.1. Constituents associated with hydrothermal wells

Major-ion data for wells with sufficient data were plotted on Piper diagrams (Fig. 6). Piper diagrams show the relative abundance of major cations and anions (on a charge equivalent basis) as a percentage of the total ion content of the water (Piper, 1944). In a majority of the GW wells, Ca plus Mg were the dominant cations, and HCO_3 generally accounted for a majority of the total anions, however some GW samples had more Na and K cations. In the MW wells, Na plus K were the dominant cations, and HCO_3 also accounted for a majority of the total anions. As such, the GW wells are described as Ca–Mg– HCO_3 type waters, while the MW wells are described as Na–K– HCO_3 type waters. The HC and HSON wells are described as Na–Cl waters.

In addition to elevated concentrations of Na and Cl, the multivariate statistical analyses employed indicate that the hydrothermal fluids from the HC wells also have higher values of water temperature, W, Li, F, B, As, Al and $^3\text{He}/^4\text{He}$, and are depleted in Mg when compared with GW wells. Of these constituents $^3\text{He}/^4\text{He}$, measured temperature, Cl, B and Li are the most likely to provide a means of evaluating the contribution of the hydrothermal system

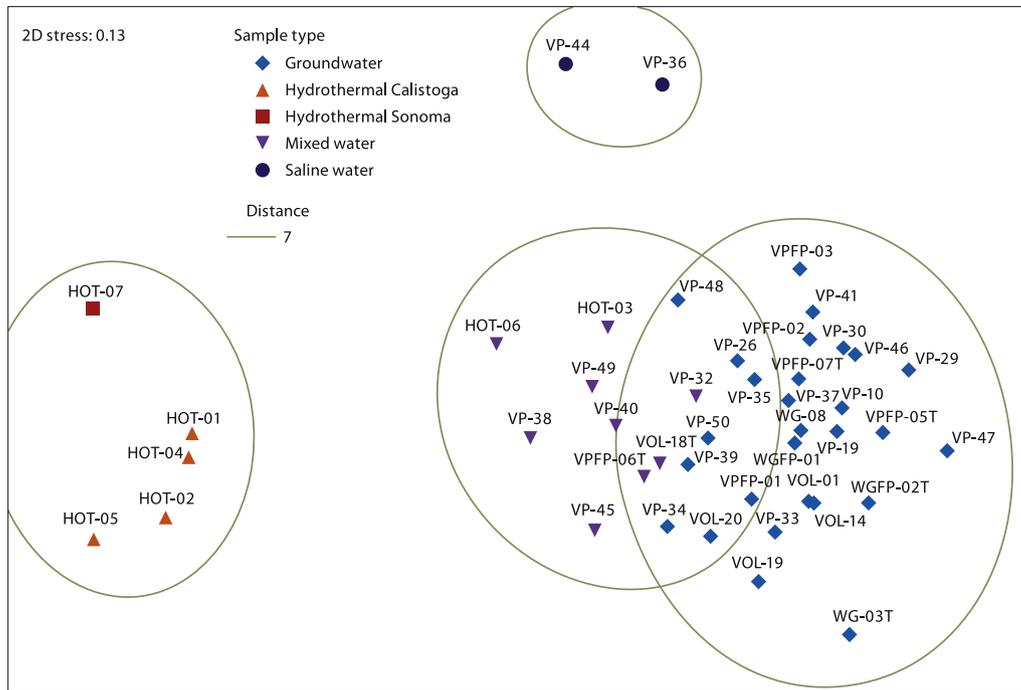


Fig. 3. Multidimensional Scaling (MDS) Map. The proximity of the well samples to each other indicates how similar they are to each other. The 2-D stress result of 0.13 indicates that the MDS is a useful representation of the data.

