

Prepared in cooperation with the California State Water Resources Control Board

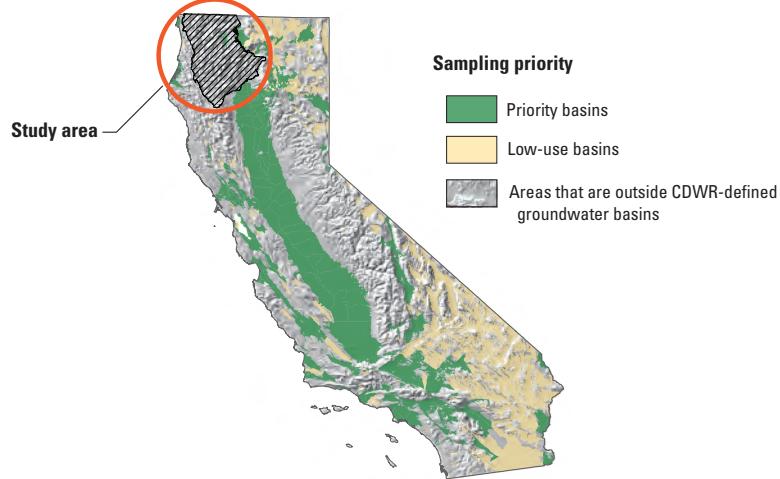
A product of the California Groundwater Ambient Monitoring and Assessment (GAMA) Program

Status and Understanding of Groundwater Quality in the Klamath Mountains Study Unit, 2010: California GAMA Priority Basin Project



Scientific Investigations Report 2014–5065

Front Cover Map: Groundwater basins categorized by sampling priority. Location of groundwater basin boundaries from California Department of Water Resources (CDWR, 2003).



Cover photographs:

Front cover: Water-quality sampling vehicle and well house near Lewiston, California. (Photograph taken by Tracy Davis, U.S. Geological Survey.)

Back cover: Well house and deer near Lewiston, California. (Photograph taken by Tracy Davis, U.S. Geological Survey.)

Status and Understanding of Groundwater Quality in the Klamath Mountains Study Unit, 2010: California GAMA Priority Basin Project

By George L. Bennett V, Miranda S. Fram, and Kenneth Belitz

A product of the California Groundwater Ambient Monitoring and Assessment
(GAMA) Program

Prepared in cooperation with the California State Water Resources Control Board

Scientific Investigations Report 2014–5065

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

U.S. Department of the Interior
SALLY JEWELL, Secretary

U.S. Geological Survey
Suzette M. Kimball, Acting Director

U.S. Geological Survey, Reston, Virginia: 2014

For more information on the USGS—the Federal source for science about the Earth, its natural and living resources, natural hazards, and the environment, visit <http://www.usgs.gov> or call 1–888–ASK–USGS.

For an overview of USGS information products, including maps, imagery, and publications, visit <http://www.usgs.gov/pubprod>

To order this and other USGS information products, visit <http://store.usgs.gov>

Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the U.S. Government.

Although this information product, for the most part, is in the public domain, it also may contain copyrighted materials as noted in the text. Permission to reproduce copyrighted items must be secured from the copyright owner.

Suggested citation:

Bennett, G.L., V. Fram, M.S., and Belitz, Kenneth, 2014, Status and understanding of groundwater quality in the Klamath Mountains study unit, 2010—California GAMA Priority Basin Project: U.S. Geological Survey Scientific Investigations Report 2014–5065, 58 p., <http://dx.doi.org/10.3133/sir20145065>

ISBN 978-1-4113-3790-9

ISSN 2328-0328 (online)
ISSN 2328-031X (print)

Contents

Abstract	1
Introduction.....	2
Purpose and Scope	4
Methods.....	6
Status Assessment.....	6
Water-Quality Benchmarks and Relative-Concentrations	6
Datasets Used for Status Assessment.....	7
U.S. Geological Survey Grid Sites.....	7
California Department of Public Health Grid Sites.....	7
Additional Data Used for Spatially Weighted Calculations	10
Selection of Constituents for Additional Evaluation in the Status Assessment.....	10
Calculation of Aquifer-Scale Proportions.....	12
Understanding Assessment.....	12
Selection of Constituents for Additional Evaluation in the Understanding Assessment	12
Statistical Tests of Relations between Potential Explanatory Factors and Groundwater Quality.....	13
Hydrogeologic Setting and Potential Explanatory Factors.....	13
Aquifer Lithology	14
Land Use.....	16
Hydrologic Conditions	19
Depth and Groundwater Age Characteristics of the Primary Aquifer System.....	21
Geochemical Conditions in the Primary Aquifer System	21
Status and Understanding of Groundwater Quality.....	23
Inorganic Constituents.....	25
Trace Elements	28
Factors Affecting Boron	28
Nutrients.....	28
Radioactive Constituents.....	28
Constituents with SMCL Benchmarks.....	30
Factors Affecting Iron and Manganese	30
Organic Constituents.....	32
Potential Factors Affecting Chloroform	34
Summary.....	34
Acknowledgments.....	35
References.....	35
Appendix A. Attribution of Potential Explanatory Factors	41
Appendix B. Grid Cells and Sites	50
Appendix C. Calculation of Aquifer-Scale Proportions	55
Appendix D. Comparison of CDPH and USGS–GAMA Data.....	56

Figures

1.	Map showing hydrogeologic provinces of California and the location of the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project	3
2.	Map showing geographic features and locations of sampled sites in the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	5
3.	Map showing locations of grid sites, the understanding site, and CDPH sites sampled for the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	8
4.	Map showing geology of the Klamath Mountains study unit, California GAMA Priority Basin Project.....	15
5.	Ternary diagram of the percentages of urban, agricultural, and natural land use surrounding individual USGS-grid and USGS-understanding sites, and land-use averages in the study unit, around grid sites, and around CDPH sites in the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project	16
6.	Map showing land use, CDWR groundwater basins, and locations of sampled sites within the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	17
7.	Graph showing well depths and depths to tops of screened or open intervals for USGS-grid sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	21
8.	Map showing groundwater age classes of sampled sites within the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	22
9.	Graph showing maximum relative-concentrations in USGS-grid sites for constituents detected, by type of constituent, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	25
10.	Graphs showing relative-concentrations of selected trace elements, radioactive constituents, and constituents with non-regulatory aesthetic-based benchmarks in USGS-grid sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project	26
11.	Graphs showing relations between dissolved oxygen concentration and iron and manganese, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project	31
12.	Graph showing iron and manganese concentrations by groundwater age class, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project	32
13.	Graph showing detection frequency and maximum relative-concentration for organic constituents detected in USGS-grid sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	33
14.	Graphs showing maximum relative-concentration and detection frequency for the trihalomethane chloroform detected in USGS-grid sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	34

Tables

1.	Summary of constituent groups and numbers of constituents sampled for each constituent group by the U.S. Geological Survey in the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	9
2.	Numbers of constituents analyzed and detected, by benchmark and constituent type, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	11
3.	Constituents historically (June 14, 1984, to November 30, 2007) reported at concentrations greater than benchmarks in the California Department of Public Health database, but not during the 3-year period used in the status assessment, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	11
4.	Results of Wilcoxon rank-sum tests for differences in values of land-use factors, hydrologic conditions, geochemical conditions, and selected water-quality constituents between samples classified into groups by 2-factor age class, redox class, or aquifer lithology class, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.....	18
5.	Results of Spearman's rho (ρ) tests for correlations between selected potential explanatory factors and selected water-quality constituents, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project	20
6.	Constituents selected for additional evaluation in the status assessment of groundwater quality in the Klamath Mountains study unit, California GAMA Priority Basin Project	24
7A.	Summary of aquifer-scale proportions for inorganic constituent classes with health-based and aesthetic-based benchmarks, Klamath Mountains study unit, 2010, California GAMA Priority Basin Program	27
7B.	Summary of aquifer-scale proportions for organic constituent classes with health-based benchmarks, Klamath Mountains study unit, 2010, California GAMA Priority Basin Program.....	27
8.	Aquifer-scale proportions from grid-based and spatially weighted methods for constituents that met criteria for additional evaluation in the status assessment, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project	29

Conversion Factors, Datums, and Abbreviations and Acronyms

Inch/foot/mile to International System of Units (SI)

Multiply	By	To obtain
Length		
inch (in.)	2.54	centimeter (cm)
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter (m)
mile (mi)	1.609	kilometer (km)
Area		
square foot (ft ²)	0.09290	square meter (m ²)
square mile (mi ²)	2.590	square kilometer (km ²)
Radioactivity		
picocurie per liter (pCi/L)	0.037	becquerel per liter (Bq/L)
picocurie per liter (pCi/L)	0.313	tritium units (TU)

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

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

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

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

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$). One milligram per liter is equivalent to 1 part per million (ppm); 1 microgram per liter is equivalent to 1 part per billion (ppb); 1 per mil is equivalent to 1 part per thousand.

Concentrations of noble gases used for modeling recharge temperatures are given as the atom ratio (for helium-3/helium-4) or as cubic centimeters of gas at standard temperature and pressure per gram of water (cm³ STP/g).

Activities of radioactive constituents in water (except uranium and tritium) are given in picocuries per liter (pCi/L).

Concentrations of tritium are presented in tritium units (TU). One TU equals 3.19 pCi/L.

Datums

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88). Land-surface datum (LSD), as used in this report, refers to a horizontal plane that is approximately at land surface at each site, at a specific elevation relative to NAVD 88.

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

Abbreviations and Acronyms

AL-US	U.S. Environmental Protection Agency action level
E	estimated or having a higher degree of uncertainty
GAMA	Groundwater Ambient Monitoring and Assessment Program
HAL-US	U.S. Environmental Protection Agency lifetime health advisory level
HBSL	health-based screening level
KLAM	Klamath Mountains study unit
TRL	laboratory reporting level
LSD	land-surface datum
LUFT	leaking (or formerly leaking) underground fuel tank
MCL	maximum contaminant level
MCL-CA	California Department of Public Health maximum contaminant level
MCL-US	U.S. Environmental Protection Agency maximum contaminant level
MDL	method detection limit
na	not available
NAVD 88	North American Vertical Datum of 1988
NL-CA	California Department of Public Health notification level
ns	not significant
RSD5-US	U.S. Environmental Protection Agency risk-specific dose at a risk factor of 10^{-5}
SI	International System of Units
SMCL-CA	California Department of Public Health secondary maximum contaminant level
SMCL-US	U.S. Environmental Protection Agency secondary maximum contaminant level
TEAP	terminal electron acceptor process

Organizations

CDPH	California Department of Public Health
CDPR	California Department of Pesticide Regulation
CDWR	California Department of Water Resources
LLNL	Lawrence Livermore National Laboratory
SWRCB	California State Water Resources Control Board
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey

Selected Constituent Names

¹⁴ C	carbon-14
DO	dissolved oxygen
H ₂ O	water
MTBE	methyl <i>tert</i> -butyl ether
TDS	total dissolved solids
THM	trihalomethane
VOC	volatile organic compound

Selected Symbols and Units of Measure

α	critical level
cm ³ STP/g	cubic centimeters of gas at standard temperature and pressure per gram of water
δ/E	delta notation; the ratio of a heavier isotope of an element, ⁱ E, to the more common lighter isotope of an element, relative to a standard reference material, expressed as per mil
L	liter
m	meter
mg/L	milligrams per liter
$\mu\text{g}/\text{L}$	micrograms per liter
$\mu\text{S}/\text{cm}$	microsiemens per centimeter
p	attained significance level (probability)
pM	percent modern
pmc	percent modern carbon
ρ	rho (test statistic from Spearman's rank-order correlation test)
TU	tritium unit
yr	year
>	greater than
<	less than
\leq	less than or equal to
%	percent
\%	per mil

Status and Understanding of Groundwater Quality in the Klamath Mountains Study Unit, 2010: California GAMA Priority Basin Project

By George L. Bennett V, Miranda S. Fram, and Kenneth Belitz

Abstract

Groundwater quality in the Klamath Mountains (KLAM) study unit was investigated as part of the Priority Basin Project of the California Groundwater Ambient Monitoring and Assessment (GAMA) Program. The study unit is located in Del Norte, Humboldt, Shasta, Siskiyou, Tehama, and Trinity Counties. The GAMA Priority Basin Project is being conducted by the California State Water Resources Control Board in collaboration with the U.S. Geological Survey (USGS) and the Lawrence Livermore National Laboratory.

The GAMA Priority Basin Project was designed to provide a spatially unbiased, statistically robust assessment of the quality of untreated (raw) groundwater in the primary aquifer system. The assessment is based on water-quality data and explanatory factors for groundwater samples collected in 2010 by the USGS from 39 sites and on water-quality data from the California Department of Public Health (CDPH) water-quality database. The primary aquifer system was defined by the depth intervals of the wells listed in the CDPH water-quality database for the KLAM study unit. The quality of groundwater in the primary aquifer system may be different from that in the shallower or deeper water-bearing zones; shallow groundwater may be more vulnerable to surficial contamination.

This study included two types of assessments: (1) a *status assessment*, which characterized the status of the current quality of the groundwater resource by using data from samples analyzed for volatile organic compounds, pesticides, and naturally occurring inorganic constituents, such as major ions and trace elements, and (2) an *understanding assessment*, which evaluated the natural and human factors potentially affecting the groundwater quality. The assessments were intended to characterize the quality of groundwater resources in the primary aquifer system of the KLAM study unit, not the quality of treated drinking water delivered to consumers by water purveyors.

Relative-concentrations (sample concentrations divided by the health- or aesthetic-based benchmark concentrations)

were used for evaluating groundwater quality for those constituents that have Federal or California regulatory or non-regulatory benchmarks for drinking-water quality. A relative-concentration greater than ($>$) 1.0 indicates a concentration greater than a benchmark, and a relative-concentration less than or equal to (\leq) 1.0 indicates a concentration less than or equal to a benchmark. Relative-concentrations of organic constituents were classified as "high" (relative-concentration > 1.0), "moderate" ($0.1 < \text{relative-concentration} \leq 1.0$), or "low" (relative-concentration ≤ 0.1). For inorganic constituents, the boundary between low and moderate relative-concentration was set at 0.5.

Aquifer-scale proportion was used in the status assessment as the primary metric for evaluating regional-scale groundwater quality. High aquifer-scale proportion is defined as the percentage of the area of the primary aquifer system with a relative-concentration greater than 1.0 for a particular constituent or class of constituents; percentage is based on an areal rather than a volumetric basis. Moderate and low aquifer-scale proportions were defined as the percentages of the primary aquifer system with moderate and low relative-concentrations, respectively.

The KLAM study unit includes more than 8,800 square miles (mi^2), but only those areas near the sampling sites, about 920 mi^2 , are included in the areal assessment of the study unit. Two statistical approaches—grid-based and spatially weighted—were used to evaluate aquifer-scale proportions for individual constituents and classes of constituents. To confirm this methodology, 90 percent confidence intervals were calculated for the grid-based high aquifer-scale proportions and were compared to the spatially weighted results, which were found to be within these confidence intervals in all cases. Grid-based results were selected for use in the status assessment unless, as was observed in a few cases, a grid-based result was zero and the spatially weighted result was not zero, in which case, the spatially weighted result was used.

The *status assessment* showed that inorganic constituents with human-health benchmarks were detected at high relative-concentrations in 2.6 percent of the primary

2 Status and Understanding of Groundwater Quality in the Klamath Mountains Study Unit, 2010

aquifer system and at moderate relative-concentrations in 10 percent of the system. The high aquifer-scale proportion for inorganic constituents mainly reflected the high aquifer-scale proportions of boron. Inorganic constituents with secondary maximum contaminant levels were detected at high relative-concentrations in 13 percent of the primary aquifer system and at moderate relative-concentrations in 10 percent of the system. The constituents present at high relative-concentrations included iron and manganese.

Organic constituents with human-health benchmarks were not detected at high relative-concentrations, but were detected at moderate relative-concentrations in 1.9 percent of the primary aquifer system. The 1.9 percent reflected a spatially weighted moderate aquifer-scale proportion for the gasoline additive methyl *tert*-butyl ether. Of the 148 organic constituents analyzed, 14 constituents were detected. Only one organic constituent had a detection frequency of greater than 10 percent—the trihalomethane, chloroform.

The second component of this study, the *understanding assessment*, identified the natural and human factors that may have affected the groundwater quality in the KLAM study unit by evaluating statistical correlations between water-quality constituents and potential explanatory factors. The potential explanatory factors evaluated were aquifer lithology, land use, hydrologic conditions, depth, groundwater age, and geochemical conditions. Results of the statistical evaluations were used to explain the occurrence and distribution of constituents in the KLAM study unit.

Groundwater age distribution (modern, mixed, or pre-modern), redox class (oxic, mixed, or anoxic), and dissolved oxygen concentration were the explanatory factors that best explained occurrence patterns of the inorganic constituents. High concentrations of boron were found to be associated with groundwater classified as mixed or pre-modern with respect to groundwater age. Boron was also negatively correlated to dissolved oxygen and positively correlated to specific conductance. Iron and manganese concentrations were strongly associated with low dissolved oxygen concentrations, anoxic and mixed redox classifications, and pre-modern groundwater. Specific conductance concentrations were found to be related to pre-modern groundwater, low dissolved oxygen concentrations, and high pH.

Chloroform was selected for additional evaluation in the *understanding assessment* because it was detected in more than 10 percent of wells sampled in the KLAM study unit. Septic tank density was the only explanatory factor that was found to relate to chloroform concentrations.

Introduction

To assess the quality of ambient groundwater in aquifers used for drinking-water supply and to establish a baseline groundwater-quality monitoring program, the California State Water Resources Control Board (SWRCB), in collaboration

with the U.S. Geological Survey (USGS) and Lawrence Livermore National Laboratory (LLNL), implemented the Groundwater Ambient Monitoring and Assessment (GAMA) Program (California State Water Resources Control Board, 2010, website at <http://www.waterboards.ca.gov/gama/>). The statewide GAMA Program was initiated in 2000 in response to Legislative mandates (State of California, 1999, 2001a). The program currently consists of four projects: (1) the GAMA Priority Basin Project, conducted by the USGS (U.S. Geological Survey, 2010, website at <http://ca.water.usgs.gov/gama/>); (2) the GAMA Domestic Well Project, conducted by the SWRCB; (3) the GAMA Special Studies, conducted by LLNL; and (4) the GeoTracker GAMA web-based groundwater information system, developed by the SWRCB. On a statewide basis, the GAMA Priority Basin Project focused on the primary aquifer system, typically the deep portion of the groundwater resource, and the SWRCB Domestic Well Project generally focused on the shallow aquifer systems.

The GAMA Priority Basin Project was initiated in response to the Groundwater Quality Monitoring Act of 2001 to assess and monitor the quality of groundwater in California (State of California, 2001b). The GAMA Priority Basin Project is a comprehensive assessment of statewide groundwater quality designed to improve the understanding of and to identify risks to groundwater resources and to increase the availability of information about groundwater quality to the public. The USGS, in collaboration with the SWRCB, developed a monitoring plan to assess groundwater basins through direct sampling of groundwater and other statistically reliable sampling approaches (Belitz and others, 2003; California State Water Resources Control Board, 2003). Additional partners in the GAMA Priority Basin Project include the California Department of Public Health (CDPH), the California Department of Pesticide Regulation (CDPR), the California Department of Water Resources (CDWR), and local water agencies and well owners (Kulongsiki and Belitz, 2004).

The ranges of hydrologic, geologic, and climatic conditions in California were considered in this statewide assessment of groundwater quality. Belitz and others (2003) partitioned the State into 10 hydrogeologic provinces, each with distinctive hydrologic, geologic, and climatic characteristics ([fig. 1](#)). These hydrogeologic provinces include groundwater basins and subbasins designated by the CDWR (California Department of Water Resources, 2003). Groundwater basins generally consist of relatively permeable, unconsolidated deposits of alluvial origin. Eighty percent of California's approximately 16,000 active or standby public-supply wells or springs listed in the statewide water-quality database maintained by the CDPH (hereinafter referred to as CDPH sites) are located within CDWR-designated groundwater basins (Belitz and others, 2003). These basins were prioritized for sampling on the basis of the number of CDPH sites in the basin, with secondary consideration given to municipal groundwater use, agricultural pumping, the number of historically leaking underground fuel tanks,

and the number of square-mile sections having registered pesticide applications (Belitz and others, 2003). Of the 472 CDWR-designated basins and subbasins, 116 basins contain approximately 95 percent of CDPH sites located in CDWR-designated groundwater basins and were defined as priority

basins (Belitz and others, 2003). The remaining 356 basins were defined as low-use basins. All of the priority basins, selected low-use basins, and selected areas outside of basins were grouped into 35 USGS–GAMA study units that together represent approximately 95 percent of all CDPH sites.



Figure 1. Hydrogeologic provinces of California and the location of the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

4 Status and Understanding of Groundwater Quality in the Klamath Mountains Study Unit, 2010

The Klamath Mountains (KLAM) study unit corresponds to the Klamath Mountains hydrogeologic province described by Belitz and others (2003) ([fig. 1](#)), which is composed primarily of areas outside of CDWR-designated groundwater basins. About 99 percent of the total area and approximately 85 percent of the CDPH sites in the province are outside of CDWR-designated groundwater basins (Belitz and others, 2003). Of the approximately 16,000 CDPH sites throughout the State, only about 1 percent are located in the KLAM study unit. The KLAM study unit includes one *priority basin* (Scott River Valley) and six *low-use basins* (Seiad Valley, Hoopa Valley, Hyampom Valley, Happy Camp Town Area, Hayfork Valley, and Wilson Point Area) (Belitz and others, 2003; California Department of Water Resources, 2003) ([fig. 2](#)).

The goal of the GAMA Priority Basin Project is to produce three types of water-quality assessments for each study unit: (1) Status: assessment of the current quality of the groundwater resource, (2) Understanding: identification of the natural and human factors affecting groundwater quality and explanation of the relations between water quality and selected explanatory factors, and (3) Trends: detection of changes in groundwater quality (Kulogoski and Belitz, 2004). The assessments are intended to characterize the quality of groundwater within the primary aquifer system of the study unit, not the treated drinking water delivered to consumers by water purveyors. The primary aquifer system for a study unit is defined by the depths of the screened or open intervals of the wells listed in the CDPH water-quality database for the study unit. The CDPH water-quality database lists wells used for public drinking-water supplies and includes wells from systems classified as community (such as cities, towns, and mobile-home parks), non-transient, non-community (such as schools, workplaces, and restaurants), and transient, non-community (such as campgrounds and parks). Groundwater quality in the primary aquifer system may differ from that in shallower or deeper parts of the aquifer system. In particular, shallower groundwater may be more vulnerable to contamination from the land surface.

Purpose and Scope

The purposes of this report are to provide a (1) *study unit description*: description of the hydrogeologic setting of the KLAM study unit, (2) *status assessment*: assessment of the status of the current quality of groundwater in the primary aquifer system in the KLAM study unit, and (3) *understanding assessment*: identification of the natural and anthropogenic factors affecting groundwater quality. Assessments are made for chemical constituents only; microbiological indicators of groundwater quality are not discussed in this report. Trends in groundwater quality are not discussed in this report.

Features of the hydrogeologic setting are described on the scale of the entire KLAM study unit; features of specific alluvial basins and delineated hard-rock aquifers are not discussed. Geology, land-use patterns, and hydrology of the study unit are summarized. Characteristics of the primary aquifer system, including aquifer lithology, land use, hydrologic conditions, depth, groundwater age, and geochemical conditions are described by using explanatory factor data compiled for the 39 groundwater sites sampled by USGS–GAMA for the study unit.

The status assessment includes analyses by the USGS of water-quality data for 39 sites, 38 of which were selected for spatial coverage of 1 site per grid cell (hereinafter referred to as USGS-grid sites), across the KLAM study unit. The details of sample collection, analysis, and quality-assurance procedures for the KLAM study unit and all of the water-quality data collected are reported by Mathany and Belitz (2014). Water-quality data from the CDPH water-quality database were used to supplement data collected by the USGS for the GAMA Program. The resulting set of water-quality data from USGS-grid sites and CDPH sites was considered to be representative of the primary aquifer system in the KLAM study unit; the primary aquifer system is defined by the depths of the screened or open intervals of the sites listed in the CDPH water-quality database for the KLAM study unit. GAMA status assessments were designed to provide a statistically robust characterization of groundwater quality in the primary aquifer system at the basin-scale (Belitz and others, 2003, 2010). The statistically robust design also allows basins to be compared and results to be synthesized regionally and statewide. This report describes methods used in designing the sampling network, identifying CDPH data for use in the status assessments, estimating aquifer-scale proportions of relative-concentrations, and assessing the status of groundwater quality by statistical and graphical approaches.

To provide context, the water-quality data discussed in this report were compared to California and Federal regulatory and non-regulatory benchmarks for drinking water. This study does not attempt to evaluate the quality of water delivered to consumers; after withdrawal from the ground, water typically is treated, disinfected, or blended with water from other sources to maintain acceptable water quality. Regulatory benchmarks apply to drinking water that is delivered to the consumer, not to untreated groundwater.

The understanding assessment is based on water-quality data from 39 sites sampled by the USGS for the GAMA Program (Mathany and Belitz, 2014). The potential explanatory factors affecting water quality in the primary aquifer system evaluated are aquifer lithology, land use, hydrologic conditions, depth, groundwater age, and geochemical conditions. Connections between potential explanatory factors and water quality were evaluated by using statistical tests for correlations and by analysis of graphical relations.

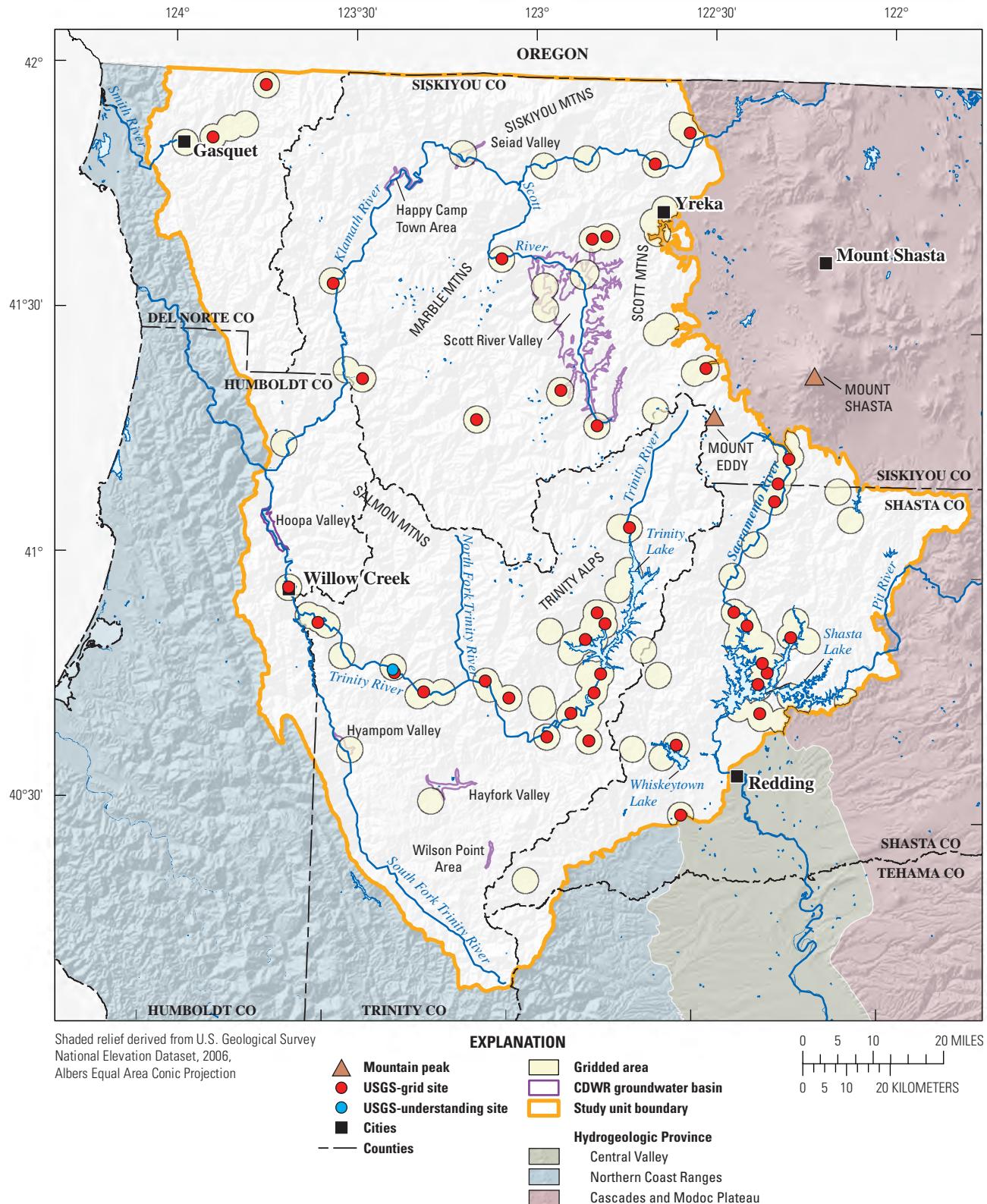


Figure 2. Geographic features and locations of sampled sites in the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Methods

This section describes the methods used for the status assessment and understanding assessment for water quality in the KLAM study unit. Methods used for compiling data for the potential explanatory factors are described in [appendix A](#).

Status Assessment

The *status assessment* is intended to characterize the quality of groundwater resources in the primary aquifer system of the KLAM study unit. Methods used for the status assessment included (1) assembling water-quality benchmarks, (2) assembling datasets for use in the status assessment and calculating relative-concentrations, (3) selecting constituents for additional evaluation, and (4) calculating aquifer-scale proportions for these constituents.

Water-Quality Benchmarks and Relative-Concentrations

To provide context for water-quality data, measured concentrations of constituents may be compared to water-quality benchmarks established by the U.S. Environmental Protection Agency (USEPA) and CDPH that are typically applied to finished drinking water (U.S. Environmental Protection Agency, 1999, 2009, 2012a; California Department of Public Health, 2010, 2013). The benchmarks used for each constituent were selected in the following order of priority:

1. Regulatory, health-based CDPH and USEPA maximum contaminant levels (MCL-CA and MCL-US), action levels (AL-US), and treatment technique levels (TT-US).
2. Non-regulatory CDPH and USEPA secondary maximum contaminant levels (SMCL-CA and SMCL-US). For constituents with recommended and upper SMCL-CA levels, the values for the upper levels were used.
3. Non-regulatory, health-based CDPH notification levels (NL-CA), USEPA lifetime health advisory levels (HAL-US), and USEPA risk-specific doses for 1:100,000 (RSD5-US).

For constituents with multiple types of benchmarks, this hierarchy may not result in selection of the benchmark with the lowest concentration. Additional information on the types of benchmarks and listings of the benchmarks for all constituents analyzed are provided by Mathany and Belitz (2014).

Groundwater-quality data are presented as relative-concentrations, the concentrations of constituents measured in groundwater relative to regulatory and non-regulatory benchmarks used to evaluate drinking-water quality:

$$\text{Relative-concentration} = \frac{\text{Sample concentration}}{\text{Benchmark concentration}} \quad (1)$$

Relative-concentrations less than 1.0 indicate a sample concentration less than the benchmark, and relative-concentrations greater than 1.0 indicate a sample concentration greater than the benchmark. The use of relative-concentrations also permits comparison on a single scale of constituents present at a wide range of concentrations. Relative-concentrations can only be computed for constituents with water-quality benchmarks; therefore, constituents without water-quality benchmarks are not included in the *status assessment*.

The two microbial indicators analyzed in samples from the KLAM study unit, total coliform bacteria and *Escherichia coli* (*E. coli*), have drinking-water-quality benchmarks, but are not included in the status assessment because the results will be presented in one report for all 35 GAMA Priority Basin Project public-supply aquifer study units (Carmen Burton, U.S. Geological Survey, written commun., 2014).

Toccalino and others (2004), Toccalino and Norman (2006), and Rowe and others (2007) previously used the ratio of measured sample concentration to the benchmark concentration [either MCL-US or health-based screening levels (HBSLs)] and defined this ratio as the benchmark quotient. HBSLs were not used in this report because HBSLs are not currently used as benchmarks by California drinking-water regulatory agencies. Because different water-quality benchmarks may be used to calculate relative-concentrations and benchmark quotients, the terms are not interchangeable.

For ease of discussion, relative-concentrations of constituents were classified into low, moderate, and high categories:

Category	Relative-concentrations for organic constituents	Relative-concentrations for inorganic constituents
High	> 1	> 1
Moderate	> 0.1 and ≤ 1	> 0.5 and ≤ 1
Low	≤ 0.1	≤ 0.5

For organic constituents, a relative-concentration of 0.1 was used as a threshold to distinguish between low and moderate relative-concentrations for consistency with other studies and reporting requirements (U.S. Environmental Protection Agency, 1998; Toccalino and others, 2004). For inorganic constituents, a relative-concentration of 0.5 was used as a threshold to distinguish between low and moderate relative-concentrations. The primary reason for using a higher threshold was to focus attention on the inorganic constituents of greatest concern (Fram and Belitz, 2012). The naturally occurring inorganic constituents tend to be more prevalent than organic constituents in groundwater. Although more complex classifications could be devised based on the properties and sources of individual constituents, use of a single moderate/low threshold value for each of the two major groups of constituents provided a consistent objective criteria for distinguishing constituents present at moderate rather than low concentrations.

Datasets Used for Status Assessment

Groundwater-quality data used for the status assessment came from sites sampled by the USGS and from the CDPH water-quality database. To obtain a spatially unbiased representation of the KLAM study unit, a grid-based approach was used, which relied on sites sampled by the USGS (USGS-grid sites) supplemented by data from CDPH sites (CDPH-grid sites) selected to provide a more complete coverage of the gridded area. Combined, they are referred to as the grid-site dataset. Additional data from the CDPH water-quality database were used for a spatially weighted approach described later. This section describes how these datasets was constructed.

U.S. Geological Survey Grid Sites

The primary data used for the grid-based calculations of aquifer-scale proportions of relative-concentrations were from sites sampled by USGS-GAMA. Detailed descriptions of the methods used to identify sites for sampling are given in Mathany and Belitz (2014). Briefly, the KLAM study unit was divided into 40 equal-area grid cells, and the objective was for the USGS to collect water-quality samples from one CDPH site in each cell. The KLAM study unit had relatively few CDPH sites, and these CDPH sites were not evenly distributed ([fig. 3](#)). To minimize the number of cells without any sampled sites, only the parts of the study unit near CDPH sites were included in the gridded area. A 1.86-mile (mi) (3-kilometer [km]) radius circle was drawn around each CDPH site, and the collective area encompassed by the circles was divided into forty 23-square-mile (mi²) (60-square-kilometer [km²]) grid cells, as described by Scott (1990) and shown in [appendix B, figs. B1–B5](#). One CDPH site was randomly selected for sampling in each cell. If a cell had no accessible CDPH sites, then an appropriate site was selected by door-to-door canvassing. The USGS sampled sites in 38 of the 40 grid cells (hereinafter referred to as USGS-grid sites). Of the 38 USGS-grid sites, 33 were listed in the CDPH water-quality database, and the other 5 sites were screened or had open intervals at depths similar to those of sites listed in the CDPH water-quality database. USGS-grid sites were named with an alphanumeric GAMA identification consisting of the prefix “KLAM” and a number indicating the order of sample collection ([appendix B, figs. B1–B5](#)). One additional site was sampled by USGS-GAMA. This “USGS-understanding” site was given the identification number KLAM-U-01. This site was sampled in error and is in the same cell as the USGS-grid site KLAM-15. Samples collected from USGS-grid sites were analyzed for 216 constituents ([table 1](#)). The collection, analysis, and quality-control data for the constituents listed in [table 1](#) are described by Mathany and Belitz (2014).

California Department of Public Health Grid Sites

The CDPH data were used in three ways in the *status assessment*: (1) to supplement the USGS data for the grid-based calculations of aquifer-scale proportions, (2) to select constituents for additional evaluation in the assessment, and (3) to provide additional data used in the spatially weighted calculations of aquifer-scale proportions.

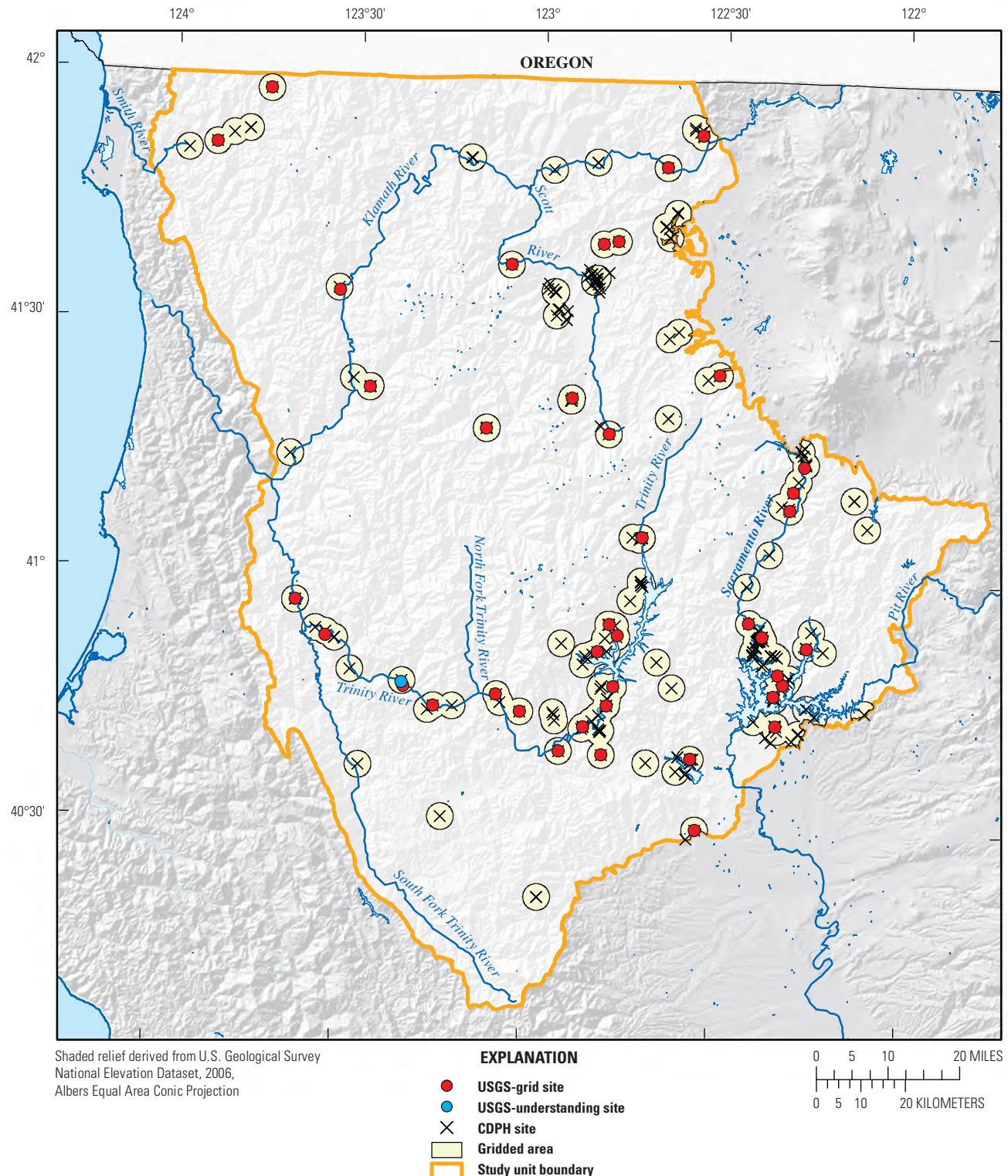


Figure 3. Locations of grid sites, the understanding site, and California Department of Public Health (CDPH) sites sampled for the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Table 1. Summary of constituent groups and numbers of constituents sampled for each constituent group by the U.S. Geological Survey (USGS) in the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[Abbreviations and symbols: B, boron; C, carbon; H, hydrogen; He, helium; O, oxygen; Sr, strontium; δ , delta notation, the ratio of a heavier isotope of an element. Unless otherwise noted, constituent analyses were performed at the USGS National Water Quality Laboratory]

Site summary	
	Number of constituents analyzed
Total number of sites	39
Number of grid sites sampled	38
Number of understanding sites sampled	1
Inorganic constituents	
Alkalinity and total dissolved solids (TDS)	2
Gross alpha and beta radioactivity ¹	2
Trace elements and major and minor ions	35
Nutrients	5
Radon-222	1
Specific conductance (field) ²	1
Uranium isotopes ³	1
Organic constituents	
Pesticides and pesticide degradates	63
Volatile organic compounds (VOCs) ⁴	85
Tracers	
Arsenic and iron species	2
$\delta^{11}\text{B}$ in water ⁵	1
Carbon-14 and $\delta^{13}\text{C}$ of dissolved carbonates	2
Dissolved oxygen, pH, and temperature (field) ²	3
$\delta^2\text{H}$ and $\delta^{18}\text{O}$ stable isotopes of water	2
Dissolved noble gases (helium, neon, argon, krypton, xenon), ${}^3\text{He}/{}^4\text{He}$ of helium, and tritium ⁶	7
${}^{87}\text{Sr}/{}^{86}\text{Sr}$ of dissolved strontium ⁵	1
Tritium ⁷	1
Microbial indicators	
Total coliforms and <i>Escherichia coli</i> (<i>E. coli</i>) ²	2
Sum:	216

¹ Gross alpha particle and gross beta particle activities were measured after 72-hour and 30-day holding times; data from the 72-hour measurements are used in this report.

² Analyzed by USGS field staff.

³ Uranium activity equals the sum of the three uranium isotopes measured: uranium-234, uranium-235, and uranium-238.

⁴ Includes 10 constituents classified as fumigants or fumigant synthesis byproducts.

⁵ Analyzed at the USGS Metals Isotope Research Laboratory, Menlo Park, California.

⁶ Analyzed at Lawrence Livermore National Laboratory, Livermore, California.

⁷ Analyzed at USGS Stable Isotope and Tritium Laboratory, Menlo Park, California.

Data collected by USGS–GAMA at the USGS-grid sites (Mathany and Belitz, 2014) provided the majority of the data used for the *status assessment* for inorganic constituents. Although other organizations also collect water-quality data, the CDPH database is the only statewide database of groundwater-chemistry data available for comprehensive analysis. The CDPH water-quality database contains records from more than 25,000 sites, necessitating targeted retrievals to effectively access relevant water-quality data. For example, for the area representing the KLAM study unit, the CDPH water-quality database contains 16,801 records from 204 sites for the period of record before this study (June 14, 1984, to November 30, 2007). To provide additional data in grid cells that did not have wells sampled by USGS–GAMA, two CDPH sites were selected from the CDPH water-quality database to provide inorganic constituent data. CDPH sites with data available for the time period December 1, 2007, through December 31, 2010, were considered, and if a site had more than one analysis for a constituent, data from the most recent sampling event were selected. The selected CDPH sites (hereinafter referred to as CDPH-grid sites) were named with an alphanumeric GAMA identification consisting of the prefix “KLAM-DPH” and the next number in the sequence of grid sites. One of the cells without a USGS-grid site contained two CDPH sites, and both sites only had data for nutrients. One site was randomly selected from the two to be the CDPH-grid site. The other cell without a USGS-grid site contained one CDPH site. This site was selected as the CDPH-grid site, and it provided data for nutrients and a subset of trace elements ([table C1](#)).

CDPH data were not used to provide grid values for volatile organic compounds (VOCs) or pesticides because a larger number of VOCs and pesticide compounds were analyzed for the USGS–GAMA Program than were available from the CDPH water-quality database. In addition, method detection limits for USGS–GAMA analyses were one to two orders of magnitude less than the reporting levels for analyses compiled by the CDPH (Fram and Belitz, 2012).

Additional Data Used for Spatially Weighted Calculations

The spatially weighted calculations of aquifer-scale proportions of relative-concentrations used data from all KLAM study unit sites sampled by USGS–GAMA and from all sites in the CDPH water-quality database with water-quality data collected during the 3-year interval December 1, 2007, through December 31, 2010. For sites and constituents with USGS and CDPH data, only the USGS data were used. Ninety-two CDPH sites that were not also USGS-grid sites had data for at least one water-quality constituent; however, for 66 of these sites, data were only available for nutrients. Water-quality information from the CDPH wells used in the spatially weighted analysis is available from the GeoTracker GAMA web-based groundwater information system, developed by the SWRCB (California State Water Resources Control Board, 2011).