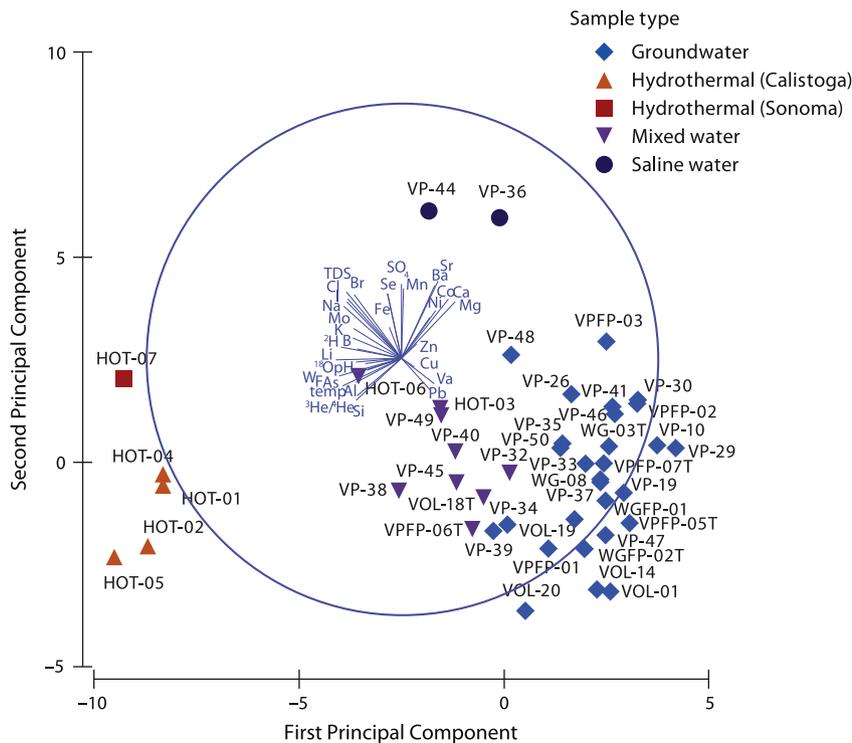


Fig. 4. Principal components analysis (PCA) ordination of well samples.

to drinking water wells because they generally behave conservatively, and their concentrations are not usually controlled by temperature- and pressure-dependent chemical reactions involving rock minerals (Ellis, 1970; Brondi et al., 1973; Henley and Ellis, 1983). Helium isotope ratios are extremely sensitive indicators of magma-related hydrothermal activity because the contrast in

$^3\text{He}/^4\text{He}$ ratios between crustal (typical $^3\text{He}/^4\text{He} < 0.02\text{Ra}$, where Ra is the $^3\text{He}/^4\text{He}$ ratio of air = 1.4×10^{-6}) and magmatic systems (typical $^3\text{He}/^4\text{He} \sim 8\text{Ra}$) provides a means of identifying even small amounts of mantle input (Kulongoski and Hilton, 2011). Elevated B concentrations have also been attributed to hydrothermal contamination in multiple locations, including Mexico (Birkle and Merkel,

Table 5

Coefficients in the linear combinations of variables making up PC's (Eigenvectors), and % Variation explained by each PC.

| PC | Eigenvalues | % Variation | Cum. % variation | | |
|-------------------------------------|-------------|-------------|------------------|--------|--------|
| <i>Principal component analysis</i> | | | | | |
| 1. | 13.5 | 40.8 | 40.8 | | |
| 2. | 4.23 | 12.8 | 53.6 | | |
| 3. | 2.89 | 8.8 | 62.4 | | |
| 4. | 1.8 | 5.5 | 67.9 | | |
| 5. | 1.65 | 5.0 | 72.9 | | |
| Variable | PC1 | PC2 | PC3 | PC4 | PC5 |
| <i>Eigenvectors</i> | | | | | |
| Temp | -0.243 | 0.109 | -0.035 | -0.031 | -0.106 |
| ³ He/ ⁴ He | -0.176 | 0.142 | -0.035 | -0.149 | -0.010 |
| B | -0.240 | -0.047 | -0.098 | 0.049 | -0.112 |
| Li | -0.261 | 0.001 | -0.060 | -0.066 | -0.084 |
| As | -0.199 | 0.054 | 0.034 | 0.011 | -0.126 |
| Mo | -0.188 | -0.118 | 0.046 | 0.201 | 0.087 |
| Sr | 0.137 | -0.304 | -0.171 | -0.024 | 0.065 |
| Na | -0.230 | -0.205 | -0.037 | 0.040 | 0.088 |
| Cl | -0.210 | -0.233 | -0.111 | -0.128 | 0.029 |
| F | -0.245 | 0.060 | -0.002 | -0.037 | -0.180 |
| Si | -0.180 | 0.160 | 0.229 | -0.080 | -0.072 |
| SO ₄ | -0.001 | -0.295 | -0.227 | -0.096 | -0.328 |
| Mg | 0.207 | -0.227 | 0.088 | 0.089 | 0.038 |
| K | -0.189 | -0.081 | 0.249 | 0.035 | 0.052 |
| Ca | 0.167 | -0.221 | -0.171 | -0.101 | 0.211 |
| Br | -0.188 | -0.255 | -0.121 | -0.043 | -0.051 |
| I | -0.217 | -0.225 | 0.007 | 0.065 | 0.122 |
| Al | -0.182 | 0.089 | -0.181 | -0.172 | -0.077 |
| W | -0.251 | 0.064 | -0.032 | -0.081 | -0.125 |
| TDS | -0.216 | -0.263 | -0.067 | 0.015 | 0.069 |
| δ ¹⁸ O | -0.182 | 0.010 | 0.167 | 0.386 | -0.072 |
| δD | -0.177 | -0.040 | 0.158 | 0.430 | -0.068 |
| Ba | 0.127 | -0.289 | 0.045 | 0.357 | 0.086 |
| Cu | 0.047 | 0.032 | -0.384 | 0.228 | -0.293 |
| Fe | -0.050 | -0.128 | 0.424 | -0.223 | 0.069 |
| Mn | 0.007 | -0.281 | 0.306 | 0.006 | -0.013 |
| Pb | 0.109 | 0.119 | -0.144 | 0.233 | -0.233 |
| Ni | 0.110 | -0.166 | 0.137 | -0.255 | -0.413 |
| Va | 0.122 | 0.093 | -0.098 | 0.154 | -0.080 |
| Zn | 0.059 | -0.067 | 0.109 | 0.280 | -0.363 |
| Co | 0.130 | -0.188 | 0.214 | -0.104 | -0.332 |
| Se | -0.058 | -0.260 | -0.242 | -0.122 | -0.052 |
| pH | -0.145 | 0.018 | -0.203 | 0.146 | 0.333 |

2000), Ethiopia (Reimann et al., 2003), Argentina (Kasemann et al., 2004), Greece (Dotsika et al., 2006), Turkey (Dogdu and Bayari, 2005), and China (Guo et al., 2008).