Selection of Constituents for Additional Evaluation in the Status Assessment

As many as 216 constituents were analyzed in samples from KLAM study unit sites; however, only subsets of these constituents were identified for additional evaluation in the status assessment. Of the 216 constituents analyzed, 100 constituents did not have benchmarks ([table 2](#)). Because relative-concentrations cannot be calculated for constituents without benchmarks, these 100 constituents were not evaluated in this report. The 116 constituents having benchmarks were assessed, and a subset of these constituents were selected for additional evaluation in the status assessment on the basis of the following three criteria:

- Constituents present at high or moderate relative-concentrations in the CDPH water-quality database within the 3-year interval (December 1, 2007, through December 31, 2010), hereinafter referred to as the current sampling period;
- Constituents present at high or moderate relative-concentrations in the USGS-grid sites or USGS-understanding site; or
- Organic constituents with detection frequencies of greater than 10 percent in the USGS-grid site dataset for the study unit.

These criteria identified 13 inorganic and 3 organic constituents for additional evaluation in the status assessment. A complete list of the constituents investigated by USGS–GAMA in the KLAM study unit may be found in the data report (Mathany and Belitz, 2014).

The CDPH water-quality database also was used to identify constituents with high relative-concentrations historically, but not currently. The historical period was defined as extending from the earliest record maintained in the CDPH water-quality database for sites in the KLAM study unit to November 30, 2007 (June 14, 1984, to November 30, 2007). Constituent concentrations may have been historically high, but not currently high, because of improvement of groundwater quality with time or abandonment of sites with high concentrations. Historically high concentrations of constituents that did not otherwise meet the criteria for additional evaluation are not considered representative of potential groundwater-quality concerns in the study unit from 2007 to 2010.

For the KLAM study unit, eight inorganic constituents had high concentrations reported in the CDPH water-quality database during the historical period, but did not have high concentrations reported during the current period or in the USGS–GAMA dataset ([table 3](#)). Of these eight constituents, two were also detected at moderate relative-concentrations during the current period (chloride and gross alpha radioactivity).

Table 2. Numbers of constituents analyzed and detected, by benchmark and constituent type, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[Benchmark type: Regulatory health-based benchmarks include: MCL-US, USEPA maximum contaminant level; AL-US, USEPA action level; MCL-CA, CDPH maximum contaminant level. Non-regulatory health-based benchmarks include HAL-US, USEPA lifetime health advisory level; NL-CA, CDPH notification level. Non-regulatory aesthetic benchmarks include SMCL-CA, CDPH secondary maximum contaminant level. **Abbreviations:** USEPA, U.S. Environmental Protection Agency; CDPH, California Department of Public Health]

Benchmark type	Constituent type								Sum of all constituents	
	Inorganic constituents		Organic constituents		Age tracers		Microbial indicators		Number analyzed	Number detected
	Number analyzed	Number detected	Number analyzed	Number detected	Number analyzed	Number detected	Number analyzed	Number detected	Number analyzed	Number detected
Regulatory health-based	20	20	36	11	1	1	2	2	59	34
Non-regulatory health-based	5	5	42	2	0	0	0	0	47	7
Non-regulatory aesthetic-based	9	9	0	0	1	1	0	0	10	10
No benchmark	13	13	70	1	17	17	0	0	100	31
Total:	47	47	148	14	19	19	2	2	216	82

Table 3. Constituents historically (June 14, 1984, to November 30, 2007) reported at concentrations greater than benchmarks in the California Department of Public Health database, but not during the 3-year period used in the status assessment, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[Benchmark type: Regulatory, health-based benchmarks: MCL-US, USEPA maximum contaminant level; AL-US, USEPA action level; MCL-CA, CDPH maximum contaminant level. Non-regulatory, health-based benchmarks: HAL-US, USEPA lifetime health advisory level. Non-regulatory, aesthetic-based benchmarks: SMCL-CA, CDPH secondary maximum contaminant level. **Benchmark units:** mg/L, milligrams per liter; µg/L, micrograms per liter; pCi/L, picocuries per liter. **Other abbreviations:** GAMA, Groundwater Ambient Monitoring and Assessment Program; USEPA, U.S. Environmental Protection Agency; CDPH, California Department of Public Health]

Constituent	Typical use or source	Benchmark			Date of most recent high value	Number of sites with historical data	Number of sites with a high value
		Type ¹	Value	Units			
Aluminum	Naturally occurring	MCL-CA	1,000	µg/L	05/19/98	58	1
Chloride ²	Naturally occurring	SMCL-CA	500	mg/l	06/24/99	57	1
Fluoride	Naturally occurring	MCL-CA	2	µg/L	11/07/01	68	1
Gross alpha particle activity ²	Naturally occurring	MCL-US	15	pCi/L	05/05/89	41	1
Lead	Naturally occurring	AL-US	15	µg/L	03/09/04	57	2
Nickel	Naturally occurring	MCL-CA	100	µg/L	09/14/99	53	1
Radium-226	Naturally occurring	MCL-US	5	pCi/L	05/05/89	2	1
Zinc	Naturally occurring	SMCL-CA	5,000	µg/L	03/10/98	57	2

¹ Maximum contaminant level benchmarks are listed as MCL-US when the MCL-US and MCL-CA are identical, and as MCL-CA when the MCL-CA is lower than the MCL-US or no MCL-US exists.

Sources of benchmarks: MCL-CA: California Department of Public Health (2013); MCL-US and AL-US: U.S. Environmental Protection Agency (2012a); SMCL-CA: California Department of Public Health (2013).

² Constituent was detected at moderate relative-concentrations within the grid-site dataset and therefore was selected for additional evaluation in the status assessment for the study unit.

Calculation of Aquifer-Scale Proportions

Two statistical approaches, grid-based and spatially weighted (Belitz and others, 2010), were selected to evaluate the proportions of the primary aquifer system in the KLAM study unit with high, moderate, and low relative concentrations of constituents. For ease of discussion, these proportions are referred to as “high,” “moderate,” and “low” aquifer-scale proportions. Calculations of aquifer-scale proportions were made for individual constituents, as well as for classes of constituents. The classes consisted of groups of related individual constituents.

The grid-based calculation uses the grid-site dataset assembled from the USGS-grid and CDPH-grid sites. For each constituent, the high aquifer-scale proportion was calculated by dividing the number of cells represented by a high relative-concentration (> 1.0) for that constituent by the total number of grid cells with data for that constituent. The moderate and low aquifer-scale proportions were calculated using the numbers of cells with moderate and low relative concentrations, respectively. Confidence intervals on the grid-based results for the high aquifer-scale proportions for individual constituents were computed using the Jeffreys interval for the binomial distribution (Brown and others, 2001; Belitz and others, 2010). For calculation of high aquifer-scale proportion for a class of constituents, cells were considered high if any of the constituents in that class had high relative concentrations. Cells were considered moderate if any of the constituents in the class had moderate relative concentrations, but no high relative concentrations. The grid-based estimate is designed to be spatially unbiased. However, the grid-based approach may not detect constituents that are present at high or moderate concentrations in small proportions of the primary aquifer system; therefore, a spatially weighted calculation was performed to complement the grid-based approach.

The spatially weighted calculation used the dataset assembled from all CDPH and USGS–GAMA sites. For each constituent, the high aquifer-scale proportion was calculated by computing the proportion of sites with one or more high relative-concentrations in each cell and then averaging the proportions for all cells (Isaaks and Srivastava, 1989; Belitz and others, 2010). The moderate aquifer-scale proportion was calculated similarly. For calculation of high aquifer-scale proportion for a class of constituents, the aquifer-scale proportion was considered high if any of the constituents in that class were high. The aquifer-scale proportion was considered moderate if any of the constituents in the class were moderate, but none were high.

In addition, for each constituent, the raw detection frequencies of high and moderate aquifer-scale proportions for individual constituents were calculated using the same dataset as used for the spatially weighted calculations. Raw detection frequencies are not spatially unbiased, however, because the sites in the CDPH water-quality database are not uniformly distributed throughout the KLAM study unit (fig. 3). For example, if a constituent were present at high concentrations

in a small region of the aquifer with a high density of sites, the raw detection frequency of high values would be greater than the high aquifer-scale proportion. Raw detection frequencies are provided for reference but were not used to assess aquifer-scale proportions (see [appendix C](#) for additional details about the statistical approaches).

The grid-based high aquifer-scale proportions were used to represent proportions in the primary aquifer system unless the spatially weighted proportions were significantly different from the grid-based values. Significantly different results were defined as follows:

- If the grid-based high aquifer-scale proportion was zero and the spatially weighted proportion was non-zero, then the spatially weighted result was used. This situation can happen when the relative-concentration of a constituent is high in a small fraction of the primary aquifer system.
- If the grid-based high aquifer-scale proportion was non-zero and the spatially weighted proportion was outside the 90 percent confidence interval (based on the Jeffreys interval for the binomial distribution), then the spatially weighted proportion was used.

The grid-based moderate and low aquifer-scale proportions were used in most cases because the reporting levels for many organic constituents and some inorganic constituents in the CDPH water-quality database were higher than the threshold between moderate and low categories. However, if the grid-based moderate proportion was zero and the spatially weighted proportion non-zero, then the spatially weighted value was used as a minimum estimate for the moderate proportion.

Understanding Assessment

Methods used for the understanding assessment included (1) selecting constituents for additional evaluation in the understanding assessment, and (2) applying statistical tests of relations between potential explanatory factors and groundwater quality.

Selection of Constituents for Additional Evaluation in the Understanding Assessment

The understanding assessment places groundwater quality within a physical and chemical context based on the potential explanatory factors. A subset of constituents was selected for additional evaluation in the understanding assessment on the basis of the following two criteria:

- Constituents with high aquifer-scale proportions of greater than 2 percent. These constituents were selected to focus the assessment for understanding on those constituents that have the greatest effect on groundwater quality.

- Classes of organic constituents that included constituents with study-unit detection frequencies of greater than 10 percent, regardless of concentration.

These criteria resulted in selection of three inorganic constituents and one organic constituent for additional evaluation in the understanding assessment. The understanding assessment was based on the 39 wells sampled by USGS–GAMA (Mathany and Belitz, 2014). Other CDPH wells were not used because data for many of the potential explanatory factors were not available.

Statistical Tests of Relations between Potential Explanatory Factors and Groundwater Quality

Nonparametric statistical methods were used to test the significance of correlations among potential explanatory factors and between water-quality parameters and potential explanatory factors. Nonparametric statistics are robust techniques that generally are not affected by outliers and do not require that the data follow any particular distribution (Helsel and Hirsch, 2002). The attained significance level (p), which was attained from the data and used for hypothesis testing for this report, was compared to a critical level (α) of 5 percent ($\alpha=0.05$) to evaluate whether the relation was statistically significant ($p < \alpha$).

Three different statistical tests were used because the set of potential explanatory factors included categorical and continuous variables. Groundwater age class, aquifer lithology, and oxidation-reduction class were treated as categorical variables. Land use, septic tank density, leaking (or formerly leaking) underground fuel tank (LUFT) density, aridity index, elevation, well depth, depth to top of screened or open interval, pH, and dissolved oxygen were treated as continuous variables. Concentrations of water-quality constituents were treated as continuous variables.

Correlations between potential explanatory factors and water-quality constituents were tested for significance.

- Correlations between continuous variables were evaluated by using the Spearman's rho test to calculate the rank-order coefficient (ρ , rho) and to determine whether the correlation was significant ($p < \alpha$). Values of ρ could range from -1 (complete correlation in opposite directions) to 0 (no correlation) to 1 (complete correlation in the same direction).
- Relations between categorical variables and continuous variables were evaluated by using the Wilcoxon rank-sum test. The null hypothesis for the test is that the median values of the continuous variable are not significantly different from one another.
- Relations between categorical variables were evaluated using contingency tables (Helsel and Hirsch, 2002).

For a contingency table analysis, the data are recorded as a matrix of counts. One variable is assigned to the columns and the other to the rows, and the entries in the cells of the matrix are the number of observations, O_{ij} , which fall into the i th row and the j th column of the matrix. A test statistic (X_{ct}) is computed by comparing the observed counts (O_{ij}) to the counts expected if the two variables are independent, and significance is determined by comparing the test statistic to the $(1-\alpha)$ quantile of the chi-squared distribution. If the contingency table yielded a result of significance, the relation of the variables was determined by comparing the relative difference in magnitudes of the test statistics in each cell of the contingency table.

Hydrogeologic Setting and Potential Explanatory Factors

The KLAM study unit covers an area of approximately 8,806 mi² (22,809 km²) in parts of Del Norte, Humboldt, Shasta, Siskiyou, Tehama, and Trinity Counties in northern California ([fig. 2](#)) and consists primarily of mountainous terrain composed of relatively low-permeability rocks. The area of the study unit covered by grid cells (gridded area) is about 920 square miles (2,400 square kilometers). The gridded area is commonly located near rivers and lakes throughout the study unit. The study unit is bounded on the east by the volcanic rocks of the Cascades Range and Modoc Plateau, on the west by the Northern Coast Ranges, and on the south by the sediments of the Central Valley. The northern boundary is the Oregon State line.

Features of the hydrogeologic setting are described on the scale of the entire KLAM study unit; features of specific alluvial basins and delineated hard-rock aquifers are not discussed. Geology, land-use patterns, and hydrology of the study unit are summarized. Characteristics of the primary aquifer system are described using explanatory factor data compiled for the 39 sites sampled by USGS–GAMA for the study unit. Explanatory factors are grouped in three categories for discussion: geologic factors (aquifer lithology), land-use factors (percentages of agricultural, natural, and urban land use, and septic and underground fuel tank densities), and hydrologic conditions (elevation, aridity index, site type, well depth, groundwater age, and geochemical conditions). The presence of correlations among explanatory factors may confound interpretation of correlations between explanatory factors and groundwater quality, so correlations among explanatory factors are discussed in this section. The methods used for assigning values for each of the explanatory factors to the 39 sites sampled by USGS–GAMA in the KLAM study unit are described in [appendix A](#).

For this report, the primary aquifer system is defined by the depth intervals over which public-supply wells listed in the CDPH water-quality database are screened or open. The use of the term “primary aquifer system” does not imply that there exists a discrete aquifer unit. In most groundwater basins, public-supply wells generally are screened or open at greater (deeper) depths than are domestic wells (for example, Burow and others, 2008; Burton and others, 2012). Thus, the primary aquifer system generally corresponds to the deeper portion of the aquifer system tapped by public drinking-water supply wells. However, this segregation between the depths used for public drinking-water supply and domestic drinking-water supply wells commonly does not apply in areas outside of groundwater basins defined by the CDWR. Wells in fractured-rock aquifers are most productive at depths where fractures in the local rock are saturated with water, and the density of fractures typically decreases with depth (Freeze and Cherry, 1979; Page and others, 1984; Borchers, 1996; Ingebritsen and Sanford, 1998). The definition of the primary aquifer system in the KLAM study unit is further complicated by the abundance of spring sites among the CDPH sites and the sites sampled by USGS–GAMA. A screened or open interval cannot be defined for springs; although groundwater from a spring may be collected at or near land-surface datum, the depth interval of origin is generally unknown.

Aquifer Lithology

The geologic history of the Klamath Mountains is complex. It is characterized by multiple episodes of oceanic crustal accretion and plutonic emplacement along the Pacific Northwest tectonic boundary between the Juan de Fuca and North American tectonic plates. Accretionary episodes within the KLAM study unit likely began in the early Paleozoic and extended through the Late Jurassic if not middle Cenozoic (Snoke and Barnes, 2006). Each accretionary episode is generally recognized as a unique tectonostratigraphic terrane. The terranes are stacked against one another with high-angle east-dipping faults separating them, with the oldest terranes in the east and progressively younger terranes to the west (Irwin and Wooden, 1999). Regional studies conducted by the USGS and others often divide the Klamath Mountain geologic region into distinct geologic belts or terranes (Irwin and Wooden, 1999; Alt and Hyndman, 2000; Snoke and Barnes, 2006). Each terrane is a complex of similar assemblages of rocks that share a similar history or origin. The terranes of the Klamath Mountains are primarily composed of metasedimentary (metamorphosed oceanic and other sedimentary rocks), granite, and ultramafic rock types ([fig. 4](#)). The granitic rocks are the result of intrusions into the terranes, which emplaced plutons of varying composition and size throughout the Klamath Mountains during their development, while the ultramafic rocks are remnants of oceanic seafloor (Alt and Hyndman, 2000; Snoke and Barnes, 2006).

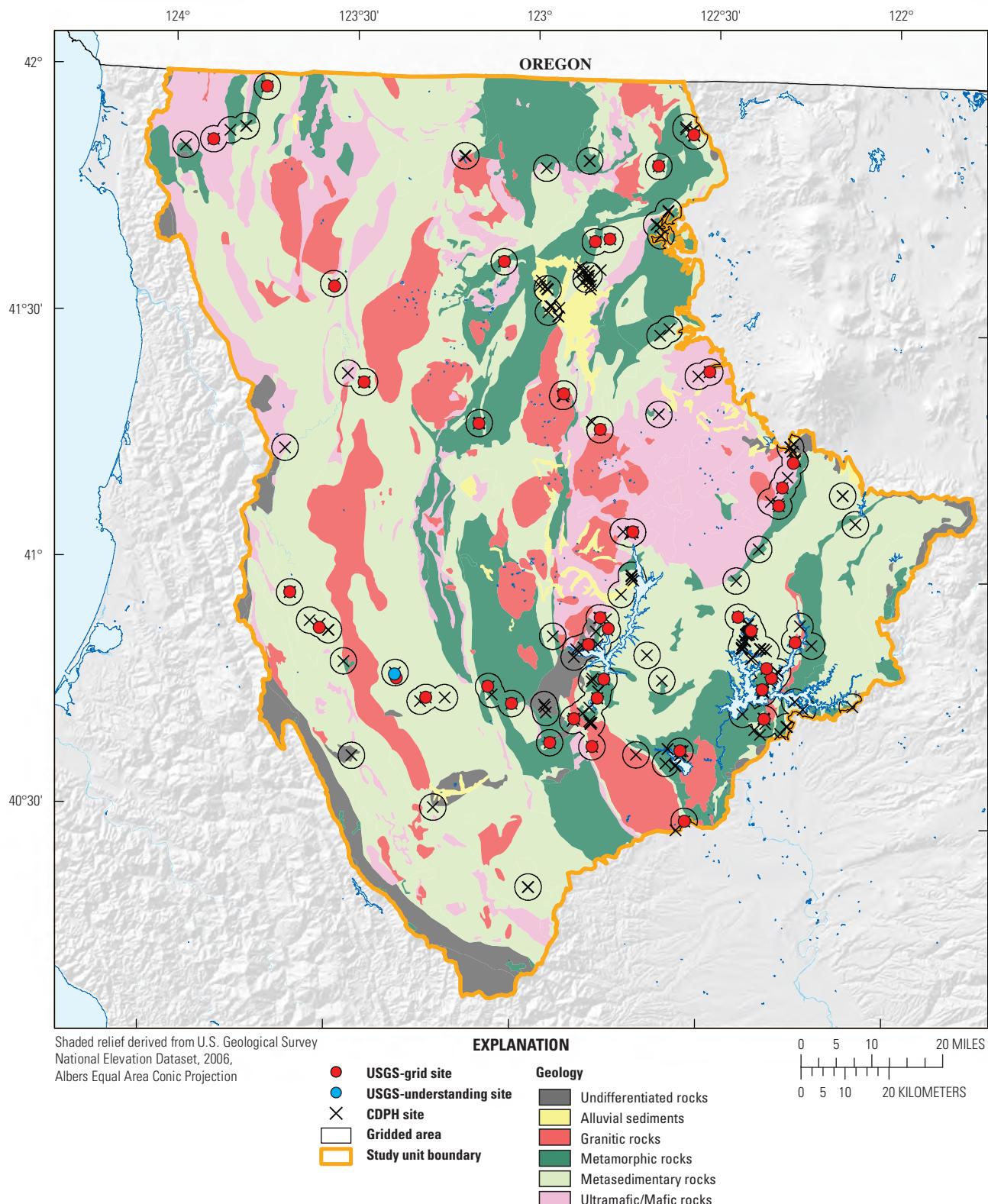


Figure 4. Geology of the Klamath Mountains study unit, California GAMA Priority Basin Project (modified from Saucedo and others, 2000).

For the purpose of examining broad relations between aquifer lithology and groundwater quality, the geologic units represented on the State geologic map (Jennings, 1977; Saucedo and others, 2000) in the KLAM study unit were simplified into six rock types ([fig. 4](#); [appendix A](#)):

- Granitic rocks: Primarily Mesozoic granitic rocks with some Paleozoic granitic rocks;
- Metamorphic rocks (other than metasedimentary): Mesozoic, Paleozoic, and pre-Cenozoic metavolcanic rocks;
- Metasedimentary rocks: Metamorphosed Mesozoic and Paleozoic marine rocks;
- Ultramafic/mafic rocks: Chiefly Mesozoic ultramafic, mafic, or gabbroic rocks;
- Alluvial sediments: Chiefly Quaternary alluvial sediments;
- Undifferentiated rocks.

The specific tectonostratigraphic terranes for each sampling site were not taken into account. In a previous GAMA study in the Sierra Nevada, significant differences in groundwater quality were observed when comparing results based on different rock types (Fram and Belitz, 2012).

The area of each rock type as a percentage of the total area of the KLAM study unit was metasedimentary, 46 percent; metamorphic, 18 percent; ultramafic/mafic, 16 percent; granitic, 13 percent; undifferentiated, 4 percent; and alluvial sediment, 2 percent. The percentages of wells sampled in each rock type were similar to the areal proportions of rock types identified in the study unit. Of the 38 cells with grid wells in the KLAM study unit, 17 wells represent the metasedimentary rock type (45 percent of grid wells), 10 wells represent the metamorphic rock type (26 percent of grid wells), 7 wells represent the ultramafic/mafic rock type (18 percent of grid wells), and 4 wells represent the granitic rock type (10 percent of grid wells). No sampled wells represented either the alluvial sediment or undifferentiated rock types ([table A1](#)). About 12 percent of CDPH wells are located in alluvial sediments, and 6 percent are located in undifferentiated rocks; however, these aquifer lithology classes only represent 2 and 4 percent, respectively, of the KLAM study unit area. The understanding well was in the metasedimentary rock type.

Land Use

Land use was described by three land-use types: natural, urban, and agricultural ([appendix A](#)). Percentages of the three types were calculated for the study unit as whole and for areas within a radius of 500 meters (m) (500-m buffers) around sites (USGS and CDPH) (Johnson and Belitz, 2009). As of 1992, land use in the KLAM study unit was 97 percent natural, 2 percent urban, and 1 percent agricultural ([figs. 5, 6](#); Nakagaki and others, 2007). Nearly all of the agricultural land was located in the Scott River Valley groundwater basin in the northeastern part of the study unit ([fig. 2](#)). No sites were sampled within the Scott River Valley groundwater basin.