Murray et al. (1985) reported concentrations of B and Cl from hydrothermal fluids from the upper Napa Valley near Calistoga that are similar to those from this study, and found a close grouping in the proportions of Cl and B. The present data indicate a similar grouping in the proportions of Cl and B from the HC samples, suggesting a single source aquifer. The Cl/B ratios of the HC samples from this study are fairly uniform, ranging from 16.8 to 19.1 (median = 17.3; Table 3); HOT-03, the MW well that was collected within 50 m of the HC well HOT-02, also has a very similar Cl/B ratio of 20.3. In contrast to these results, the Cl/B ratios from the HSON wells in this study (HOT-06 and HOT-07) are more variable (71.4 and 36.8, respectively), suggesting that these two wells in Sonoma may be derived from two distinct hydrothermal reservoirs (e.g. Goff et al., 1993), however additional data are needed. The Cl/B ratios in the MW wells range from 6.7 to 209 (median = 33.0), and Cl/B ratios in the GW samples are highly variable, ranging from 7.3 to 3885 (median = 153.3).

The elements F and As are also useful in determining whether hydrothermal contamination is occurring, despite the fact that they may be affected by water-rock interaction. Fluoride occurrence in

groundwater is dependent upon the geology of the area, and is often associated with volcanic or marine deposits. Fluoride mobility in hydrothermal waters is temperature dependent; above ~250 °C dissolved F concentrations increase as a result of the dissolution of F-bearing minerals, while at temperatures below ~250 °C F concentrations decrease due to rock alteration and precipitation of F-bearing phases (Seyfried and Ding, 1995; Valentino and Stanzone, 2003). Hydrothermal fluids commonly exceed recommended water quality criteria for F (Ellis and Mahon, 1967), which has a US EPA MCL of 4.0 mg/L, and a secondary standard (SMCL) at 2.0 mg/L. This is important because skeletal fluorosis may develop after long-term intake of drinking water with a F concentration above 4 mg/L, and crippling fluorosis is observed at F concentrations >10 mg/L (Disanayake, 1991). The incidence of dental and skeletal fluorosis is well documented within the Rift Valley in Ethiopia, and the geographical distribution suggests a hydrothermal origin for high F concentrations in drinking water wells (Reimann et al., 2003). Similarly, in the Choma District of Zambia, a study found that all schoolchildren who drank water from hot springs had moderate to severe fluorosis, while the majority of the pupils who drank water from other sources had no dental fluorosis (Shitumbanuma et al., 2007). All hydrothermal wells from this study exceed the MCL for F, and the median F concentration for the HC and HSON wells is 10.2 mg/L. The median F concentration for MW wells is 0.38 mg/L (Table 3), but HOT-06 has a F concentration of 2.01, and HOT-03 has a F concentration of 1.9 (Table 2). The median F concentration for GW wells is 0.17 mg/L (Table 3).

The concentration of As in rock is not determinative of its concentration in surrounding porewater (Ballantyne and Moore, 1988), as As mobility is controlled by the redox conditions in the aquifer (Kulongoski and Belitz, 2010). Along a groundwater flow path, As may become enriched in groundwater by rock leaching or depleted by precipitation, ion exchange, or surface complexation (Aiuppa et al., 2003; Kulongoski and Belitz, 2010). However, high temperatures will leach As from rock, which explains the high concentrations of As in many hydrothermal fluids. In the Cimino-Vico volcanic area in central Italy, As in groundwater is mainly associated with upflowing fluids from deep hydrothermal systems, and elevated As concentrations (from 20 to 100 µg/L) occur due to mixing between deep groundwater and water recharged by infiltration in the volcanic aquifer, indicating that hydrothermal areas and faulted zones in the units underlying the shallow aquifer represent lower quality drinking water (Angelone et al., 2009).

It appears that similar processes and pathways are occurring in Northern California, with potentially harmful concentrations of As occurring in hydrothermal wells, and public supply wells contaminated with geothermal fluids. Nearly all of the HC and HSON wells (except HOT-07), and five of the MW wells HOT-03, HOT-06, VP-45, VP-49, and VP-38 have As concentrations exceeding the MCL for drinking water of 10 µg/L. The As concentrations in the HC wells (HOT-01, HOT-02, HOT-04, HOT-05) range from 50.2 µg/L to 128 µg/L (median = 67.55 µg/L) (Table 3), and the shallow MW well HOT-03 collected within 50 m of the HC well HOT-02 also has a highly elevated As concentration (30.9 µg/L).

4.2. Utility of multivariate statistics

Due to the presence of three or more distinct water types and the occurrence of admixtures of hydrothermal fluids and groundwaters in this study, multivariate statistics were required to adequately identify and characterize the constituents associated with each well. Cluster Analyses (CA) and Multidimensional Scaling (MDS) provide excellent visual representations of the groupings of the wells, and a relative assessment of contamination levels indicated by the proximity of the mixed water wells to the hydrothermal wells. Principal Components Analyses offers more

Table 6
Similarity Percentage Analyses (SIMPER) of differences between ground water from public supply wells (Group GW) and hydrothermal wells from Calistoga (Group HC).

| Variable | Group GW | | Group HC | | | |
|----------------------------------|-----------|-----------|--------------|-------------|-----------|--------|
| | Av. value | Av. value | Av. sq. dist | Sq. dist/SD | Contrib % | Cum. % |
| Temp | -0.488 | 2.7 | 10.6 | 2.59 | 7.16 | 7.16 |
| W | -0.457 | 2.74 | 10.3 | 5.20 | 7.00 | 14.16 |
| Li | -0.542 | 2.42 | 8.88 | 5.34 | 6.02 | 20.18 |
| F | -0.449 | 2.44 | 8.55 | 2.80 | 5.79 | 25.97 |
| B | -0.515 | 2.19 | 7.5 | 3.32 | 5.08 | 31.06 |
| Al | -0.326 | 2.02 | 7.5 | 0.93 | 5.08 | 36.14 |
| As | -0.4 | 2.18 | 7.14 | 1.92 | 4.84 | 40.98 |
| Mg | 0.264 | -2.07 | 6.04 | 1.68 | 4.09 | 45.08 |
| ³ He/ ⁴ He | -0.353 | 1.96 | 5.62 | 2.62 | 3.81 | 48.89 |
| δ ¹⁸ O | -0.439 | 1.78 | 5.49 | 1.72 | 3.72 | 52.61 |
| Si | -0.401 | 1.57 | 4.68 | 1.28 | 3.17 | 55.78 |
| Ca | 0.206 | -1.77 | 4.63 | 1.39 | 3.14 | 58.92 |
| δD | -0.462 | 1.51 | 4.53 | 1.60 | 3.07 | 61.99 |
| Cl | -0.485 | 1.57 | 4.41 | 2.58 | 2.99 | 64.98 |
| Na | -0.589 | 1.42 | 4.29 | 2.30 | 2.91 | 67.89 |
| Br | -0.43 | 1.53 | 4.16 | 2.21 | 2.82 | 70.71 |
| TDS | -0.586 | 1.37 | 4.04 | 2.29 | 2.74 | 73.45 |
| Ba | 0.104 | -1.65 | 3.91 | 1.24 | 2.65 | 76.10 |
| I | -0.505 | 1.4 | 3.9 | 2.37 | 2.64 | 78.74 |
| Co | 0.216 | -1.3 | 3.31 | 1.00 | 2.24 | 80.99 |
| Zn | 6.57E-2 | -0.362 | 2.89 | 0.85 | 1.96 | 82.95 |
| Mo | -0.503 | 1.03 | 2.85 | 1.41 | 1.93 | 84.88 |
| Va | 0.294 | -0.927 | 2.83 | 0.86 | 1.92 | 86.80 |
| Sr | 0.173 | -1.03 | 2.62 | 1.07 | 1.77 | 88.57 |
| K | -0.527 | 0.86 | 2.43 | 1.57 | 1.65 | 90.22 |

Groups GW vs HC.

Average squared distance = 147.50.

Table 7
Similarity Percentage Analyses (SIMPER) of differences between ground water from public supply wells (Group GW) and mixed hydrothermal/meteoric wells (Group MW).