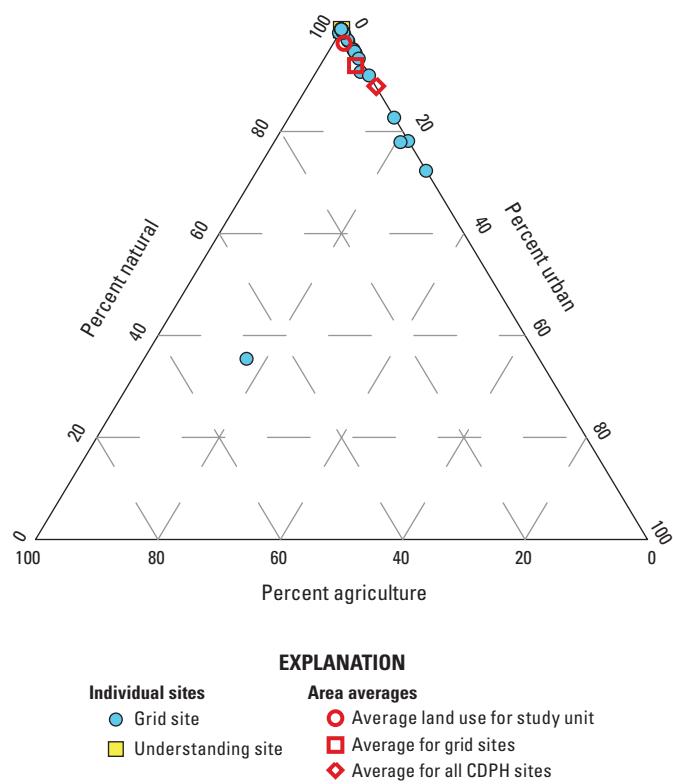


Figure 5. Percentages of urban, agricultural, and natural land use surrounding individual USGS-grid and USGS-understanding sites, and land-use averages in the study unit, around grid sites, and around CDPH sites in the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

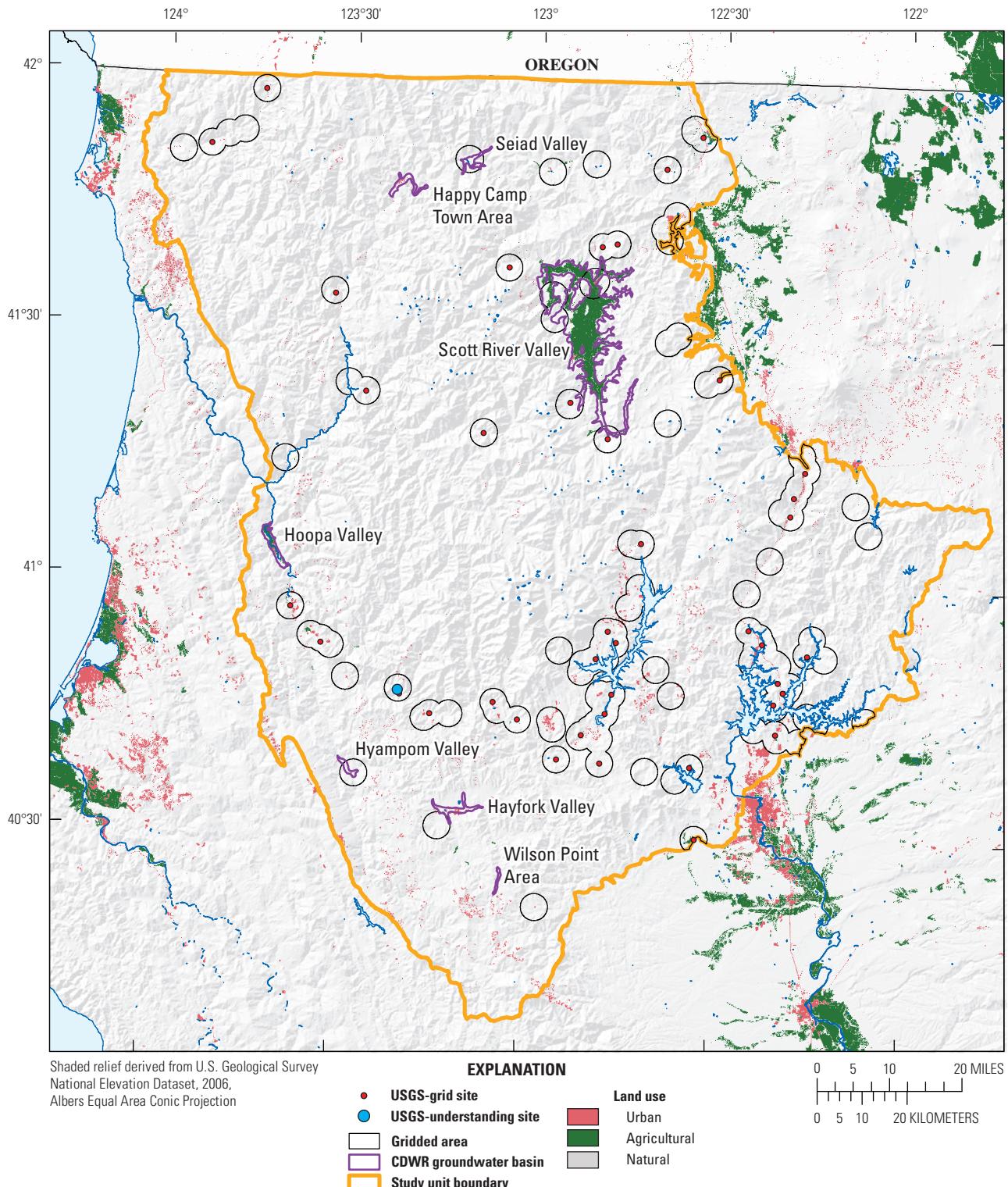


Figure 6. Land use, California Department of Water Resources (CDWR) groundwater basins, and locations of sampled sites within the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Similar to the study unit percentages, land use within the 500-m buffers surrounding the sampled sites was primarily natural. The biggest difference was in the percentage of urban land use. Urban land use in the areas within 500 m of the grid sites was 4 percent, as compared to only 2 percent throughout the entire study unit. Around individual grid sites, urban land use ranged from less than 1 to 28 percent urban, with only 5 of 39 wells surrounded by greater than 10 percent urban land use (fig. 6; table A1).

Septic tanks and LUFTs are also markers of land-use patterns. The density of LUFTs calculated using Thiessen polygons and the density of septic tanks in the 500-m radius area around a site may be indicators of potential sources of anthropogenic contaminants from the land surface. The density of LUFTs around grid sites ranged from 0 to 0.11 tanks

per square kilometer (tanks/km²), and the median density was 0.01 tanks/km² (table A1). A description of how Thiessen polygons were used to calculate LUFT density is included in appendix A. The density of septic tanks around grid sites ranged from 0.09 to 10.85 tanks/km², and the median density was 0.54 tanks/km² (table A1).

Results of Wilcoxon rank-sum tests indicate that none of the land-use factors were significantly correlated to any of the geologic rock types (table 4). Agricultural land use within the KLAM study unit was found to be primarily concentrated in areas of alluvial sediment rock type which generally coincide with CDWR groundwater basins in the KLAM study unit (fig. 6). The statistical analysis may not have identified a correlation with agricultural land use and geology because no wells were sampled in the CDWR-defined groundwater basins.

Table 4. Results of Wilcoxon rank-sum tests for differences in values of land-use factors, hydrologic conditions, geochemical conditions, and selected water-quality constituents between samples classified into groups by 2-factor age class, redox class, or aquifer lithology class, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[The relation of median values in sample groups tested is shown if they were determined to be significantly different (two-sided test) on the basis of p-values (not shown) less than threshold value of (a) of 0.05; ns, test indicated no significant differences between the sample groups. **Aquifer lithology class:** G, granitic rocks; M, metamorphic rocks; MS, metasedimentary rocks; UM, ultra-mafic rocks. **Other abbreviations:** >, greater than; LUFT, leaking (or formerly leaking) underground fuel tank]

	Significant differences		
	Age class (Modern, Mixed/Pre-modern)	Redox class (Oxic, Anoxic/Mixed)	Aquifer lithology class (G, M, MS, UM)
Land-use factors			
Percent agricultural land use	ns	ns	ns
Percent natural land use	ns	ns	ns
Percent urban land use	ns	ns	ns
LUFT density	ns	ns	ns
Septic tank density	ns	ns	ns
Hydrologic conditions			
Aridity index	ns	ns	ns
Elevation of land-surface datum	ns	ns	ns
Depth to top of screened or open interval	ns	ns	ns
Well depth	ns	ns	MS > M and G > M
Geochemical conditions			
pH	Mixed/Pre-modern > Modern	ns	ns
Dissolved oxygen (DO)	Modern > Mixed/Pre-modern	Oxic > Anoxic/Mixed	ns
Selected water-quality constituents			
Boron	Mixed/Pre-modern > Modern	ns	ns
Iron	Mixed/Pre-modern > Modern	Anoxic/Mixed > Oxic	ns
Manganese	Mixed/Pre-modern > Modern	Anoxic/Mixed > Oxic	ns
Specific conductance	Mixed/Pre-modern > Modern	ns	ns
Chloroform	ns	ns	ns

Explanation: How to read results for significant differences. "Mixed/Pre-modern > Modern" for pH means the following: The pH values in mixed/pre-modern age class sites are significantly greater than pH values in modern age class sites.

Hydrologic Conditions

Hydrologic conditions are represented by elevation and aridity index at the site ([table A1](#)). Land-surface elevations in the study area range from about 400 feet (ft) (122 m) near the town of Gasquet, to over 9,000 ft (2,743 m) on Mount Eddy, located just west of the city of Mount Shasta ([fig. 2](#)). The topography is characterized by high peaks and continuous ridgelines separated by deep river gorges. These gorges separate the study unit into several distinct mountain ranges, including the Trinity Alps and the Siskiyou, Scott, Marble, and Salmon Mountains. Most of the aquifer systems in the KLAM study unit consist of fractured hard rock and may not be interconnected, and recharge is not limited to the highest elevations. Because of the topographic and geologic complexity of the Klamath Mountains, many local flow cells of different scales are likely superimposed on an overall generalized regional groundwater flow pattern (Toth, 1963). In large groundwater basins, regional-scale groundwater flow patterns can develop; however, in steep mountainous terranes, groundwater flow patterns are controlled at much more localized scales that are dependent on local topography and the arrangement of discharge zones (Toth, 1963).

The primary aquifer system in the KLAM study unit is made up of localized areas of fractured bedrock that are confined to semi-confined. In addition to the production wells that are bored into the bedrock, there are numerous springs and horizontal wells. The CDWR-defined groundwater basins (Happy Camp Town Area, Hayfork Valley, Hoopa Valley, Hyampom Valley, Seiad Valley, Scott River Valley, and Wilson Point Area) consist of alluvial fan, stream channel, and floodplain deposits of Quaternary age (California Department of Water Resources, 2004a–c; [fig. 2](#)). No KLAM study unit sample sites were located within these groundwater basins, and the effect that these alluvial deposits have on the hard rock aquifer system is unknown. Groundwater recharge in the study unit occurs from the ambient recharge of runoff and snowmelt that penetrates the bedrock through faults and fractures at higher elevations (California Department of Water Resources, 1984).

The climate in the study unit is typical of mountainous areas in northern California, with warm, dry summers and cold, wet winters (U.S. Department of Commerce, National Climatic Data Center, 2012). Average annual precipitation in the study unit ranges from about 69 inches (in.) on the western edge of the study unit along the Northern Coast Ranges to about 40 in. in the central and eastern parts of the study unit (Western Regional Climate Center, 2012; U.S. Department of Commerce, National Climatic Data Center, 2012). The general decrease in precipitation from west to east reflects the rain-shadow effect of the mountain ranges within the study unit. The proportion of the annual precipitation that falls as snow ranges from 2 to 80 percent, with the greatest proportions of snow generally occurring at higher elevations in the central to northern parts of the study unit (U.S. Department of Commerce, National Climatic Data Center, 2012; Western Regional Climate Center, 2012).

The aridity index was used as an indicator of climate. Aridity index is defined as average annual precipitation divided by average annual evapotranspiration and is equal to the United Nations Educational, Scientific, and Cultural Organization aridity index (United Nations Educational, Scientific, and Cultural Organization, 1979; United Nations Environment Programme, 1997). The aridity index was inversely correlated to elevation in the KLAM study unit ([table 5](#)), meaning that drier conditions were observed at higher elevations. The inverse correlation is a result of the fact that the mountains in the central and eastern portions of the study unit are at higher elevations than those in the west. The central and eastern portions of the study unit are generally drier because of the rain-shadow effect caused by the westernmost mountain ranges.

Aridity index values at USGS–GAMA sampling sites ranged from 0.43 to 2.43 ([table A1](#)). Ninety percent of 39 sites sampled in the study unit had an aridity index in the humid or wet category (aridity index > 0.65) as defined by the United Nations Environment Programme (1997), with only four sites being dry subhumid or semi-arid.

Table 5. Results of Spearman's rho (ρ) tests for correlations between selected potential explanatory factors and selected water-quality constituents, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[*p* values are shown for tests in which the variables were determined to be significantly correlated on the basis of *p* values (not shown) being less than the critical level (α) of 0.05; LUFTs, leaking (or formerly leaking) underground fuel tanks; ns, Spearman's test indicates no significant correlation between factors; blue text, significant positive correlation; red text, significant negative correlation]

ρ	Elevation	Depth to top of screened or open interval	Well depth	Percent agricultural land use	Percent natural land use	Percent urban land use	Density of LUFTs	Density of septic tanks	pH	Dissolved oxygen	Boron	Iron	Manganese	Specific conductance	Chloroform
Aridity index	-0.54	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Elevation of land-surface datum		ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Depth to top of screened or open interval		0.80	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Well depth			ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Percent agricultural land use				-0.42	ns	ns	ns	ns	ns	0.32	ns	ns	0.41	ns	ns
Percent natural land use					-0.98	ns	ns	ns	ns	ns	-0.34	ns	ns	ns	ns
Percent urban land use						ns	ns	ns	ns	ns	0.38	ns	ns	ns	ns
Density of LUFTs							0.36	ns	ns	ns	ns	ns	ns	ns	ns
Density of septic tanks								ns	ns	ns	ns	ns	ns	ns	0.36
pH								ns	ns	ns	ns	ns	ns	0.64	ns
Dissolved oxygen									-0.38	-0.42	-0.56	-0.33			ns
Boron										ns	0.33	0.49			
Iron											0.78	ns	0.35		
Manganese												0.37	0.35		
Specific conductance													ns		

Depth and Groundwater Age Characteristics of the Primary Aquifer System

The primary aquifer system in the KLAM study unit is defined as the depth interval over which wells in the CDPH water-quality database are screened or open. Sites sampled by USGS–GAMA are considered representative of the primary aquifer system, thus, depth characteristics of these sites can be used to define the primary aquifer system.

Seven of the 39 sites sampled by USGS–GAMA are springs. In this report, springs are not assigned values for the depths to the top and bottom of screened or open intervals, and are therefore not included in tests involving depth as a continuous variable. Springs emerge at land surface, but the geometry of the fracture network in the subsurface is unknown.

Well depth information was available for 22 of the 32 wells sampled. Depths of USGS-grid sites ranged from 25 to 400 ft (8 to 122 m) below land surface; the median depth was 122 ft (37 m) (fig. 7; table A2). Depths of tops of screened or open intervals were available for 16 of those 22 wells with construction information. Depths to the tops of the screened or open intervals ranged from 24 to 300 ft (7 to 91 m), with a median of 74 ft (22 m). The screened or open interval length ranged from 8 to 223 ft (68 m), with a median of 46 ft (14 m) (Mathany and Belitz, 2014).

Groundwater “age” refers to the length of time that the water has resided in the aquifer system, which is the amount of time elapsed since the water was last in contact with the atmosphere. Groundwater samples were assigned age classes

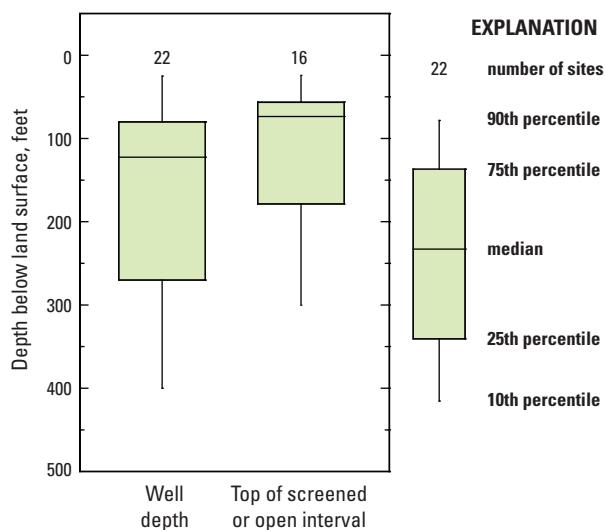


Figure 7. Well depths and depths to tops of screened or open intervals for USGS-grid sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

on the basis of the tritium and carbon-14 (^{14}C) contents of the samples (see section “Groundwater Age” in appendix A). Groundwater with tritium activity greater than 1 tritium unit (TU) was defined as “modern,” and groundwater with tritium activity less than or equal to 1 TU was defined as “pre-modern.” Modern groundwater contains a substantial component of water recharged since 1952. The presence of pre-modern groundwater also was identified using the ^{14}C data: samples with percent modern carbon (pmc) less than 90 percent were considered to contain a substantial component of pre-modern groundwater. Samples with tritium activity greater than 1 TU and pmc less than 90 percent were classified as “mixed.” Samples from 26 sites were classified as modern, samples from 11 sites were classified as mixed, and samples from 2 sites were classified as pre-modern (table A4). Sites classified as pre-modern or mixed were mostly located in the eastern part of the study unit (fig. 8). Groundwater age was treated as a 2-factor classification for tests of statistical relations between potential explanatory factors and water quality. Because so few sites had pre-modern water, two of the three groundwater age classes (mixed and pre-modern) were merged for the statistical tests, resulting in two categories: modern and mixed/pre-modern.

Groundwater age was compared to the top of the screened or open interval to determine whether a classification system based on site depth could be established and used as an additional potential explanatory factor. However, the relative difference between the median depths to top-of-perforations among the three age classes was not significant enough to establish unique depth classes based on age. Wilcoxon rank-sum tests comparing the median depths to the top of the screened or open intervals in each groundwater age class did not indicate significant differences.

Geochemical Conditions in the Primary Aquifer System

Oxidation-reduction (redox) conditions for the 39 sites sampled by USGS–GAMA were classified by using the redox classification framework of McMahon and Chapelle (2008) and Jurgens and others (2009) (table A3). Groundwater conditions were primarily oxic (31 of 39 sites). Samples from four sites had anoxic conditions, and the remaining four sites had mixed redox conditions. The pH ranged from 5.9 to 9.4 (table A3). Contingency table tests indicated that anoxic or mixed redox conditions were statistically more often associated with groundwater classified as mixed or pre-modern in age and that wells with oxic redox conditions were significantly associated with groundwater classified as modern in age (attained significance level [p] = 0.005).

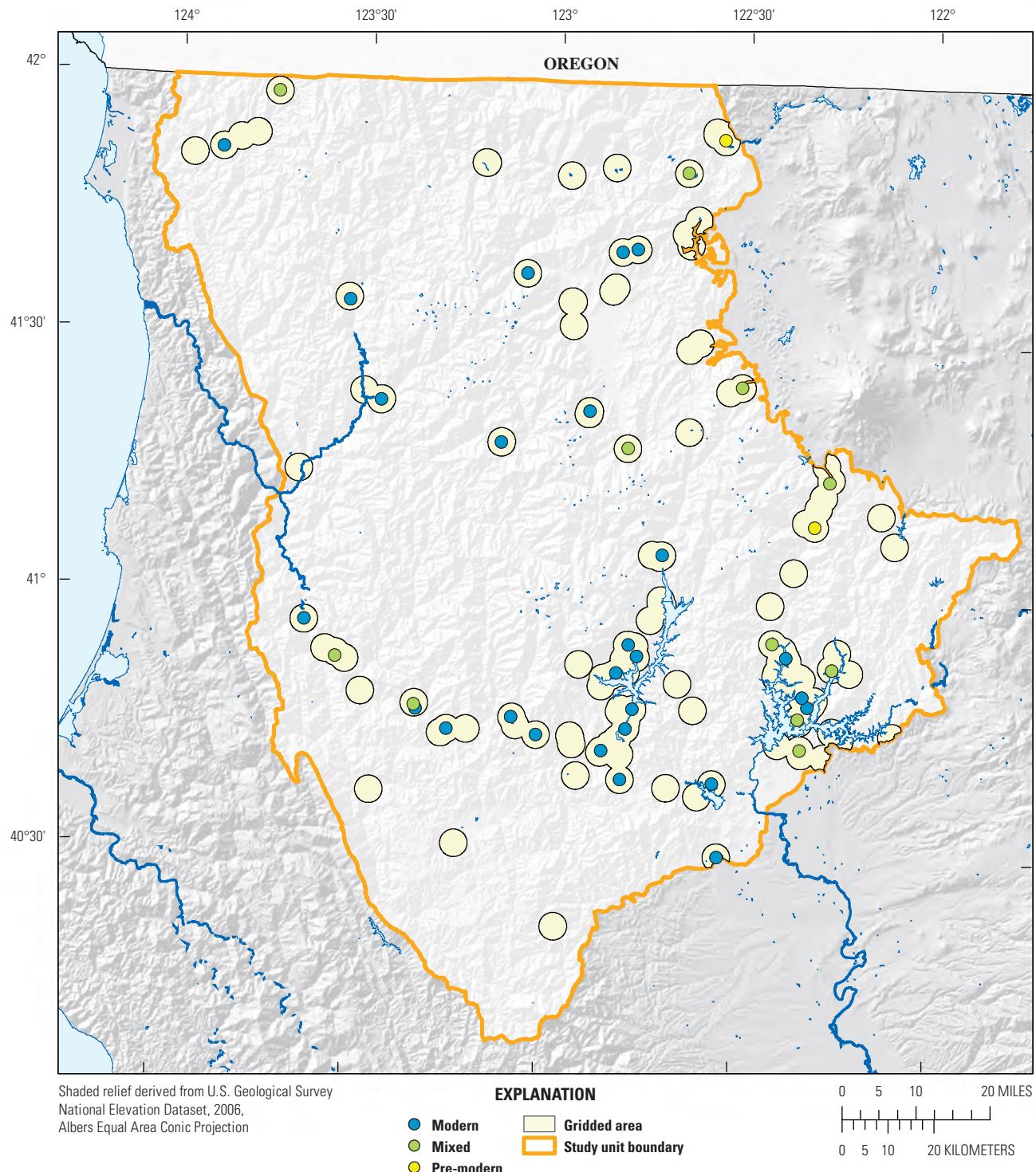


Figure 8. Groundwater age classes of sampled sites within the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Status and Understanding of Groundwater Quality

The status assessment was designed to identify the constituents or classes of constituents most likely to be water-quality concerns because of their high relative-concentrations or their prevalence. The assessment applies only to constituents having regulatory or non-regulatory health-based or aesthetic-based benchmarks established by the USEPA or the CDPH (U.S. Environmental Protection Agency, 1999, 2009, 2012a; California Department of Public Health, 2010, 2013). USGS sample analyses, plus additional data from the CDPH water-quality database, were included in the assessment of groundwater quality for the KLAM study unit. The spatially distributed, randomized approach to grid-site selection and data analysis yields a view of groundwater quality in which all areas of the primary aquifer system are weighted equally; regions with a high density of groundwater use or with high density of potential contaminants were not preferentially sampled (Belitz and others, 2010).

The understanding assessment was designed to help answer the question of why selected constituents are, or are not, detected in the groundwater, and may improve understanding of how natural and anthropogenic factors affect groundwater quality. The assessment addresses a subset of the constituents selected for additional evaluation in the status assessment and is based on statistical correlations between water quality and a set of potential explanatory factors. The assessment was not designed to identify specific sources of specific constituents to specific wells.

The following discussion of the status and understanding assessment results is divided into two parts for inorganic and organic constituents. Each part begins with a survey of how many constituents in each constituent class were detected at any concentration compared to the number of constituents analyzed for in each constituent class and a graphical summary of the relative-concentrations of constituents detected in the grid sites. Results are presented for the subset of constituents that met criteria for selection for additional evaluation in the *status assessment* based on relative-concentration, or for organic constituents, prevalence. Of the 216 constituents analyzed and the 82 constituents detected, 16 met the criteria for additional evaluation in the status assessment ([table 6](#)). Of these 16 constituents, 4 met the criteria for further evaluation in the understanding assessment. The results of the understanding assessment for each of these four constituents are presented immediately following the status assessment results for each constituent.

The 216 constituents include 2 microbial indicators that were detected in samples from USGS grid sites (Mathany and Belitz, 2014). Microbial indicators were not evaluated in the status assessment because the drinking-water benchmarks for these constituents cannot be directly applied to the data collected for this study (see section “[Water-Quality Benchmarks and Relative-Concentrations](#)”).

24 Status and Understanding of Groundwater Quality in the Klamath Mountains Study Unit, 2010

Table 6. Constituents selected for additional evaluation in the status assessment of groundwater quality in the Klamath Mountains study unit, California GAMA Priority Basin Project.

[Inorganic constituents selected if maximum concentration measured in USGS–GAMA samples or reported in CDPH database during the 3-year time period used for the status assessment was greater than 0.5 times the benchmark concentration. Organic constituents selected if maximum concentration was greater than 0.1 times the benchmark concentration, or if detection frequency at any concentration was greater than 10 percent. **Benchmark type:** *Regulatory, health-based benchmarks:* MCL-US, USEPA maximum contaminant level; AL-US, USEPA action level; MCL-CA, CDPH maximum contaminant level. *Non-regulatory health-based benchmarks:* HAL-US, USEPA lifetime health advisory level; NL-CA, CDPH notification level. *Non-regulatory aesthetic-based benchmarks:* SMCL-CA, CDPH secondary maximum contaminant level. **Benchmark units:** mg/L, milligrams per liter; µg/L, micrograms per liter; µS/cm, microsiemens per centimeter; pCi/L, picocuries per liter. **Other abbreviations:** USGS, U.S. Geological Survey; GAMA, Groundwater Ambient Monitoring and Assessment Program; USEPA, U.S. Environmental Protection Agency; CDPH, California Department of Public Health]

Constituent	Source or typical use	Benchmarks			
		Type ¹	Value	Units	
Inorganic constituents with health-based benchmarks					
Trace elements					
Antimony	Naturally occurring	MCL-US	6	µg/L	
Arsenic	Naturally occurring	MCL-US	10	µg/L	
Barium	Naturally occurring	MCL-CA	1,000	µg/L	
Boron	Naturally occurring	NL-CA	1,000	µg/L	
Copper	Naturally occurring	AL-US	1,300	µg/L	
Nutrient					
Nitrate ²	Natural, fertilizer, sewage	MCL-US	10	mg/L	
Radioactive constituents					
Gross alpha particle radioactivity	Naturally occurring	MCL-US	15	pCi/L	
Radon-222	Naturally occurring	Proposed MCL-US	4,000	pCi/L	
Inorganic constituents with aesthetic-based benchmarks					
Chloride	Naturally occurring	SMCL-CA	500	mg/L	
Iron	Naturally occurring	SMCL-CA	300	µg/L	
Manganese	Naturally occurring	SMCL-CA	50	µg/L	
Specific conductance, field	Naturally occurring	SMCL-CA	1,600	µS/cm	
Total dissolved solids (TDS)	Naturally occurring	SMCL-CA	1,000	mg/L	
Organic constituents with health-based benchmarks					
Volatile organic compounds					
Chloroform	Disinfection byproduct	MCL-US ³	80	µg/L	
1,2-Dichloroethane	Solvent, fumigant, plastics	MCL-CA	0.5	µg/L	
Methyl <i>tert</i> -butyl ether (MTBE)	Gasoline oxygenate	MCL-CA	13	µg/L	

¹ Maximum contaminant level benchmarks are listed as MCL-US when the MCL-US and MCL-CA are identical, and as MCL-CA when the MCL-CA is lower than the MCL-US or no MCL-US exists. Sources of benchmarks: MCL-CA: California Department of Public Health (2013); MCL-US: U.S. Environmental Protection Agency (2012b); SMCL-CA: California Department of Public Health (2013); NL-CA: California Department of Public Health (2010); HAL-US: U.S. Environmental Protection Agency (2012b); Proposed MCL-US: U.S. Environmental Protection Agency (1999).

² Selected on the basis of concentrations reported in the CDPH database. Constituent also detected by USGS–GAMA at low relative-concentrations.

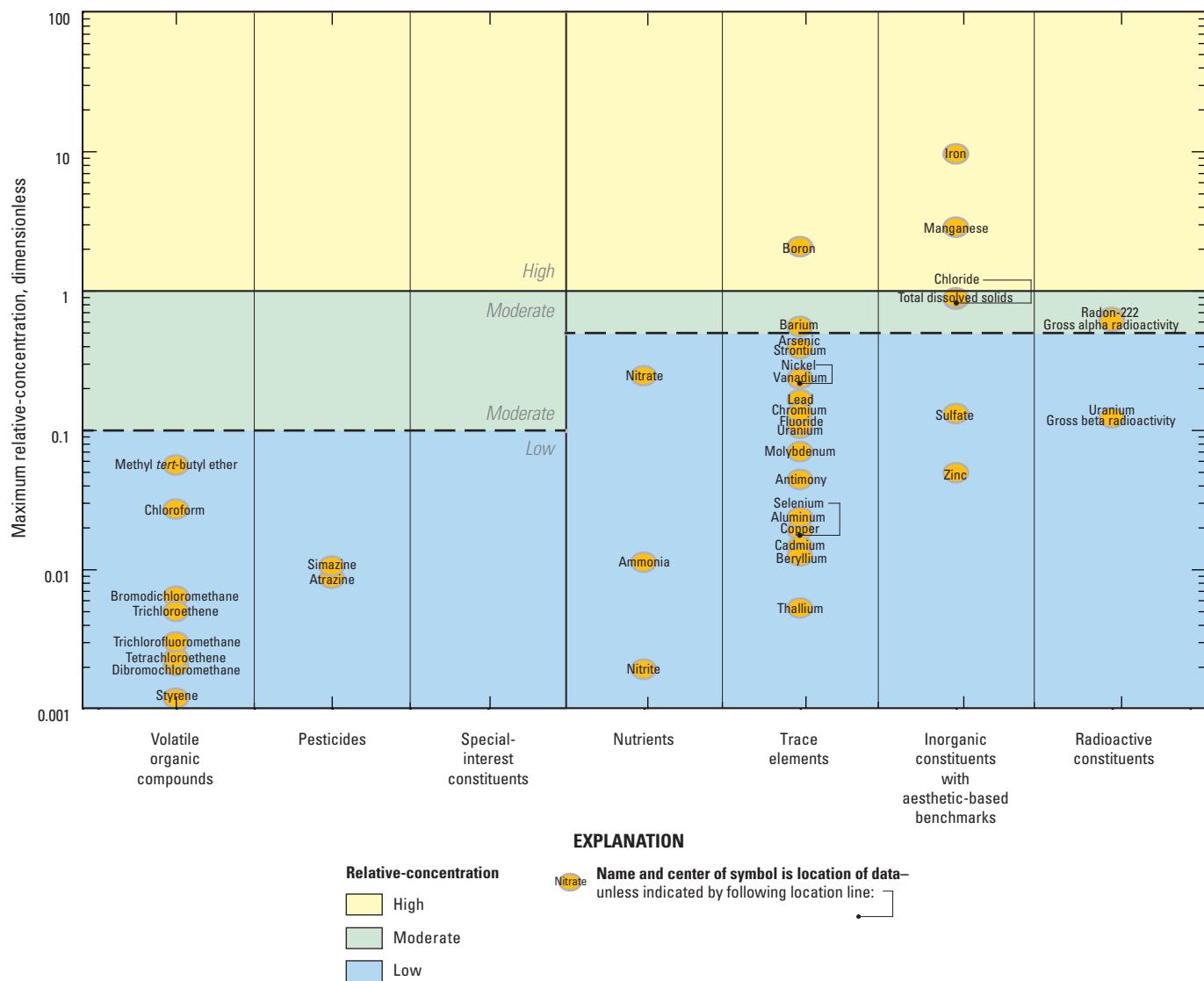
³ MCL-US benchmark for trihalomethanes is for the sum of chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

Inorganic Constituents

Inorganic constituents generally occur naturally in groundwater, although their concentrations may be influenced by human as well as natural factors. All 47 inorganic constituents analyzed by the USGS–GAMA were detected in the Klam study unit. Of these 47 constituents, 25 had regulatory or non-regulatory health-based benchmarks, 9 had non-regulatory aesthetic-based benchmarks, and 13 had no established benchmarks (table 2). Most of the constituents without benchmarks are major or minor ions that are present in nearly all groundwater.

Eight inorganic constituents were selected for additional evaluation in the status assessment because they were detected

at moderate or high relative-concentrations in the grid sites: the trace elements barium and boron, the radioactive constituents gross alpha radioactivity and radon-222, and the constituents with aesthetic-based benchmarks, chloride, iron, manganese, and total dissolved solids (table 6; figs. 9, 10). Four other inorganic constituents—antimony, arsenic, copper, and nitrate—were selected for additional evaluation because they were reported at high or moderate concentrations in the CDPH water-quality database during the current sampling period, December 1, 2007, to December 31, 2010. Boron, iron, and manganese were selected for further evaluation in the understanding assessment because they were present at high relative-concentrations in greater than 2 percent of the primary aquifer system.



Two volatile organic compounds (carbon disulfide and toluene), one pesticide (hexazinone), and one inorganic constituent (silver) with an aesthetic-based benchmark were detected at relative-concentrations less than 0.001 and are not shown on the figure.

Upper water-quality benchmark used when calculating relative-concentrations for constituents with an upper and a recommended secondary maximum contaminant level.

Figure 9. Maximum relative-concentrations in USGS-grid sites for constituents detected, by type of constituent, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

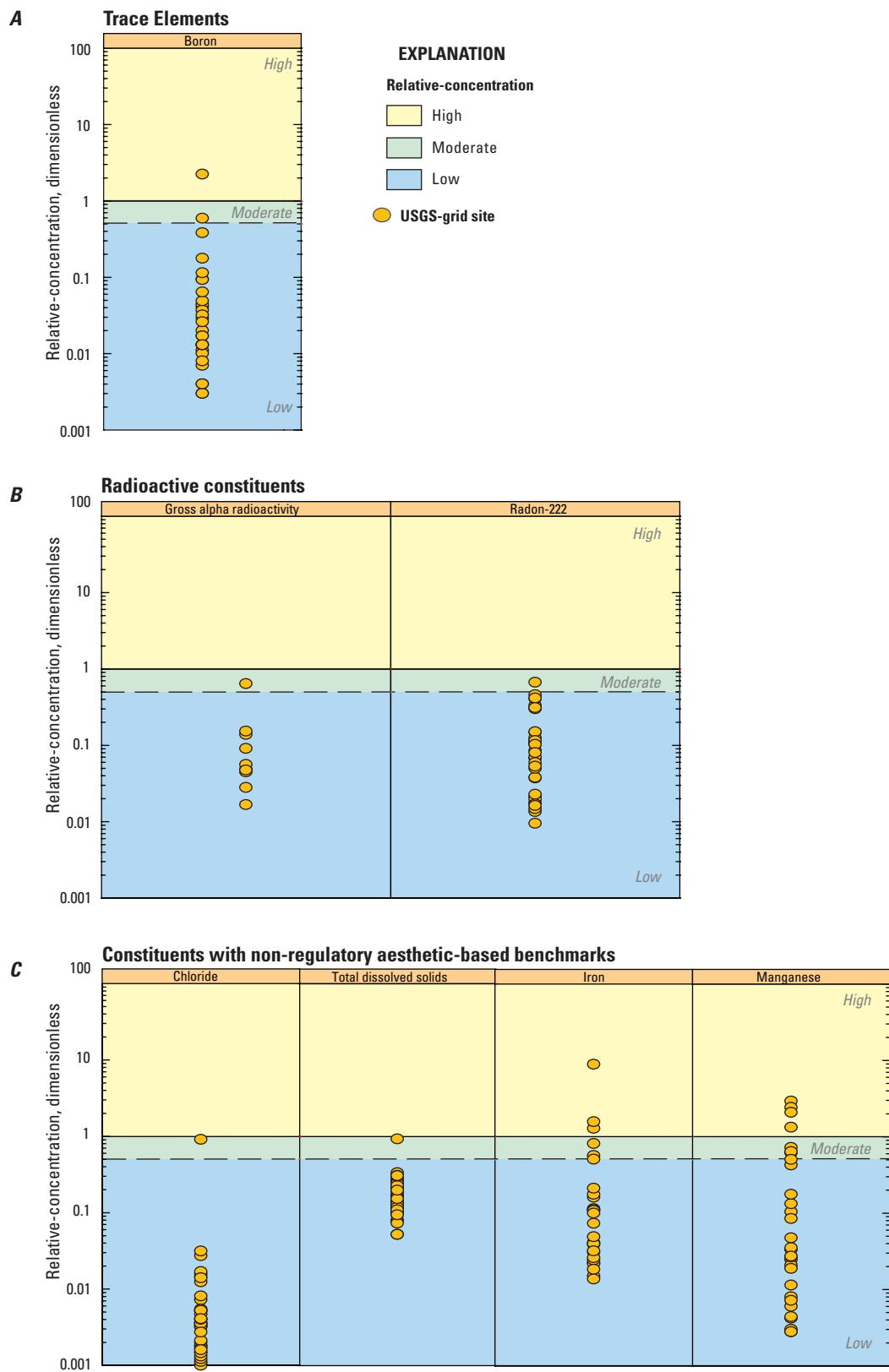


Figure 10. Relative-concentrations of selected trace elements, radioactive constituents, and constituents with non-regulatory aesthetic-based benchmarks in USGS-grid sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Inorganic constituents having human-health benchmarks, as a group (trace elements and radioactive constituents), were detected at high relative-concentrations in 2.6 percent of the primary aquifer system, at moderate relative-concentrations in 10 percent, and at low relative-concentrations in 87 percent ([table 7A](#)). Inorganic constituents having aesthetic-based

benchmarks, as a group, were detected at high relative-concentrations in 13 percent of the primary aquifer system, at moderate relative-concentrations in 10 percent, and at low relative-concentrations in 77 percent.

Table 7A. Summary of aquifer-scale proportions for inorganic constituent classes with health-based and aesthetic-based benchmarks, Klamath Mountains study unit, 2010, California GAMA Priority Basin Program.

[**Relative-concentration categories:** high, concentration of at least one constituent in group greater than water-quality benchmark; moderate, concentration of at least one constituent in group greater than 0.5 of benchmark and no constituents in group with concentration greater than benchmark; low, concentrations of all constituents in group are less than or equal to 0.5 of benchmark. **Abbreviations:** TDS, total dissolved solids]

	Number of grid cells	Aquifer-scale proportion (percent) ¹		
		Low	Moderate	High
Inorganic constituents with health-based benchmarks				
Trace elements ²	39	92	5.2	2.6
Radioactive constituents ³	38	95	5.3	0
Any inorganic constituent with health-based benchmarks	39	87	10	2.6
Inorganic constituents with aesthetic-based benchmarks				
Trace elements	39	77	10	13
Major ions and TDS	38	97	2.6	0
Any inorganic constituent with aesthetic-based benchmarks	39	77	10	13

¹ Aquifer-scale proportions by class calculated using the grid-based approach unless otherwise noted.

² Boron was only analyzed for 38 grid cells.

³ Radon-222 was only analyzed for 37 grid cells.

Table 7B. Summary of aquifer-scale proportions for organic constituent classes with health-based benchmarks, Klamath Mountains study unit, 2010, California GAMA Priority Basin Program.

[**Relative-concentration categories:** high, concentration of at least one constituent in group greater than water-quality benchmark; moderate, concentration of at least one constituent in group greater than 0.1 of benchmark and no constituents in group with concentration greater than benchmark; low, concentrations of all constituents in group are less than or equal to 0.1 of benchmark]

	Number of grid cells	Aquifer-scale proportion (percent) ¹		
		Not detected	Low	Moderate
Organic constituents with health-based benchmarks				
Volatile organic compounds	38	53	45	¹ 1.9
Pesticides and pesticide degradates	38	87	13	0
Any organic constituent	38	50	48	¹ 1.9

¹ Spatially weighted aquifer-scale proportion.

Trace Elements

Trace elements with health-based benchmarks, as a class, were detected at high relative-concentrations (for one or more constituents) in 2.6 percent of the primary aquifer system, at moderate relative-concentrations in 5.2 percent, and at low relative-concentrations in 92 percent ([table 7A](#)). Boron was the only trace element present at high relative-concentrations in the grid-site network ([fig. 9](#)).

Boron was detected at high relative-concentrations in 2.6 percent of the primary aquifer system and at moderate relative-concentrations in 2.6 percent ([table 8](#)). Boron is a naturally occurring metalloid element that is highly soluble in water. Natural sources of boron include evaporate minerals, such as borax, ulexite, and colemanite, and boron-bearing silicate minerals, such as tourmaline, that are primarily found in igneous rocks (Hem, 1985; Klein and Hurlbut, 1993). Boron concentrations in seawater can be as high as 4,500 micrograms per liter ($\mu\text{g/L}$), and boron is also associated with thermal springs and volcanic activity (Hem, 1985). Because borax is a component of many detergents, boron can be associated with wastewater. Borosilicate glass, boric acid insecticides, chemical reagents, and fertilizers are other anthropogenic uses of boron. Boron is an essential nutrient for plants, but is toxic to plants at high concentrations. The comparison benchmark used for boron in this study was the NL-CA of 1,000 $\mu\text{g/L}$. Boron also has a HAL-US of 6,000 $\mu\text{g/L}$. High concentrations of boron may adversely affect fetal development (U.S. Environmental Protection Agency, 2008b).

Antimony and arsenic had high aquifer-scale proportions (spatially weighted) of 1.3 percent. Antimony is a naturally occurring semi-metallic trace element. Chemically, it behaves similarly to arsenic, but it is about one-tenth as prevalent in rocks as arsenic is (Hem, 1985). The most common natural source of antimony is the mineral stibnite. Common anthropogenic sources of antimony include brake linings, tires, and vehicle exhaust. Antimony is often added as an alloy to lead and tin to make those metals stronger and harder. The MCL-US for antimony is 6 $\mu\text{g/L}$. Arsenic is a semi-metallic trace element. Natural sources of arsenic in groundwater include dissolution of arsenic-bearing minerals and desorption of arsenic from mineral surfaces. Pyrite, the most common sulfide mineral in aquifer materials, is sometimes partially composed of arsenic. Potential anthropogenic sources of arsenic include copper ore smelting, coal combustion, and wood preservatives. The MCL-US for arsenic was lowered from 50 $\mu\text{g/L}$ to 10 $\mu\text{g/L}$ in 2002; chronic exposure to arsenic concentrations between 10 and 50 $\mu\text{g/L}$ in drinking water has been linked to increased cancer risk and to non-cancerous effects including skin damage and circulatory problems (U.S. Environmental Protection Agency, 2012a).

Barium and copper were not reported at high relative-concentrations and were detected at moderate spatially

weighted aquifer-scale proportions of 2.6 and 1.5 percent, respectively. Barium is a naturally occurring alkaline-earth metal that occurs most commonly in the mineral barite. Concentrations of barium in natural waters appear to be controlled by the solubility of the mineral barite and adsorption of barium to metal oxides or hydroxides (Hem, 1985). Anthropogenic sources of barium are numerous, with compounds containing barium being used in well drilling fluids, paints, rubber, and pyrotechnics. The MCL-CA for barium is 1,000 $\mu\text{g/L}$. Copper is a naturally occurring metallic element with a wide range of uses, from electronics and plumbing to agricultural pesticides. Organic and inorganic forms of copper are more abundant in the environment than its average abundance in rocks might suggest (Hem, 1985). The AL-US for copper is 1,300 $\mu\text{g/L}$.

Factors Affecting Boron

Boron concentrations were significantly greater in groundwater classified as mixed or pre-modern age than in groundwater classified as modern age ([table 4](#)). Boron concentrations were significantly negatively correlated with dissolved oxygen (DO) concentration ([table 5](#)). The negative correlation with DO likely reflects that DO concentrations were significantly lower in groundwater with mixed or pre-modern ages than in groundwater with modern ages ([table 4](#)). Boron was also significantly positively correlated with specific conductance ([table 5](#)), and the only site with a high relative-concentration of boron also had a high relative-concentration of specific conductance (KLAM-06).