| Variable | Group GW | | Group MW | | | |
|----------------------------------|-----------|-----------|--------------|-------------|-----------|--------|
| | Av. value | Av. value | Av. sq. dist | Sq. dist/SD | Contrib % | Cum. % |
| K | -0.527 | 0.957 | 3.23 | 1.10 | 6.26 | 6.26 |
| Mo | -0.503 | 0.685 | 2.6 | 0.78 | 5.04 | 11.30 |
| Cu | 0.121 | -0.25 | 2.35 | 0.70 | 4.57 | 15.87 |
| Pb | 0.276 | -0.341 | 2.29 | 0.68 | 4.44 | 20.30 |
| Si | -0.401 | 0.668 | 2.12 | 0.88 | 4.11 | 24.42 |
| Na | -0.589 | 0.575 | 2.02 | 0.98 | 3.91 | 28.33 |
| ³ He/ ⁴ He | -0.353 | 0.455 | 2.01 | 0.98 | 3.89 | 32.22 |
| Ni | 0.269 | -0.385 | 1.96 | 0.66 | 3.80 | 36.03 |
| Fe | -0.19 | 0.319 | 1.95 | 0.91 | 3.79 | 39.81 |
| δD | -0.462 | 0.367 | 1.86 | 0.92 | 3.62 | 43.43 |
| SO ₄ | -2.64E-2 | -0.388 | 1.85 | 0.80 | 3.58 | 47.01 |
| As | -0.4 | 0.302 | 1.81 | 0.98 | 3.52 | 50.53 |
| pH | -0.27 | 5.43E-2 | 1.79 | 0.70 | 3.47 | 54.00 |
| Mn | -0.115 | 0.364 | 1.77 | 0.87 | 3.44 | 57.44 |
| Co | 0.216 | -4.88E-2 | 1.7 | 0.71 | 3.30 | 60.75 |
| δ ¹⁸ O | -0.439 | 0.252 | 1.69 | 0.89 | 3.29 | 64.03 |
| Va | 0.294 | -0.162 | 1.66 | 0.76 | 3.22 | 67.25 |
| TDS | -0.586 | 0.477 | 1.56 | 1.03 | 3.03 | 70.27 |
| Se | -0.151 | -9.49E-2 | 1.55 | 0.84 | 3.01 | 73.28 |
| Ca | 0.206 | 6.97E-3 | 1.33 | 0.73 | 2.58 | 75.86 |
| B | -0.515 | 0.361 | 1.29 | 0.85 | 2.50 | 78.35 |
| Cl | -0.485 | 0.101 | 1.23 | 0.63 | 2.39 | 80.74 |
| Sr | 0.173 | -0.249 | 1.2 | 1.07 | 2.33 | 83.08 |
| Zn | 6.57E-2 | -0.157 | 1.13 | 0.68 | 2.20 | 85.27 |
| Li | -0.542 | 0.344 | 1.11 | 0.76 | 2.15 | 87.42 |
| Ba | 0.104 | 0.109 | 1.09 | 0.89 | 2.11 | 89.53 |
| I | -0.505 | 0.163 | 0.967 | 0.91 | 1.88 | 91.41 |

Groups GW vs. MW.

Average squared distance = 51.55.

detailed information regarding the significance of specific constituents that are indicative of hydrothermal contamination. Similarity Percentage Analyses further refines these differences, and identifies the constituents providing the greatest contributions to the differences between each of the well types.

The Multivariate Mixing and Mass-balance model (M3) was particularly useful in determining the percentage of hydrothermal contamination occurring in the mixed water wells. However, this method is constrained by the necessity to identify individual wells that best represent end-members for each water type, which

Table 8

Similarity Percentage Analyses (SIMPER) of differences between hydrothermal wells from Calistoga (Group HC) and wells from mixed hydrothermal/meteoric wells (Group MW).

| Variable | Group HC | Group MW | | | | |
|----------------------------------|-----------|-----------|--------------|-------------|-----------|--------|
| | Av. value | Av. value | Av. sq. dist | Sq. dist/SD | Contrib % | Cum. % |
| W | 2.74 | 0.107 | 7.16 | 2.76 | 8.07 | 8.07 |
| Temp | 2.7 | 0.301 | 6.22 | 1.79 | 7.02 | 15.09 |
| Al | 2.02 | 0.107 | 5.32 | 0.81 | 6.00 | 21.08 |
| F | 2.44 | 0.174 | 5.31 | 2.88 | 5.99 | 27.07 |
| Mg | -2.07 | 8.03E-2 | 5.16 | 1.75 | 5.82 | 32.89 |
| As | 2.18 | 0.302 | 4.7 | 0.94 | 5.29 | 38.18 |
| Li | 2.42 | 0.344 | 4.6 | 2.58 | 5.19 | 43.36 |
| Ca | -1.77 | 6.97E-3 | 3.84 | 1.43 | 4.33 | 47.69 |
| B | 2.19 | 0.361 | 3.68 | 1.91 | 4.15 | 51.84 |
| Ba | -1.65 | 0.109 | 3.37 | 1.87 | 3.80 | 55.64 |
| ³ He/ ⁴ He | 1.96 | 0.455 | 3.37 | 0.79 | 3.80 | 59.43 |
| Br | 1.53 | -0.136 | 3.07 | 1.89 | 3.46 | 62.89 |
| δ ¹⁸ O | 1.78 | 0.252 | 3.06 | 1.08 | 3.45 | 66.33 |
| Cl | 1.57 | 0.101 | 2.84 | 1.44 | 3.20 | 69.54 |
| Zn | -0.362 | -0.157 | 2.32 | 1.09 | 2.61 | 72.15 |
| SO ₄ | -9.36E-2 | -0.388 | 2.3 | 0.82 | 2.60 | 74.74 |
| Co | -1.3 | -4.88E-2 | 2.23 | 0.96 | 2.52 | 77.26 |
| δD | 1.51 | 0.367 | 1.94 | 1.00 | 2.19 | 79.45 |
| I | 1.4 | 0.163 | 1.83 | 1.39 | 2.07 | 81.52 |
| Se | 0.196 | -9.49E-2 | 1.73 | 0.97 | 1.95 | 83.47 |
| pH | 0.863 | 5.43E-2 | 1.71 | 0.77 | 1.93 | 85.40 |
| Pb | -0.877 | -0.341 | 1.48 | 0.70 | 1.66 | 87.06 |
| Va | -0.927 | -0.162 | 1.46 | 0.67 | 1.65 | 88.72 |
| Mn | -0.502 | 0.364 | 1.42 | 0.83 | 1.60 | 90.31 |

Groups HC vs. MW.