Nutrients

Nutrients, as a class, were not detected at high relative-concentrations, but were detected at moderate relative-concentrations in 0.7 percent (spatially weighted) of the primary aquifer system. Nitrate was the nutrient present at moderate relative-concentrations ([table 8](#)). Nitrate has anthropogenic and natural sources to groundwater; however, concentrations greater than 2 milligrams per liter (mg/L) as nitrogen (relative-concentration of 0.2) generally are considered to indicate the presence of nitrate from anthropogenic sources (Mueller and Helsel, 1996).

Radioactive Constituents

Radioactive constituents, as a class, were not detected at high relative-concentrations, but were detected at moderate relative-concentrations in 5.3 percent of the primary aquifer system ([table 7A](#)). The moderate aquifer-scale proportions for gross alpha radioactivity and radon-222 were 2.6 and 2.7 percent, respectively ([table 8](#)).

Table 8. Aquifer-scale proportions from grid-based and spatially weighted methods for constituents that met criteria for additional evaluation in the status assessment, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[Grid-based aquifer-scale proportions for organic constituents are based on samples collected by the U.S. Geological Survey from 38 grid sites during October to December 2010. Spatially weighted aquifer proportions are based on CDPH data from the period December 1, 2007, to December 31, 2010, in combination with grid site and understanding site data. **Relative-concentration categories:** high, concentrations greater than benchmark; moderate, concentrations less than benchmark and greater than or equal to 0.1 (for organic constituents) or 0.5 (for inorganic constituents) of benchmark; low, concentrations less than 0.1 (for organic constituents) or 0.5 (for inorganic constituents) of benchmark; SMCL, secondary maximum contaminant level]

Constituent	Raw detection frequency ¹			Spatially weighted aquifer-scale proportion ¹			Grid-based aquifer-scale proportion ²			90 percent confidence interval for grid-based high proportion ³	
	Number of sites	Percent		Number of cells	Proportion, in percent		Number of cells	Proportion, in percent		Limit, in percent	
		Moderate	High		Moderate	High		Moderate	High	Lower	Upper
Trace elements											
Antimony	57	0	1.8	39	0	1.3	39	0	0	0	4.8
Arsenic	56	0	1.8	39	0	1.3	39	0	0	0	4.8
Barium	56	1.8	0	39	2.6	0	39	2.6	0	0	4.8
Boron	40	2.5	5.0	39	2.6	3.8	38	2.6	2.6	0.5	9.8
Copper	55	3.7	0	39	1.5	0	39	0	0	0	4.8
Nutrients											
Nitrate	151	1.3	0	40	0.7	0	40	0	0	0	4.7
Radioactive constituents											
Gross alpha radioactivity	52	1.9	0	38	1.3	0	38	2.6	0	0	4.9
Radon-222	38	2.6	0	38	2.6	0	37	2.7	0	0	5.0
Inorganic constituents with aesthetic-based benchmarks											
Chloride	51	1.9	0	38	2.6	0	38	2.6	0	0	4.9
Iron	64	6.2	18	38	6.6	15	38	7.9	7.9	2.9	17
Manganese	56	13	13	38	13	12	38	11	11	4.5	21
Total dissolved solids (TDS)	54	3.7	1.9	38	2.6	0.9	38	2.6	0	0	4.9
Volatile organic compounds											
Chloroform	50	0	0	39	0	0	38	0	0	0	4.9
1,2-Dichloroethane	49	0	0	39	0	0	38	0	0	0	4.9
Methyl <i>tert</i> -butyl ether (MTBE)	50	4.0	0	39	1.9	0	38	0	0	0	4.9

¹ Based on most recent analyses for each California Department of Public Health (CDPH) site during December 1, 2007–December 31, 2010, combined with data from U.S. Geological Survey (USGS) grid sites and USGS-understanding sites.

² Grid-based aquifer-scale proportions for organic constituents are based on samples collected by the USGS from 38 grid sites between October and December 2010.

³ Based on Jeffreys interval for the binomial distribution (Brown and others, 2001).

Constituents with SMCL Benchmarks

The major ion chloride and total dissolved solids (TDS) have recommended and upper SMCL-CA values. In this report, data were compared to the upper SMCL-CA values. TDS had high relative-concentrations in 0.9 percent (spatially weighted) of the primary aquifer system ([table 8](#)). Chloride was detected at moderate relative-concentrations in 2.6 percent of the primary aquifer system. Natural sources of TDS to groundwater include weathering and dissolution of minerals in soils, sediments, and rocks; mixing with saline or brackish waters from the ocean, estuaries, or saline lakes; interactions with marine or lacustrine sediments; mixing with hydrothermal solutions; and concentration by evapotranspiration of shallow groundwater (Hem, 1985). Anthropogenic sources of TDS to groundwater include recharge of water used for irrigation, wastewater discharge, and evaporation (Hem, 1985).

Iron and manganese were present at high relative-concentrations in 7.9 and 11 percent of the primary aquifer system, respectively, and at moderate relative-concentrations in 7.9 and 11 percent, respectively ([table 8](#)). Natural sources of iron and manganese to groundwater include weathering and dissolution of minerals in soils, sediments, and rocks. Iron and manganese oxyhydroxide minerals commonly occur as coatings on mineral and sediment grains. In addition, iron-bearing silicate, sulfide, and (or) oxide minerals occur in most rocks and sediments, and manganese commonly substitutes for iron in silicate minerals. The solubilities of manganese and iron are strongly dependent on oxidation-reduction conditions; the more reduced species are much more soluble (McMahon and Chapelle, 2008).

Factors Affecting Iron and Manganese

Iron and manganese concentrations had significant negative correlations with DO concentrations and a significant positive correlation with each other ([table 5](#); [fig. 11](#)). Eight of the nine sites with high or moderate relative-concentrations of iron or manganese were sites that had anoxic or mixed (oxic and anoxic) redox conditions. The predominant redox condition in the KLAM study unit was oxic.

The dominant form of iron in solution can be identified from the ratio of iron redox species, $\text{Fe}^{+3}/\text{Fe}^{+2}$, where Fe^{+3} is the amount of iron present in the more oxidized +3 oxidation

state (ferric iron) and Fe^{+2} is the amount of iron present in the more reduced +2 oxidation state (ferrous iron). Of the 39 samples with detections of iron, the 6 samples with moderate or high relative-concentrations all had $\text{Fe}^{+3}/\text{Fe}^{+2} \leq 0.09$. Greater relative abundances of Fe^{+2} are indicative of reduced conditions (McMahon and Chapelle, 2008) ([table A3](#)). Three of the six samples with moderate or high relative-concentrations of iron had DO concentrations greater than 1 mg/L, indicating that these samples represented mixtures of oxic and iron-reducing anoxic groundwaters ([table A3](#)).

The amount of time groundwater spends in contact with aquifer materials may be related to concentrations of certain constituents. Iron and manganese concentrations were significantly greater in groundwater classified as mixed or pre-modern than in groundwater classified as modern ([table 4](#); [fig. 12](#)). Contingency table testing showed that anoxic or mixed oxidation-reduction conditions and mixed or pre-modern age groundwater are significantly positively associated.

Reducing conditions in alluvial aquifers (which were not sampled in the KLAM study unit) typically are produced by consumption of DO by oxidation of sedimentary organic matter (Appelo and Postma, 2005). Reducing conditions in aquifers not containing organic matter, such as the hard rock aquifers of the KLAM study unit, can be produced by reactions with minerals containing ferrous (Fe^{+2}) iron, given sufficiently long residence times (Gascoyne, 1997; Sidborn and Neretnieks, 2007; Fram and Belitz, 2012). In the KLAM study unit, anoxic or mixed conditions were found in sites with metasedimentary, metamorphic, and mafic/ultramafic geologic classifications. Minerals containing ferrous iron, such as biotite, chlorite, magnetite, pyrite, and hornblende, are commonly present in these rock types.

Aquifer materials can affect iron and manganese concentrations because the relative abundance of iron or manganese can vary between rock types. The sites with moderate or high relative-concentrations of iron or manganese were grouped by aquifer lithology class. The highest percentages of sites with high or moderate relative-concentrations of iron or manganese were located in metasedimentary (33 percent) and ultramafic/mafic (29 percent) aquifer lithologies. Of the 10 sites in the metamorphic category, only 1 site (KLAM-30) had high or moderate relative-concentrations of iron or manganese.

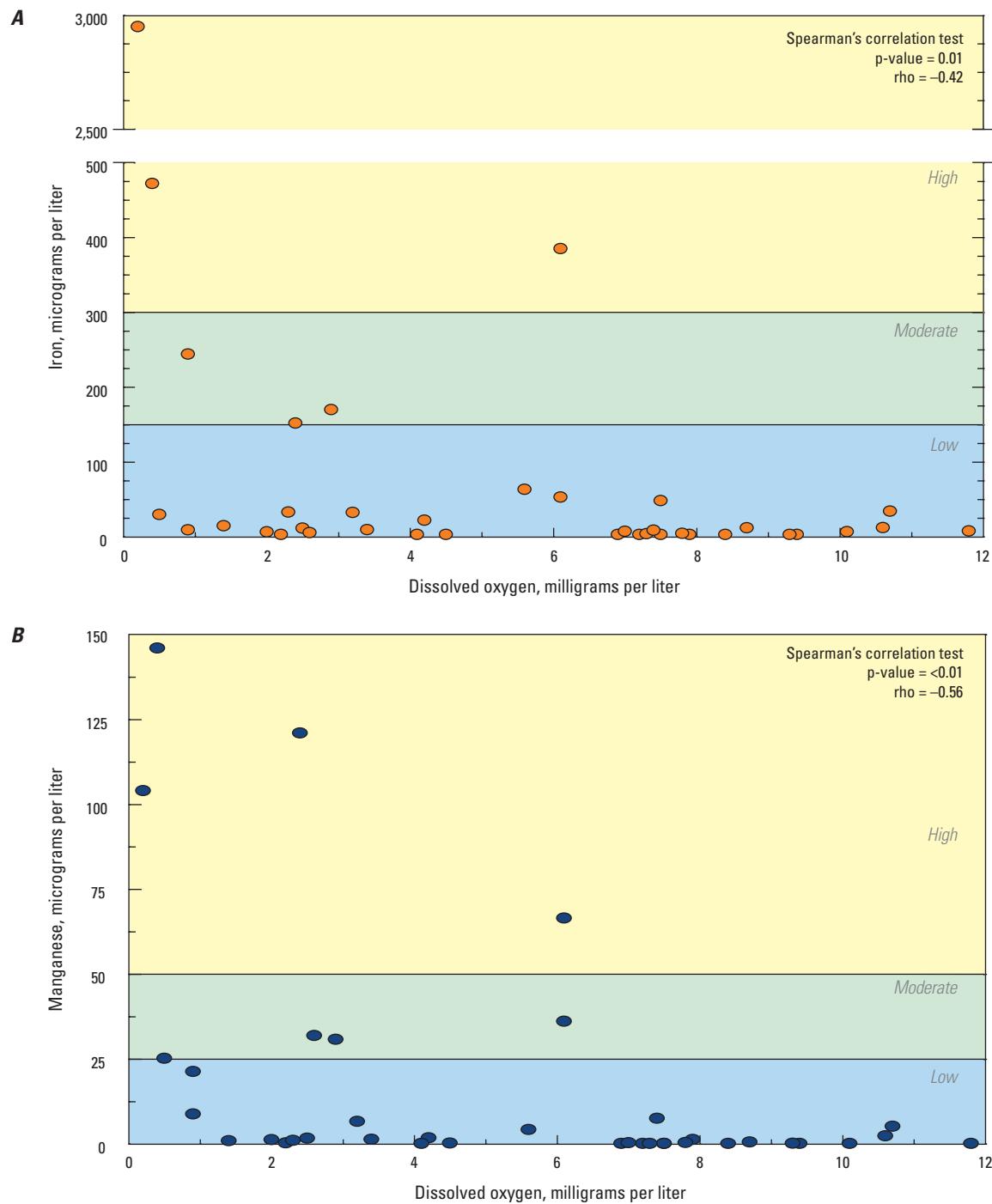


Figure 11. Relations between dissolved oxygen concentration and (A) iron and (B) manganese, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

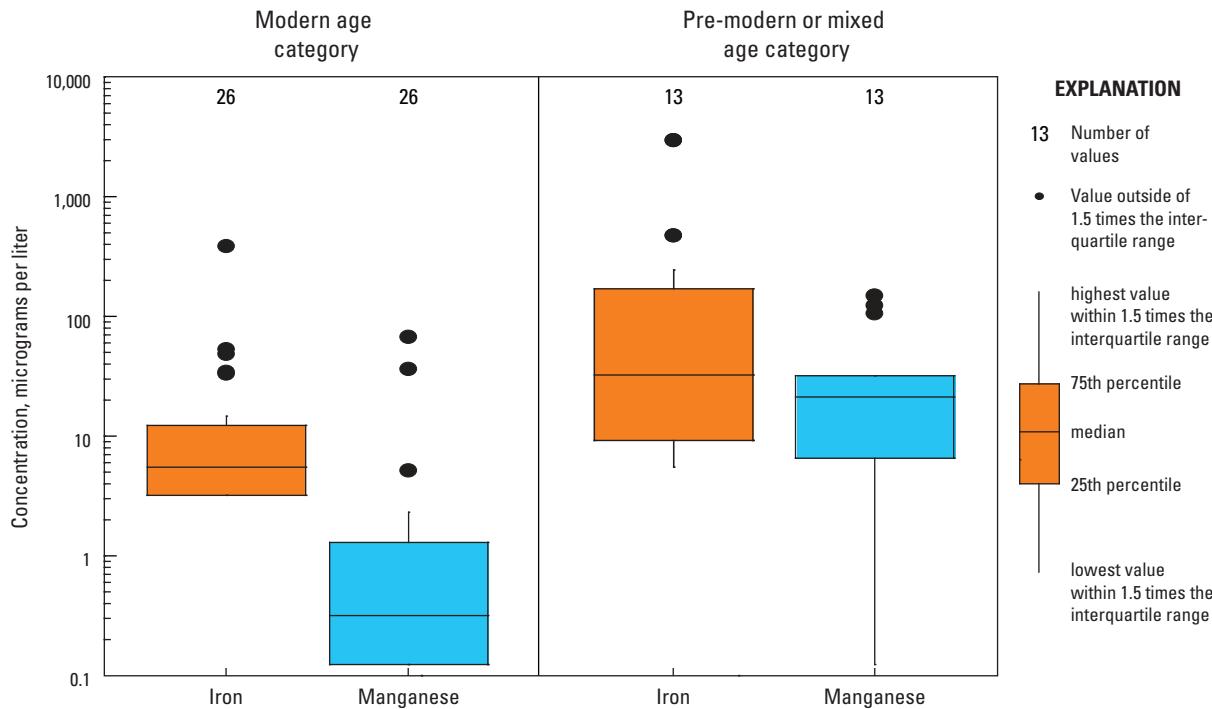


Figure 12. Iron and manganese concentrations by groundwater age class, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Organic Constituents

The organic constituents assessed in this study primarily are VOCs and pesticides. VOCs may be present in paints, solvents, fuels, refrigerants, and fumigants or may be formed as byproducts of water disinfection. VOCs are characterized by a volatile nature, or tendency to evaporate, and they generally persist longer in groundwater than in surface water because groundwater is more isolated from the atmosphere. Pesticides are used to control weeds, fungi, or insects in agricultural and urban settings. One or more organic constituents were detected in 21 of the 38 grid sites (55 percent) sampled in the study unit. Of the 148 organic constituents analyzed, 14 were detected in the KLAM study unit (table 2). Of these 14 constituents, 11 have regulatory health-based benchmarks. Organic constituents as a group were not present at high relative-concentrations in the primary aquifer system (table 7B). Organic constituents were present at moderate relative-concentrations in 1.9 percent (spatially weighted) and were present at low relative-concentrations or not detected in 98 percent of the primary aquifer system. The moderate relative-concentration of 1.9 percent was due solely to detections of methyl *tert*-butyl ether (MTBE). Three organic constituents (chloroform, 1,2-dichloroethane, and MTBE) were selected for additional evaluation in the *status assessment* on the basis of relative-concentration or prevalence. Chloroform was selected for further evaluation in the *understanding assessment* on the basis of prevalence.

The trihalomethane chloroform was detected in more than 10 percent of the grid sites. Chloroform was the most

commonly detected VOC in the KLAM study unit, with a detection frequency of 32 percent (figs. 13, 14). Chloroform is among the most commonly detected VOCs in groundwater nationally (Zogorski and others, 2006). Water used for drinking water and other household uses in domestic and public (municipal and community) systems commonly is disinfected with solutions that contain chlorine. In addition to disinfecting the water, the chlorine can react with organic matter to produce trihalomethanes (THMs) and other chlorinated or brominated disinfection byproducts. As a class, THMs were not present at high or moderate relative-concentrations in the primary aquifer system (table 8).

The solvent/fumigant 1,2-dichloroethane was reported at high relative-concentrations in the CDPH water-quality database during the period December 1, 2007, to December 31, 2010. 1,2-Dichloroethane was reported at high relative-concentrations twice in one CDPH site; however, the most recent result for that site was a non-detection, thus the high aquifer-scale proportion for 1,2-dichloroethane is 0 percent (table 8).

The gasoline oxygenate MTBE also was reported at high relative-concentrations in the CDPH water-quality database. MTBE was reported at high relative-concentrations in one CDPH site; however, the most recent result was a moderate relative-concentration of MTBE. The high aquifer-scale proportion for MTBE is 0 percent, but MTBE was present at moderate relative-concentrations in 1.9 percent of the primary aquifer system (spatially weighted) (table 8). MTBE was detected in less than 10 percent of the grid sites (fig. 13).

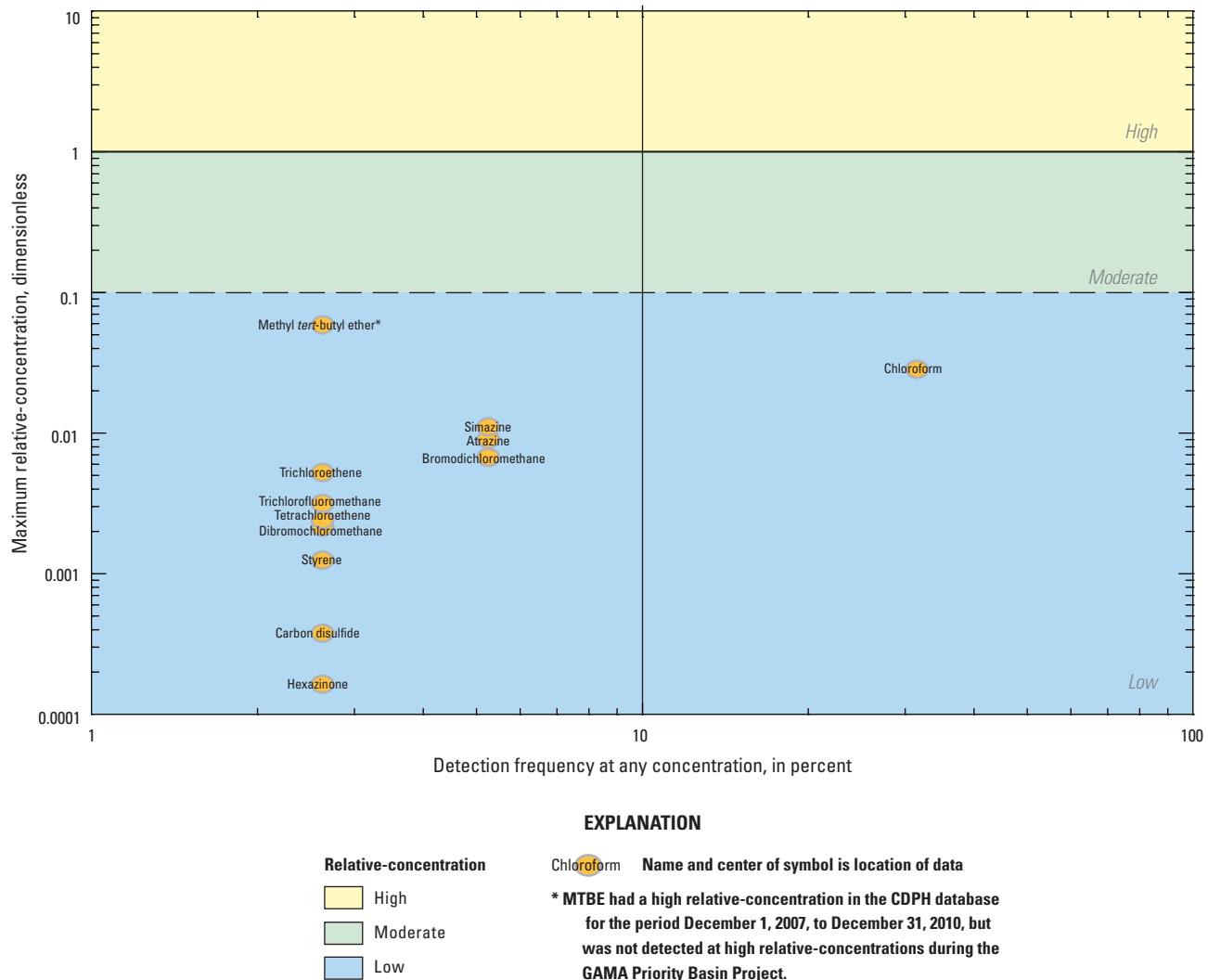


Figure 13. Detection frequency and maximum relative-concentration for organic constituents detected in USGS-grid sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

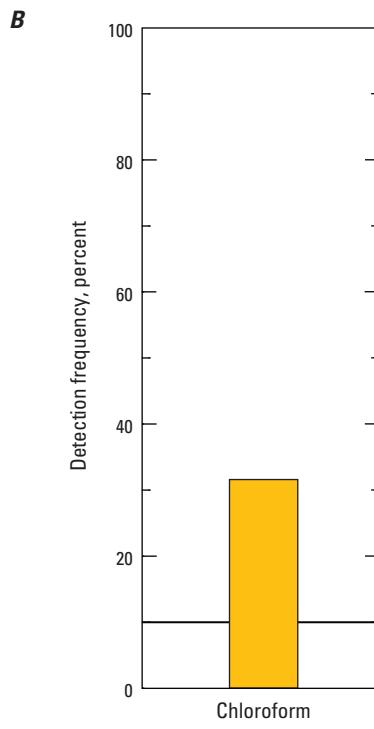
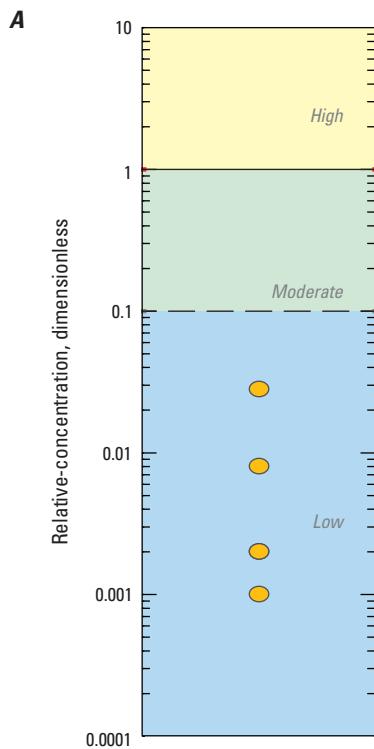


Figure 14. (A) Maximum relative-concentration and (B) detection frequency for the trihalomethane chloroform detected in USGS-grid sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Potential Factors Affecting Chloroform

Chloroform concentrations were significantly positively correlated with septic tank location density and not with any other potential explanatory factors ([table 5](#)). Chloroform and other THMs are known byproducts of drinking-water disinfection and have commonly been detected in septic tank effluent (Moran and others, 2002). Septic tank densities are generally higher in less urbanized areas. In the KLAM study unit, the percentage of urban land use was less than 5 percent. The average septic tank density in the KLAM study unit was about 1 tank/km² (0.38 per mi²).