Average squared distance = 88.71.

Table 9

Similarity Percentage Analyses (SIMPER) of differences between hydrothermal wells from Calistoga (Group HC) and the hydrothermal well from Sonoma (HSON).

| Variable | Group HC | Group HSON | | | | |
|----------------------------------|-----------|------------|--------------|-------------|-----------|--------|
| | Av. value | Av. value | Av. sq. dist | Sq. dist/SD | Contrib % | Cum. % |
| As | 2.18 | -0.217 | 5.92 | 2.61 | 12.91 | 12.91 |
| Zn | -0.362 | -2.2 | 5.31 | 0.93 | 11.58 | 24.49 |
| Se | 0.196 | 1.7 | 3.26 | 0.94 | 7.11 | 31.60 |
| I | 1.4 | 3.09 | 2.86 | 5.27 | 6.25 | 37.84 |
| temp | 2.7 | 1.16 | 2.7 | 1.26 | 5.89 | 43.74 |
| Al | 2.02 | 0.926 | 2.68 | 0.56 | 5.85 | 49.59 |
| SO ₄ | -9.36E-2 | 1.08 | 2.32 | 0.67 | 5.07 | 54.66 |
| Br | 1.53 | 3.05 | 2.3 | 7.09 | 5.02 | 59.68 |
| TDS | 1.37 | 2.86 | 2.24 | 11.99 | 4.88 | 64.56 |
| Cl | 1.57 | 2.95 | 1.91 | 26.18 | 4.17 | 68.73 |
| K | 0.86 | 2.15 | 1.66 | 12.38 | 3.61 | 72.34 |
| pH | 0.863 | 2 | 1.53 | 1.27 | 3.33 | 75.68 |
| Ba | -1.65 | -0.427 | 1.51 | 10.57 | 3.29 | 78.96 |
| Va | -0.927 | -1.88 | 1.28 | 1.12 | 2.80 | 81.76 |
| ³ He/ ⁴ He | 1.96 | 0.895 | 1.14 | 33.40 | 2.48 | 84.24 |
| Na | 1.42 | 2.48 | 1.13 | 10.71 | 2.47 | 86.71 |
| Sr | -1.03 | -1.89 | 0.986 | 0.82 | 2.15 | 88.87 |
| Mo | 1.03 | 1.88 | 0.885 | 1.06 | 1.93 | 90.79 |

Groups HC vs. HSON.

Average squared distance = 45.85.

requires *a priori* information derived from statistical analyses. The consistency of the results from the M3 analyses with the similarities and proximities of the various well types indicated by the CA, MDS, and PCA confirms that the well classifications are robust.

4.3. Significance and implications of hydrothermal contamination

This work is the first study to utilize a broad suite of statistical methods to analyze and characterize mixing between relatively shallow groundwater and deeper hydrothermal fluids in the Napa and Sonoma Valleys in California. Traditional approaches were combined to evaluate the extent and nature of this hydrothermal contamination with more detailed information gleaned from

multivariate statistical analyses, and the powerful Multivariate Mixing and Mass-balance model (M3) to determine the constituents associated with hydrothermal contamination, as well as proportions of hydrothermal fluids, saline water and fresh groundwater present in each sample. Constraining the composition and extent of hydrothermal contamination could allow agencies to confidently attribute contaminants (e.g., As anomalies) to hydrothermal sources instead of other potential origins, such as arsenical pesticides applied to grape vineyards, a major crop in the area. It will also allow agencies to isolate wells affected by hydrothermal contamination, seal well perforation intervals associated with the contaminated aquifers, and assure consumers that they are not served drinking water with constituents such as As, F, B and Li at potentially harmful levels.

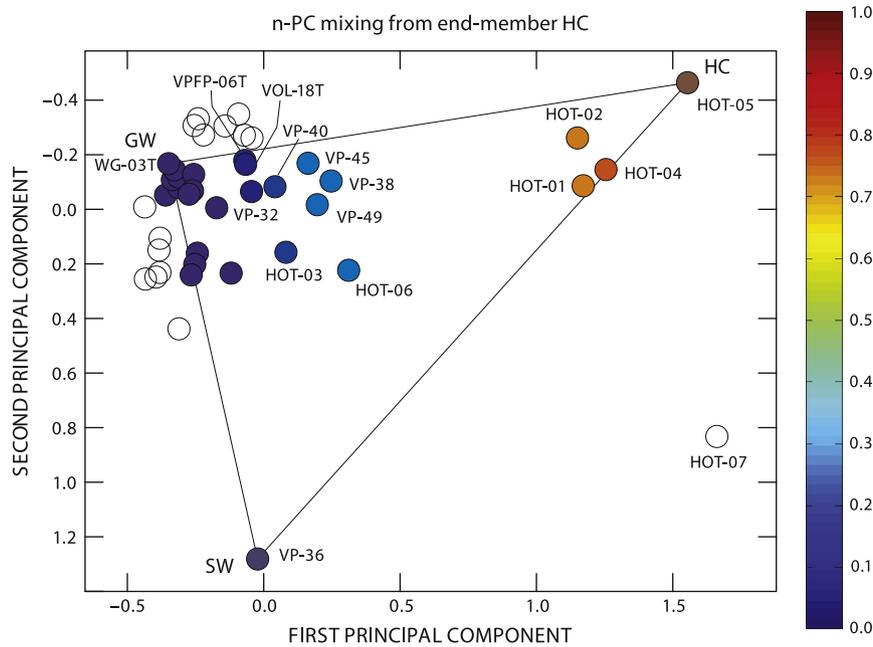


Fig. 5. Diagram showing mixing proportions from The Multivariate Mixing and Mass-balance model (M3) using the following reference waters: HOTS-05 as the reference hydrothermal well from Calistoga (HC), WG03T as the reference well for groundwater (GW), and VP-36 as the reference well for saline water (SW).

Table 10

Mixing proportions from The Multivariate Mixing and Mass-balance model, M3 using the following reference waters: HOTS-05 as the reference hydrothermal well from Calistoga (HC), WG03T as the reference well for groundwater (GW), and VP-36 as the reference well for saline water (SW).

| Well ID | Well type | % Ground water | % Saline water | % Hydrothermal water |
|----------|-----------|----------------|----------------|----------------------|
| WG-03T | GW | 1.00 | 0.00 | 0.00 |
| VP-36 | SW | 0.00 | 1.00 | 0.00 |
| HOT-05 | HC | 0.00 | 0.00 | 1.00 |
| HOT-04 | HC | 0.01 | 0.18 | 0.81 |
| HOT-02 | HC | 0.14 | 0.09 | 0.77 |
| HOT-01 | HC | 0.02 | 0.21 | 0.76 |
| VP-38 | MW | 0.60 | 0.10 | 0.30 |
| HOT-06 | MW | 0.38 | 0.33 | 0.29 |
| VP-45 | MW | 0.69 | 0.05 | 0.26 |
| VP-49 | MW | 0.58 | 0.16 | 0.26 |
| VP-40 | MW | 0.71 | 0.10 | 0.19 |
| HOT-03 | MW | 0.56 | 0.26 | 0.18 |
| VPFP-06T | MW | 0.83 | 0.02 | 0.14 |
| VOL-18T | MW | 0.83 | 0.03 | 0.14 |
| VP-32 | MW | 0.76 | 0.10 | 0.14 |
| VP-50 | GW | 0.80 | 0.13 | 0.07 |
| VP-48 | GW | 0.64 | 0.29 | 0.07 |
| VP-33 | GW | 0.92 | 0.04 | 0.04 |
| VP-19 | GW | 0.89 | 0.07 | 0.03 |
| VP-37 | GW | 0.89 | 0.08 | 0.03 |
| VP-35 | GW | 0.75 | 0.23 | 0.02 |
| WGFP-02T | GW | 0.95 | 0.04 | 0.01 |
| VP-47 | GW | 0.98 | 0.02 | 0.01 |
| VPFP-05T | GW | 0.93 | 0.06 | 0.01 |
| VP-26 | GW | 0.74 | 0.26 | 0.01 |
| WGFP-01 | GW | 0.96 | 0.04 | 0.00 |
| VP-46 | GW | 0.72 | 0.28 | 0.00 |
| WG-08 | GW | 0.93 | 0.07 | 0.00 |

5. Conclusions

Due to the presence of at least two hydrothermal systems and a saline water component, traditional methods for investigating hydrothermal systems, such as plots involving a single species (e.g. Cl or SiO₂), or ratios of elements commonly associated with the hydrothermal systems (e.g. B vs. Cl) were insufficient to characterize wells from the Napa and Sonoma Valleys. Therefore, multivariate statistical analyses and M3 modeling techniques were

essential to characterize the occurrence and extent of contamination by hydrothermal fluids.

The identification of mixing between hydrothermal fluids and meteoric waters is important to prevent contamination of drinking water. The statistical methodology implemented here accurately characterizes the chemical and isotopic differences between hydrothermal fluids and meteoric waters in the Napa and Sonoma Valleys, and provides powerful techniques to help identify mixing in wells. By recognizing mixing, and the potential for mixing, steps