Summary

Groundwater quality in the approximately 8,806-square-mile (22,809-square-kilometer) Klamath Mountains (KLAM) study unit was investigated as part of the Priority Basin Project of the Groundwater Ambient Monitoring and Assessment (GAMA) Program. The GAMA KLAM study provides a spatially unbiased characterization of untreated groundwater quality in the primary aquifer system. The assessment is based on water-quality data collected by the U.S. Geological Survey (USGS) from 39 sites in 2010 and water-quality data compiled in the California Department of Public Health (CDPH) database (for the period from December 1, 2007, to December 31, 2010).

The status of the current quality of the groundwater resource was assessed by using data from samples analyzed for volatile organic compounds (VOCs), pesticides, and naturally occurring inorganic constituents, such as trace elements and major and minor ions. The *status assessment* characterized the quality of groundwater resources in the primary aquifer system of the KLAM study unit, not the treated drinking water delivered to consumers by water purveyors.

Relative-concentrations (sample concentration divided by the health- or aesthetic-based benchmark concentration) were used for evaluating groundwater quality for those constituents that have Federal and (or) California regulatory or non-regulatory benchmarks for drinking-water quality.

Aquifer-scale proportion was used as the primary metric in the *status assessment* for evaluating regional-scale groundwater quality. High aquifer-scale proportion is defined as the percentage of the primary aquifer system with a relative-concentration greater than 1.0 for a particular constituent or class of constituents; proportion is based on an areal rather than a volumetric basis. Moderate and low aquifer-scale proportions were defined as the percentages of the primary aquifer system with moderate

and low relative-concentrations, respectively. Two statistical approaches, grid-based and spatially weighted, were used to evaluate aquifer-scale proportions for individual constituents and classes of constituents. Grid-based and spatially weighted estimates were comparable in the KLAM study unit (within 90 percent confidence intervals for all constituents). However, the spatially weighted approach was better able to identify constituents with high or moderate relative concentrations in small fractions of the aquifer.

Inorganic constituents with regulatory health-based benchmarks were present at high relative-concentrations in 2.6 percent of the primary aquifer system and at moderate relative-concentrations in 10 percent. The inorganic constituents with high aquifer-scale proportions included antimony, arsenic, and boron. The inorganic constituents with non-regulatory aesthetic-based benchmarks were present at high relative-concentrations in 13 percent of the primary aquifer system and at moderate relative-concentrations in 10 percent. The high aquifer-scale proportion primarily reflected high aquifer-scale proportions of iron and manganese.

Relative-concentrations of organic constituents were not high, but were moderate in 1.9 percent of the primary aquifer system when using the spatially weighted approach. The gasoline oxygenate methyl *tert*-butyl ether was the only constituent detected at moderate relative-concentrations. Of the 148 organic constituents analyzed, 14 constituents were detected. Only one organic constituent had a detection frequency of greater than 10 percent—the trihalomethane chloroform.

Statistical correlations between concentrations of constituents and values of selected potential explanatory factors were used in the understanding assessment to identify the factors potentially affecting the concentrations and occurrences of constituents detected at high relative-concentrations or with study-unit detections of organic constituents greater than 10 percent. The potential explanatory factors evaluated were aquifer lithology, land use, hydrologic conditions, depth, groundwater age, and geochemical conditions.

Groundwater age class (modern, mixed, or pre-modern), redox class (oxic, mixed, or anoxic), and dissolved oxygen concentration were the most significant explanatory factors with potential causative value for the inorganic constituents evaluated in the understanding assessment (boron, iron, manganese, and specific conductance). High concentrations of boron were associated with groundwater classified as mixed or pre-modern with respect to groundwater age. Boron was also negatively correlated to dissolved oxygen and positively correlated to specific conductance. Iron and manganese concentrations were strongly associated with low dissolved oxygen concentrations, anoxic and mixed

redox classifications, and pre-modern groundwater. Specific conductance concentrations were related to pre-modern groundwater, low dissolved oxygen concentrations, and high pH. The relation of specific conductance to dissolved oxygen and pH likely reflects the lower DO concentrations and greater pH values found in older groundwater in the KLAM study unit. Septic tank density was the only potential explanatory factor with any potential causative value for the one organic constituent (chloroform) selected for the *understanding assessment*.

Acknowledgments

The authors thank the following cooperators for their support: the California State Water Resources Control Board, Lawrence Livermore National Laboratory, California Department of Public Health, and California Department of Water Resources. We especially thank the site owners and water purveyors for their cooperation in allowing the U.S. Geological Survey to collect samples from their sites. Funding for this work was provided by State of California bonds authorized by Proposition 50 and administered by the State Water Resources Control Board.

References

- Alt, D., and Hyndman, D.W., 2000, Roadside geology of northern and central California: Mountain Press Publishing Company, 369 p.
- Appelo, C.A.J., and Postma, D., 2005, Geochemistry, groundwater, and pollution (2^d ed.): Leiden, Germany, A.A. Balkema Publishers, 649 p.
- Belitz, K., Dubrovsky, N.M., Burow, K.R., Jurgens, B., and Johnson, T., 2003, Framework for a ground-water quality monitoring and assessment program for California: U.S. Geological Survey Water-Resources Investigations Report 03-4166, 78 p.
- Belitz, K., Jurgens, B., Landon, M.K., Fram, M.S., and Johnson, T., 2010, Estimation of aquifer-scale proportion using equal-area grids—Assessment of regional-scale groundwater quality: Water Resources Research, v. 46, W11550, 14 p., doi:10.1029/2010WR009321. (Also available at <http://www.agu.org/pubs/crossref/2010/2010WR009321.shtml>.)

- Borchers, J.W., 1996, Ground-water resources and water-supply alternatives in the Wawona area of Yosemite National Park, California: U.S. Geological Survey Water-Resources Investigations Report 95-4229, 77 p.
- Brown, L.D., Cai, T.T., and DasGupta, A., 2001, Interval estimation for a binomial proportion: Statistical Science, v. 16, no. 2, p. 101–117.
- Burow, K.R., Dubrovsky, N.M., and Shelton, J.L., 2008, Regional nitrate and pesticide trends in ground water in the eastern San Joaquin Valley, California: Journal of Environmental Quality, v. 37, no. 5, p. S-249–S-263.
- Burton, C.A., Shelton, J.L., and Belitz, Kenneth, 2012, Status and understanding of groundwater quality in the two southern San Joaquin Valley study units, 2005–2006—California GAMA Priority Basin Project: U.S. Geological Survey Scientific Investigations Report 2011-5218, 150 p.
- California Department of Public Health, 2010, Drinking water notification levels: California Department of Public Health, accessed October 10, 2012, at <http://www.cdph.ca.gov/certlic/drinkingwater/Pages/NotificationLevels.aspx>.
- California Department of Public Health, 2013, California drinking water-related laws—Drinking water-related regulations, Title 22: California Department of Public Health, accessed October 17, 2013, at <http://www.cdph.ca.gov/certlic/drinkingwater/Pages/Lawbook.aspx>.
- California Department of Water Resources, 1984, Eastern Shasta County ground water study: State of California, The Resources Agency, Department of Water Resources, Northern District, 122 p. (Also available at http://www.water.ca.gov/pubs/groundwater/eastern_shasta_county_groundwater_study/easternshastacountygroundwaterstudydwrndjune84.pdf.)
- California Department of Water Resources, 2003, California's groundwater: California Department of Water Resources Bulletin 118, 246 p., accessed October 10, 2012, at <http://www.water.ca.gov/groundwater/bulletin118/bulletin118update2003.cfm>.
- California Department of Water Resources, 2004a, California's groundwater—Individual basin descriptions, Scott River Valley Groundwater Basin: California Department of Water Resources Bulletin 118, accessed October 10, 2012, at http://www.water.ca.gov/pubs/groundwater/bulletin_118/basindescriptions/1-5.pdf.
- California Department of Water Resources, 2004b, California's groundwater—Individual basin descriptions, Happy Camp Town Area Groundwater Basin: California Department of Water Resources Bulletin 118, accessed October 10, 2012, at http://www.water.ca.gov/pubs/groundwater/bulletin_118/basindescriptions/1-15.pdf.
- California Department of Water Resources, 2004c, California's groundwater—Individual basin descriptions, Seiad Groundwater Basin: California Department of Water Resources Bulletin 118, accessed October 10, 2012, at http://www.water.ca.gov/pubs/groundwater/bulletin_118/basindescriptions/1-16.pdf.
- California Environmental Protection Agency, 2001, Geographic Environmental Information Management System GeoTracker (GEIMS) Leaking Underground Fuel/Storage Tank database (LUFT) [digital data]: Sacramento, Calif., California Environmental Protection Agency, State Water Resources Control Board, Division of Water Quality.
- California Irrigation Management Information System, 2005, CIMIS reference evapotranspiration zones, accessed October 11, 2012, at <http://wwwcimis.water.ca.gov/cimis/pdf/CimisRefEvapZones.pdf>.
- California State Water Resources Control Board, 2003, A comprehensive groundwater quality monitoring program for California: Assembly Bill 99 Report to the Governor and Legislature, March 2003, 100 p., accessed October 10, 2012, at http://www.waterboards.ca.gov/gama/docs/final_ab_599_rpt_to_legis_7_31_03.pdf.
- California State Water Resources Control Board, 2010, GAMA—Groundwater Ambient Monitoring and Assessment Program: State Water Resources Control Board website, accessed October 10, 2012, at <http://www.waterboards.ca.gov/gama/>.
- California State Water Resources Control Board, 2011, GeoTracker GAMA Groundwater Information System, accessed September 5, 2013, at <http://geotracker.waterboards.ca.gov/gama/>.
- Centers for Disease Control and Prevention and U.S. Department of Housing and Urban Development, 2006, Healthy housing reference manual: Atlanta, U.S. Department of Health and Human Services, 231 p.
- Chapelle, F.H., 2001, Ground-water microbiology and geochemistry (2^d ed.): New York, John Wiley and Sons, Inc., 477 p.
- Chapelle, F.H., McMahon, P.B., Dubrovsky, N.M., Fuji, R.F., Oaksford, E.T., and Vroblesky, D.A., 1995, Deducing the distribution of terminal electron-accepting processes in hydrologically diverse groundwater systems: Water Resources Research, v. 31, no. 2, p. 359–371.
- Clark, I.D., and Fritz, P., 1997, Environmental isotopes in hydrogeology: New York, Lewis Publishers, 328 p.
- Cook, P.G., and Böhlke, J.K., 2000, Determining timescales for groundwater flow and solute transport, in Cook, P.G., and Herczeg, A., eds., Environmental tracers in subsurface hydrology: Boston, Kluwer Academic Publishers, p. 1–30.

- Craig, H., and Lal, D., 1961, The production rate of natural tritium: *Tellus*, v. 13, p. 85–105.
- Flint, L.E., and Flint, A.L., 2007, Regional analysis of groundwater recharge: U.S. Geological Survey Professional Paper 1703-B, p. 29–60.
- Fontes, J.C., and Garnier, J.M., 1979, Determination of the initial ^{14}C activity of the total dissolved carbon—A review of the existing models and a new approach: *Water Resources Research*, v. 15, p. 399–413.
- Fram, M.S., and Belitz, Kenneth, 2012, Status and understanding of groundwater quality in the Tahoe-Martis, Central Sierra, and Southern Sierra study units, 2006–2007—California GAMA Priority Basin Project: U.S. Geological Survey Scientific Investigations Report 2011–5216, 222 p.
- Freeze, R.A., and Cherry, J.A., 1979, *Groundwater*: Englewood Cliffs, New Jersey, Prentice-Hall, Inc., 604 p.
- Gascoyne, M., 1997, Evolution of redox conditions and groundwater composition in recharge-discharge environments on the Canadian Shield: *Hydrogeology Journal*, v. 5, no. 3, p. 4–18.
- Gilliom, R.J., Barbash, J.E., Crawford, C.G., Hamilton, P.A., Martin, J.D., Nakagaki, N., Nowell, L.H., Scott, J.C., Stackelberg, P.E., Thelin, G.P., and Wolock, D.M., 2006, The quality of our nation's waters—Pesticides in the nation's streams and ground water, 1992–2001: U.S. Geological Survey Circular 1291, 172 p. (Also available at <http://pubs.usgs.gov/circ/2005/1291/>.)
- Helsel, D.R., and Hirsch, R.M., 2002, Statistical methods in water resources: U.S. Geological Survey Techniques of Water Resources Investigations, book 4, chap. A3, 510 p., accessed January 31, 2014, at <http://pubs.usgs.gov/twri/twri4a3/>.
- Hem, J.D., 1985, Study and interpretation of the chemical characteristics of natural water (3d ed.): U.S. Geological Survey Water-Supply Paper 2254, 213 p.
- Heywood, I., Cornelius, S., and Carver, S., 1998, *An introduction to geographical information systems*: New Jersey, Prentice Hall, 278 p.
- Ingebritsen, S.E., and Sanford, W.E., 1998, *Groundwater in geologic processes*: Cambridge, England, Cambridge University Press, 341 p.
- Irwin, W.P., and Wooden, J.L., 1999, Plutons and accretionary episodes of the Klamath Mountains, California and Oregon: U.S. Geological Survey Open-File Report 99–374, 1 p.
- Isaaks, E.H., and Srivastava, R.M., 1989, *Applied geostatistics*: New York, Oxford University Press, 561 p.
- Jennings, C.W., 1977, Geologic map of California: California Department of Conservation, Division of Mines and Geology Geologic Data Map No. 2, scale 1:750,000.
- Johnson, T.D., and Belitz, Kenneth, 2009, Assigning land use to supply wells for the statistical characterization of regional groundwater quality—Correlating urban land use and VOC occurrence: *Journal of Hydrology*, v. 370, p. 100–108.
- Jurgens, B.C., Böhlke, J.K., and Eberts, S.M., 2012, *TracerLPM* (Version 1): An Excel® workbook for interpreting groundwater age distributions from environmental tracer data: U.S. Geological Survey Techniques and Methods Report 4-F3, 60 p.
- Jurgens, B.C., McMahon, P.B., Chapelle, F.H., and Eberts, S.M., 2009, An Excel® workbook for identifying redox processes in ground water: U.S. Geological Survey Open-File Report 2009–1004, 8 p. (Also available at <http://pubs.usgs.gov/of/2009/1004/>.)
- Klein, C., and Hurlbut, C.S., Jr., 1993, *Manual of mineralogy* (after James D. Dana), 21st ed.: New York, John Wiley & Sons, 681 p.
- Kulongoski, J.T., and Belitz, Kenneth, 2004, *Groundwater Ambient Monitoring and Assessment Program*: U.S. Geological Survey Fact Sheet 2004-3088, 2 p. (Also available at <http://pubs.usgs.gov/fs/2004/3088/>.)
- Kulongoski, J.T., and Belitz, Kenneth, 2011, Status and understanding of groundwater quality in the Monterey Bay and Salinas Valley Basin, 2005—California GAMA Priority Basin Project: U.S. Geological Survey Scientific Investigations Report 2011–5058, 84 p.
- Landon, M.K., Belitz, Kenneth, Jurgens, B.C., Kulongoski, J.T., and Johnson, T.D., 2010, Status and understanding of groundwater quality in the Central-Eastside San Joaquin Basin, 2006—California GAMA Priority Basin Project: U.S. Geological Survey Scientific Investigations Report 2009–5266, 97 p. (Also available at <http://pubs.usgs.gov/sir/2009/5266/>.)
- Landon, M.K., Green, C.T., Belitz, Kenneth, Singleton, M.J., and Esser, B.K., 2011, Relations of hydrogeologic factors, groundwater reduction-oxidation conditions, and temporal and spatial distributions of nitrate, Central-Eastside San Joaquin Valley, California, USA: *Hydrogeology Journal*, v. 19, no. 6, p. 1203–1224.
- Lucas, L.L., and Unterweiger, M.P., 2000, Comprehensive review and critical evaluation of the half-life of tritium: *Journal of Research of the National Institute of Standards and Technology*, v. 105, no. 4, p. 541–549.
- Manning, A.H., Solomon, D.K., and Thiros, S.A., 2005, $^3\text{H}/^3\text{He}$ age data in assessing the susceptibility of wells to contamination: *Ground Water*, v. 43, no. 3, p. 353–367.

- Mathany, T.M., and Belitz, Kenneth, 2014, Groundwater-quality data in the Klamath Mountains study unit, 2010—Results from the California GAMA Program: U.S. Geological Survey Data-Series 803, 82 p.
- McMahon, P.B., and Chapelle, F.H., 2008, Redox processes and water quality of selected principal aquifer systems: *Ground Water*, v. 46, no. 2, p. 259–271.
- Michel, R.L., 1989, Tritium deposition in the continental United States, 1953–83: U.S. Geological Survey Water-Resources Investigations Report 89–4072, 46 p.
- Michel, R.L., and Schroeder, R., 1994, Use of long-term tritium records from the Colorado River to determine timescales for hydrologic processes associated with irrigation in the Imperial Valley, California: *Applied Geochemistry*, v. 9, p. 387–401.
- Moran, M.J., Lapham, W.W., Rowe, B.L., and Zogorski, J.S., 2002, Occurrence and status of volatile organic compounds in ground water from rural, untreated, self-supplied domestic wells in the United States, 1986–99: U.S. Geological Survey Water-Resources Investigations Report 02–4085, 51 p.
- Mueller, D.K., and Helsel, D.R., 1996, Nutrients in the Nation's waters—Too much of a good thing?: U.S. Geological Survey Circular 1136, 24 p.
- Nakagaki, Naomi, Price, C.V., Falcone, J.A., Hitt, K.J., and Ruddy, B.C., 2007, Enhanced National Land Cover Data 1992 (NLCD 92): U.S. Geological Survey raster digital data, accessed January 31, 2014, at <http://water.usgs.gov/lookup/getspatial?nlcd92>.
- Nakagaki, Naomi, and Wolock, D.M., 2005, Estimation of agricultural pesticide use in drainage basins using land cover maps and county pesticide data: U.S. Geological Survey Open-File Report 2005–1188, 46 p.
- Page, R.W., Anttila, P.W., Johnson, K.L., and Pierce, M.J., 1984, Ground-water conditions and well yields in fractured rocks, southwestern Nevada County, California: U.S. Geological Survey Water-Resources Investigations Report 83–4262, 38 p.
- Piper, A.M., 1944, A graphic procedure in the geochemical interpretation of water analyses: *American Geophysical Union Transactions*, v. 25, p. 914–923.
- Plummer, L.N., Bexfield, L.M., Anderholm, S.K., Sanford, W.E., and Busenberg, E., 2004, Geochemical characterizations of groundwater flow in the Santa Fe Group aquifer system, Middle Rio Grande Basin, New Mexico: U.S. Geological Survey Water-Resources Investigations Report 03–4131, 395 p.
- Plummer, L.N., Michel, R.L., Thurman, E.M., and Glynn, P.D., 1993, Environmental tracers for age-dating young ground water, in Alley, W.M., ed., *Regional ground water quality*: New York, Van Nostrand Reinhold, p. 255–294.
- PRISM Group, Oregon State University, 2007, United States average annual precipitation, maximum and minimum temperature, 1971–2000, accessed October 11, 2012, at <http://prism.oregonstate.edu/>.
- Rowe, B.L., Toccalino, P.L., Moran, M.J., Zogorski, J.S., and Price, C.V., 2007, Occurrence and potential human-health relevance of volatile organic compounds in drinking water from domestic wells in the United States: *Environmental Health Perspectives*, v. 115, no. 11, p. 1539–1546.
- Saucedo, G.J., Bedford, D.R., Raines, G.L., Miller, R.J., and Wentworth, C.M., 2000, GIS data for the geologic map of California (version 2.0): Sacramento, Calif., California Department of Conservation, Division of Mines and Geology.
- Scott, J.C., 1990, Computerized stratified random site-selection approaches for design of a ground-water-quality sampling network: U.S. Geological Survey Water-Resources Investigations Report 90–4101, 109 p.
- Sidborn, M., and Neretnieks, I., 2007, Long term redox evolution in granitic rocks—Modelling the redox front propagation in the rock matrix: *Applied Geochemistry*, v. 22, no. 11, p. 2381–2396.
- Snoke, A.W., and Barnes, C.G., 2006, The development of tectonic concepts for the Klamath Mountains province, California and Oregon, in Snoke, A.W., and Barnes, C.G., eds., *Geological studies in the Klamath Mountains province, California and Oregon—A volume in honor of William P. Irwin*: Geological Society of America Special Paper 410, p. 1–29, doi: 10.1130/2006.2410(01).
- State of California, 1999, Supplemental Report of the 1999 Budget Act, 1999–00 Fiscal Year, Item 3940-001-0001: State Water Resources Control Board, accessed October 10, 2012, at http://www.lao.ca.gov/1999/99-00_supp_rpt_lang.html#3940.
- State of California, 2001a, Assembly Bill No. 599, Chapter 522, accessed October 10, 2012, at http://www.swrcb.ca.gov/gama/docs/ab_599_bill_20011005_chaptered.pdf.
- State of California, 2001b, Groundwater Monitoring Act of 2001, California Water Code, part 2.76, sec. 10780–10782.3, accessed October 10, 2010, at <http://www.leginfo.ca.gov/cgi-bin/displaycode?section=wat&group=10001-11000&file=10780-10783>.