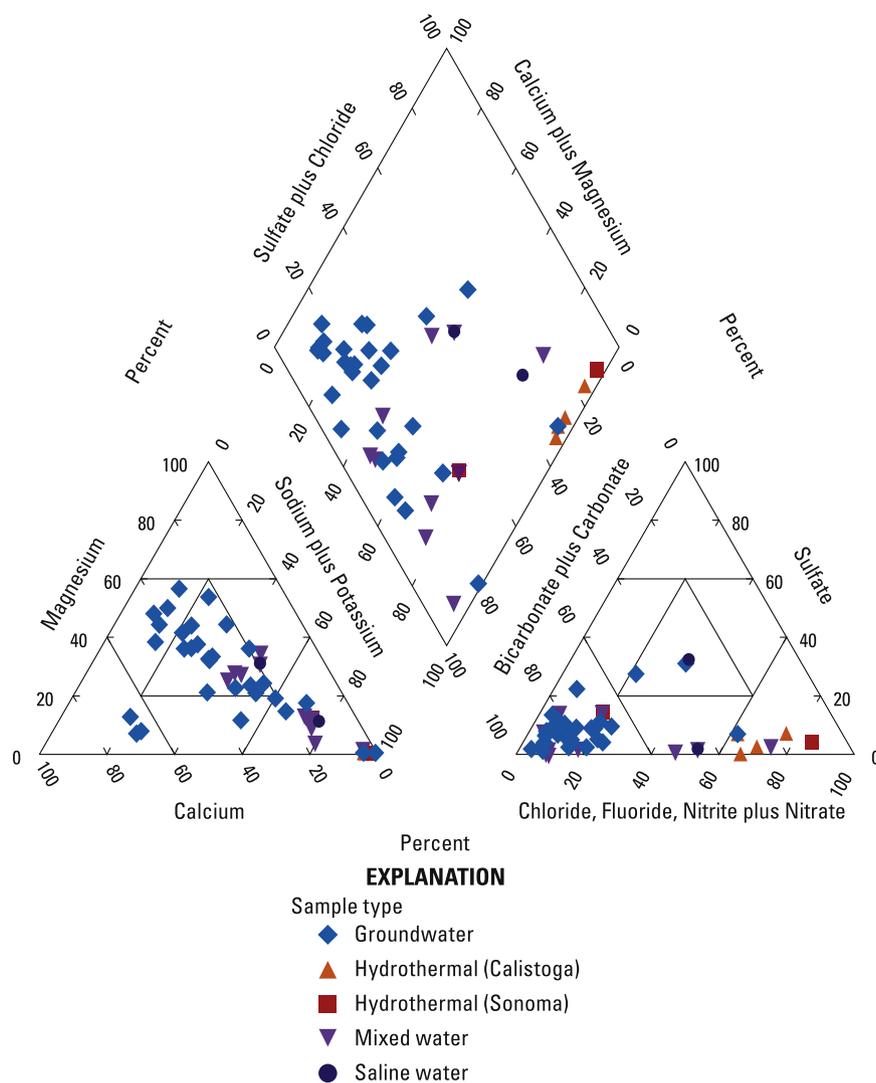


Fig. 6. Piper diagram of sampled wells. Symbols represent different well types: groundwater (GW) = Light Blue Diamonds; hydrothermal well from Calistoga (HC) = Orange Triangles; hydrothermal fluids from Sonoma (HSON) = Red Squares; mixed hydrothermal/meteoric water (MW) = Purple Upside Down Triangles; saline water (SW) = Dark Blue Circles. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

can be taken to prevent harm to the valuable resources, both potable water and hydrothermal wells.

The multivariate statistics employed in this study allowed identification of the constituents most indicative of hydrothermal fluids: water temperature, $^3\text{He}/^4\text{He}$, Li, Cl, B, As, and F, and to distinguish the wells where mixing between hydrothermal fluids and groundwater is occurring. Of these constituents, $^3\text{He}/^4\text{He}$ and measured temperature, along with the elements Li, Cl and B are most useful in evaluating the contribution of the hydrothermal system to the wells in this study because they generally behave conservatively, and are not controlled by temperature- and pressure-dependent chemical exchange involving rock minerals. Although F and As do not necessarily behave conservatively, the hydrothermal and mixed hydrothermal/ground water wells from this study generally contained elevated concentrations of F and As, often in excess of the US EPA Maximum Contamination Levels.

Results from the Multivariate Mixing and Mass-balance model (M3) confirm the initial classifications of the mixed hydrothermal/meteoric wells (MW), and indicate that the nine MW wells contain between 14% and 30% hydrothermal fluids. The results from the M3 model are consistent with those from the other multivariate statistical analyses. M3 is a valuable tool for determining

the proportions of mixing of selected reference waters present in waters from mixed origins such as in the Calistoga area. Used in tandem with multivariate statistical analyses, the M3 model provides a clear indication of the occurrence and extent of contamination of local groundwater used for drinking water by hydrothermal fluids. These methods could also be applied in other areas such as Mexico, Iceland, Japan, Turkey, Greece, Ethiopia and Italy, where the potential for mixing between ground and surface waters utilized for drinking water and crop irrigation and hydrothermal fluids also exists.

Acknowledgements

Funding for this work was provided by the California State Water Resources Control Board and the U.S. Geological Survey. Noble gas analyses were made by Jean Moran and Brad Esser at the Lawrence Livermore National Laboratory. The authors would also like to thank Marcus Laaksoharju and Birgitta Kalinowski for access and permission to use the Multivariate Mixing and Mass-balance M3 Mixing Model.

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