- Toccalino, P.L., Norman, J., Phillips, R., Kauffman, L., Stackelberg, P., Nowell, L., Krietzman, S., and Post, G., 2004, Application of health-based screening levels to groundwater quality data in a state-scale pilot effort: U.S. Geological Survey Scientific Investigations Report 2004-5174, 14 p.
- Toccalino, P.L., and Norman, J.E., 2006, Health-based screening levels to evaluate U.S. Geological Survey ground water quality data: Risk Analysis, v. 26, no. 5, p. 1339–1348.
- Tolstikhin, I.N., and Kamensky, I.L., 1969, Determination of groundwater ages by the T³He method: Geochemistry International, v. 6, p. 810–811.
- Torgersen, T., Clarke, W.B., and Jenkins, W.J., 1979, The tritium/helium-3 method in hydrology: IAEA-SM-228, v. 49, p. 917–930.
- Toth, J., 1963, A theoretical analysis of groundwater flow in small drainages: Journal of Geophysical Research, v. 63, no. 16, p. 4795–4812.
- U.S. Census Bureau, 1990, Census of population and housing, summary tape file 3A, accessed October 10, 2012, at ftp://ftp2.census.gov/census_1990/.
- U.S. Department of Commerce, National Climatic Data Center, 2012, National Climatic Data Center home page, accessed October 10, 2012, at <http://www.ncdc.noaa.gov/oa/ncdc.html>.
- U.S. Environmental Protection Agency, 1998, Code of Federal Regulations; Title 40—Protection of environment; Chapter 1—Environmental protection agency; Subchapter E—Pesticide programs; Part 159—Statements of policies and interpretations; Subpart D—Reporting requirements for risk/benefit information, 40 CFR 159.184: Washington, National Archives and Records Administration, September 19, 1997; amended June 19, 1998; accessed October 10, 2012, at <http://www.gpo.gov/fdsys/pkg/CFR-2011-title40-vol24/xml/CFR-2011-title40-vol24-part159-subpartD.xml>.
- U.S. Environmental Protection Agency, 1999, Proposed radon in drinking water regulation, accessed October 10, 2012, at <http://water.epa.gov/lawsregs/rulesregs/sdwa/radon/regulations.cfm>.
- U.S. Environmental Protection Agency, 2008a, Ground Water Rule—Source assessment guidance manual: U.S. Environmental Protection Agency 815-R-07-023, 34 p., accessed March 6, 2013, at http://www.epa.gov/ogwdw/disinfection/gwr/pdfs/guide_gwr_sourcewaterassessments.pdf.
- U.S. Environmental Protection Agency, 2008b, Drinking water health advisory for boron: U.S. Environmental Protection Agency 822-R-08-013, 53 p.
- U.S. Environmental Protection Agency, 2009, Drinking water contaminants, accessed October 12, 2012, at <http://water.epa.gov/drink/contaminants/index.cfm>.
- U.S. Environmental Protection Agency, 2012a, Drinking water science and regulatory support—Drinking water standards and health advisory tables, accessed October 10, 2012, at <http://water.epa.gov/drink/standards/hascience.cfm>.
- U.S. Environmental Protection Agency, 2012b, Arsenic in drinking water, accessed October 2012, at <http://water.epa.gov/lawsregs/rulesregs/sdwa/arsenic/index.cfm>.
- U.S. Geological Survey, 2006, National Elevation Dataset (NED): U.S. Geological Survey database, accessed January 31, 2014, at <http://ned.usgs.gov>.
- U.S. Geological Survey, 2010, What is the Priority Basin Project?, accessed October 10, 2012, at <http://ca.water.usgs.gov/gama/>.
- United Nations Educational, Scientific, and Cultural Organization (UNESCO), 1979, Map of the world distribution of arid regions—Explanatory note: MAB Technical Notes, v. 7, 42 p.
- United Nations Environment Programme, 1997, World Atlas of Desertification, 2^d ed.: London, Edward Arnold, 182 p.
- Vogel, J.C., and Ehhalt, D., 1963, The use of the carbon isotopes in groundwater studies, in Radioisotopes in hydrology: Tokyo, International Atomic Energy Agency, p. 383–395.
- Western Regional Climate Center, 2012, Western Regional Climate Center, Summary climate data for Northern California, average monthly precipitation data, accessed October 10, 2012, at <http://www.wrcc.dri.edu/summary/Climsmnca.html>.
- Zogorski, J.S., Carter, J.M., Ivahnenko, T., Lapham, W.W., Moran, M.J., Rowe, B.L., Squillace, P.J., and Toccalino, P.L., 2006, Volatile organic compounds in the Nation's ground water and drinking-water supply wells: U.S. Geological Survey Circular 1292, 101 p.

Appendix A. Attribution of Potential Explanatory Factors

Aquifer Lithology

Aquifer lithology was classified into four different categories on the basis of lithologic information from driller's logs and on the California State geologic map (Jennings, 1977; Saucedo and others, 2000) ([table A1](#)). The State geologic map shows the lithologic unit exposed at the surface, which may or may not be the same as the lithologic unit at the depth range over which the well is screened or open. When available, the lithologic category estimated from the geologic map was compared to the lithology described in the driller's log. If the lithology from the map disagreed with the lithology from the driller's log, the category from the driller's log was used. The six lithologic categories are

- Granitic rocks (G): Primarily Mesozoic granitic rocks with some Paleozoic granitic rocks (California State geologic map units: gr, grMz, and grPz);
- Metamorphic rocks (other than metasedimentary) (M): Mesozoic, Paleozoic, and pre-Cenozoic metavolcanic rocks (California State geologic map units: ls, m, mv, Mzv, Pzv, and sch);
- Metasedimentary rocks (MS): Metamorphosed Mesozoic and Paleozoic marine rocks (California State geologic map units: C, D, J, Kl, Ku, Pm, Pz, SO, and Tr);
- Ultramafic/mafic rocks (UM): Chiefly Mesozoic ultramafic, mafic, or gabbroic rocks (California State geologic map units: gb and um);
- Alluvial sediments (S): Chiefly Quaternary alluvial sediment (California State geologic map units: Q and Qg). No wells were sampled by USGS–GAMA in this unit.
- Undifferentiated rocks (X): Chiefly Franciscan formation (California State geologic map units: Ec, Kjf, Kjfs, M, Mc, Oc, QPc, Qv, Tc, Ti, Tv, and Tvp). No wells were sampled by USGS–GAMA in this unit.

Land Use

Land use was classified using an enhanced version of the satellite-derived (98-ft [30-m] pixel resolution) USGS National Land Cover Dataset (Nakagaki and others, 2007). This dataset has been used in previous national and regional studies relating land use to water quality (Gilliom and others, 2006; Zogorski and others, 2006). The dataset characterizes land cover during the early 1990s. The imagery was classified into 25 land-cover classifications (Nakagaki and Wolock, 2005). These 25 land-cover classifications were aggregated into three principal land-use classes for the purpose of general categorization of land use: urban, agricultural, and natural. Average land use (proportions of urban, agricultural, and natural) for the study unit and for areas within a radius of 1,640 ft (500 m) surrounding each site ([table A1](#)) was calculated using ArcGIS (version 9.2) (Johnson and Belitz, 2009).

LUFT and Septic Tank Densities

Density for LUFTs was determined by using a Thiessen polygon approach for spatial interpolation (Heywood and others, 1998; Tyler Johnson, U.S. Geological Survey, California Water Science Center, written commun., 2012) and data from the California Environmental Protection Agency (2001). Thiessen polygons were created by starting with the LUFT in the center of the polygon. The polygon edges were increased in all directions until they extended halfway to a neighboring LUFT (or they reached the edge of the State). The result is a unique shape for each LUFT. In most instances, there was only one LUFT per polygon, but occasionally there were multiple LUFTs in a polygon. The total number of LUFTs per polygon was divided by the area of the polygon. This generates a density of LUFTs for each polygon. The GAMA sites were then overlaid onto the Thiessen polygon map, and the GAMA site was assigned the LUFT density from the Thiessen polygon it was located within.

Septic tank density was determined from the 1990 Census of Population and Housing: Summary Tape File 3A dataset (U.S. Census Bureau, 1990). The density of septic tanks in each housing census block was calculated from the number of tanks and block area. The density of septic tanks around each USGS–GAMA grid site was then calculated from the area-weighted mean of the block densities within a 500-m radius around the site location (Tyler Johnson, U.S. Geological Survey, California Water Science Center, written commun., 2013) ([table A1](#)).

Table A1. Aquifer lithology class, land-use data, hydrologic conditions, leaking (or formerly leaking) underground fuel tank (LUFT) density, and septic tank density, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[GAMA site identification number: KLAM, Klamath Mountains study unit; KLAM-U, Klamath Mountains study unit understanding site. Other abbreviations: ft, feet; m, meter; tanks/km², tanks per square kilometer; G, granitic rocks; LSD, land-surface datum; LUFT, leaking (or formerly leaking) underground fuel tank; M, metamorphic other; MS, metasedimentary; na, not available; S, sedimentary; UM, ultramafic/mafic]

USGS-GAMA site identification number	Aquifer lithology class	Land use within 500 m of site ¹			Hydrologic conditions			LUFT density ⁵ (tanks/km ²)	Septic tank density ⁶ (tanks/km ²)
		Agricultural (percent)	Natural (percent)	Urban (percent)	Aridity index ²	Elevation of LSD (ft above NAVD 88) ³	Site type ⁴		
Klamath Mountains study unit grid sites									
KLAM-01	UM	0	98	2	2.43	723	Spring	0	0.27
KLAM-02	M	0	100	0	0.91	3,043	Spring	0	0.55
KLAM-03	M	0	99	1	0.47	1,977	Production	0.02	0.54
KLAM-04	MS	0	100	0	0.86	4,745	Spring	0.01	0.60
KLAM-05	M	0	100	0	0.60	2,989	Production	0.01	0.62
KLAM-06	MS	1	92	7	0.43	2,324	Production	0.01	0.52
KLAM-07	M	0	100	0	1.07	2,235	Production	0	0.18
KLAM-08	MS	0	98	2	2.18	2,152	Production	0	0.27
KLAM-09	MS	0	100	0	1.48	713	Production	0.01	3.83
KLAM-10	UM	0	100	0	2.03	1,063	Spring	0	0.16
KLAM-11	MS	0	100	0	1.49	647	Production	0.01	0.16
KLAM-12	MS	0	100	0	1.02	2,655	Spring	0	0.34
KLAM-13	M	0	100	0	0.92	1,412	Production	0.02	0.36
KLAM-14	MS	1	99	0	1.06	1,270	Production	0.01	0.44
KLAM-15	MS	0	100	0	1.33	1,140	Production	0.02	0.44
KLAM-16	MS	0	96	4	1.56	1,120	Production	0	1.47
KLAM-17	G	0	100	0	0.59	3,321	Production	0.01	0.18
KLAM-18	UM	0	78	22	1.14	3,301	Production	0	0.34
KLAM-19	M	0	100	0	0.90	1,788	Production	0.11	0.36
KLAM-20	UM ⁷	0	100	0	0.92	2,465	Spring	0	0.34
KLAM-21	G	0	100	0	1.04	2,620	Production	0	0.52
KLAM-22	M	0	95	5	1.48	457	Production	0.04	0.57
KLAM-23	G	0	72	28	0.80	1,794	Production	0.06	1.86

Table A1. Aquifer lithology class, land-use data, hydrologic conditions, leaking (or formerly leaking) underground fuel tank (LUFT) density, and septic tank density, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.—Continued

[GAMA site identification number: KLAM, Klamath Mountains study unit; KLAM-U, Klamath Mountains study unit understanding site. Other abbreviations: ft, feet; m, meter; tanks/km², tanks per square kilometer; G, granitic rocks; LSD, land-surface datum; LUFT, leaking (or formerly leaking) underground fuel tank; M, metamorphic other; MS, metasedimentary; na, not available; S, sedimentary; UM, ultramafic/mafic]

USGS-GAMA site identification number	Aquifer lithology class	Land use within 500 m of site ¹			Hydrologic conditions			LUFT density ⁵ (tanks/km ²)	Septic tank density ⁶ (tanks/km ²)
		Agricultural (percent)	Natural (percent)	Urban (percent)	Aridity index ²	Elevation of LSD (ft above NAVD 88) ³	Site type ⁴		
Klamath Mountains study unit grid sites—Continued									
KLAM-24	MS	0	100	0	0.71	3,436	Production	0	0.18
KLAM-25	MS	0	96	4	1.39	1,085	Production	0.03	1.48
KLAM-26	MS ⁸	48	35	17	0.96	1,093	Production	0	1.57
KLAM-27	MS	0	100	0	1.49	1,143	Production	0.01	0.70
KLAM-28	MS	0	99	1	1.73	1,091	Production	0.01	1.48
KLAM-29	UM	0	83	17	1.56	2,611	Spring	0.02	1.07
KLAM-30	M	0	96	4	1.59	2,008	Production	0	0.47
KLAM-31	UM	0	100	0	1.31	3,971	Production	0.01	1.13
KLAM-32	G	0	100	0	1.54	1,416	Production	0.01	0.69
KLAM-33	MS	0	94	6	1.67	1,250	Production	0	1.46
KLAM-34	MS	1	78	21	1.28	903	Production	0.04	10.8
KLAM-35	M	0	100	0	1.43	1,331	Production	0.02	1.16
KLAM-36	UM	0	91	9	1.32	2,479	Production	0.02	0.09
KLAM-37	MS	0	100	0	0.81	1,926	Production	0.02	1.86
KLAM-38	M	0	100	0	0.90	1,970	Production	0.01	1.86
Klamath Mountains study unit understanding site									
KLAM-U-01	MS	0	100	0	1.10	1,185	Production	0.02	0.44

¹ Land-use percentages within 500-m radius of sampled site (Nakagaki and others, 2007; Johnson and Belitz, 2009).

² Aridity index is average annual precipitation divided by average annual evapotranspiration (United Nations Educational, Scientific, and Cultural Organization, 1979).

³ Land-surface datum (LSD) is a datum plane that is approximately at land surface at each site. The elevation of the LSD is described in feet above the North American Vertical Datum of 1988 (NAVD 88).

⁴ Production sites had installed pumps which brought groundwater to the surface; springs had groundwater reaching the surface without pumps.

⁵ Leaking (or formerly leaking) underground fuel tank density within 500-m radius of sampled site (California Environmental Protection Agency, 2001).

⁶ Septic tank density within 500-m radius of sampled site (U.S. Census Bureau, 1990).

⁷ Originally identified as sedimentary rock type; however, it was reclassified based on proximity to adjacent rock type.

⁸ Perforated interval of this well in the driller's log describes its lithology as blue granite.

Hydrologic Conditions

Some of the hydrologic conditions at each site were represented by elevation and an aridity index. The aridity index is defined by the United Nations Environment Programme (1997) and United Nations Educational, Scientific, and Cultural Organization (1979) as

$$\text{aridity index} = \frac{\text{average annual precipitation}}{\text{average annual evapotranspiration}}. \quad (\text{A1})$$

Higher values of the index correspond to wetter conditions. Average annual precipitation for each site for 1971–2000 was extracted from the PRISM average annual precipitation GIS coverage (PRISM Group, Oregon State University, 2007). Average annual evapotranspiration for each site was extracted from an ESRI® ArcGIS coverage modified from Flint and Flint (2007). The modification consisted of calibrating the evapotranspiration values to the measured California Irrigation Management Information System reference evapotranspiration values (California Irrigation Management Information System, 2005; Fram and Belitz, 2012). Calculated aridity index values are listed in [table A1](#).

The range of site land-surface altitudes was large, ranging from the minimum of 457 ft (140 m) to a maximum of 4,754 ft (1,450 m). Land-surface altitudes were obtained from the U.S. Geological Survey National Elevation Dataset (2006) and are reported in feet relative to NAVD 88 ([table A1](#)).

Well Construction

Well construction data primarily were obtained from drillers' logs filed with CDWR. In some cases, well construction data were obtained from ancillary records of site owners or the USGS National Water Information System database. Well depths and depths to the tops and bottoms of the screened or open intervals for wells sampled by USGS–GAMA are listed in [table A2](#). Well construction data were not available for wells in the CDPH water-quality database. Wells drilled in hard rock commonly do not have casings; the borehole is left open. For these wells, the top of the screened or open interval was defined as the base of the sanitary seal, and the bottom was defined as the depth of the well. Springs were assigned a value of "at LSD" for the site depth and depth to top and bottom of the screened interval. Sites were classified as production wells or springs ([table A1](#)).

Table A2. Site construction information for USGS-grid and USGS-understanding sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[GAMA site identification number: KLAM, Klamath Mountains study unit; KLAM-U, Klamath Mountains study unit understanding site. Other abbreviations: ft, feet; LSD, land-surface datum; na, not available]

USGS–GAMA site identification number	Site construction information (ft below LSD ¹)		
	Well depth (ft below LSD) ²	Top of screened or open interval (ft below LSD)	Bottom of screened or open interval (ft below LSD)
Klamath Mountains study unit grid sites			
KLAM-01	at LSD	na	na
KLAM-02	at LSD	na	na
KLAM-03	40	24	32
KLAM-04	at LSD	na	na
KLAM-05	80	57	80
KLAM-06	270	170	270
KLAM-07	na	na	na
KLAM-08	400	120	180
KLAM-09	48	36	48
KLAM-10	at LSD	na	na
KLAM-11	89	49	89
KLAM-12	at LSD	na	na
KLAM-13	45	na	na
KLAM-14	na	na	na
KLAM-15	na	na	na
KLAM-16	278	55	278
KLAM-17	na	na	na
KLAM-18	320	240	300
KLAM-19	80	na	na
KLAM-20	at LSD	na	na
KLAM-21	225	na	na
KLAM-22	44	na	na
KLAM-23	305	160	305
KLAM-24	na	na	na
KLAM-25	125	na	na
KLAM-26	90	70	90
KLAM-27	320	300	320
KLAM-28	112	68	112
KLAM-29	at LSD	na	na
KLAM-30	120	60	120

Table A2. Site construction information for USGS-grid and USGS-understanding sites, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.—Continued

[GAMA site identification number: KLAM, Klamath Mountains study unit; KLAM-U, Klamath Mountains study unit understanding site. Other abbreviations: ft, feet; LSD, land-surface datum; na, not available]

USGS– GAMA site identification number	Site construction information (ft below LSD ¹)		
	Well depth (ft below LSD) ²	Top of screened or open interval (ft below LSD)	Bottom of screened or open interval (ft below LSD)
Klamath Mountains study unit grid sites—Continued			
KLAM-31	nd	na	na
KLAM-32	227	187	227
KLAM-33	249	201	249
KLAM-34	177	77	177
KLAM-35	na	na	na
KLAM-36	25	na	na
KLAM-37	na	na	na
KLAM-38	na	na	na
Klamath Mountains study unit understanding site			
KLAM-U-01	na	na	na

¹ Land-surface datum (LSD) is a datum plane that is approximately at land surface at each site. The elevation of the LSD is described in feet above the North American Vertical Datum of 1988 (NAVD 88).

² Well depths reported as “at LSD” indicate spring sites.

Geochemical Condition

Geochemical conditions were described by oxidation-reduction (redox) characteristics and pH. Redox conditions influence the mobility of many organic and inorganic constituents (McMahon and Chapelle, 2008). Along groundwater flow paths, redox conditions commonly proceed along a well-documented sequence of terminal electron acceptor processes (TEAPs); one TEAP typically dominates at a particular time and aquifer location (Chapelle and others, 1995; Chapelle, 2001). The predominant TEAPs are oxygen-reducing, nitrate-reducing, manganese-reducing, iron-reducing, sulfate-reducing, and methanogenesis. Groundwater samples may contain chemical species that suggest that more than one TEAP is occurring. Evidence for more than one TEAP may indicate mixing of waters from different redox zones upgradient of the site, a site that is screened across more than one redox zone, or spatial variability in microbial activity in the aquifer.

In this report, oxidation-reduction conditions were represented in three ways: by DO concentrations, by redox class, and by ratios of species of redox-sensitive trace elements (table A3). DO concentrations were measured in the

Table A3. Oxidation-reduction classes, dissolved oxygen concentration, pH, and ratios of oxidation-reduction species of arsenic and iron, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[Oxidation-reduction classes: Fe-red, iron reducing; Mn-red, manganese reducing; Mn-Fe-red, manganese and iron reducing. Ratio of oxidized to reduced species of iron: As⁺⁵/As⁺³, ratio of the amount of arsenic in the +5 oxidation state (arsenate) to the amount in the +3 oxidation state (arsenite); Fe⁺³/Fe⁺², ratio of the amount of iron in the +3 oxidation state (ferric) to the amount in the +2 oxidation state (ferrous). GAMA site identification number: KLAM, Klamath Mountains study unit; KLAM-U, Klamath Mountains study unit understanding site. Other abbreviations: mg/L, milligrams per liter; <, less than; >, greater than; na, not available; —, concentration too low to measure ratio]

USGS– GAMA site identification number	pH (standard units)	Dissolved oxygen (mg/L)	Oxidation- reduction class	Ratios of oxidized and reduced species of metals	
				As ⁺⁵ / As ⁺³	Fe ⁺³ / Fe ⁺²
Klamath Mountains study unit grid sites					
KLAM-01	8.2	10.1	Oxic	—	>10
KLAM-02	6.1	10.6	Oxic	—	0.11
KLAM-03	6.9	3.2	Oxic	—	0.13
KLAM-04	6.3	7.9	Oxic	—	—
KLAM-05	7.2	8.7	Oxic	—	—
KLAM-06	8.3	0.5	Anoxic	—	<0.01
KLAM-07	7.1	8.4	Oxic	>10	—
KLAM-08	7.3	0.9	Anoxic (Fe-red)	—	0.09
KLAM-09	6.5	2.9	Mixed (Fe-red)	—	0.02
KLAM-10	6.0	na	Oxic	—	—
KLAM-11	6.9	9.4	Oxic	>10	—
KLAM-12	6.6	7.5	Oxic	—	0.83
KLAM-13	6.7	7.8	Oxic	—	0.20
KLAM-14	7.2	6.9	Oxic	>10	—
KLAM-15	6.8	9.3	Oxic	—	—
KLAM-16	5.9	4.5	Oxic	—	—
KLAM-17	6.2	2.2	Oxic	>10	—
KLAM-18	6.1	6.1	Mixed (Fe-red)	—	0.04
KLAM-19	7.2	2.0	Oxic	>10	<0.01
KLAM-20	7.6	7.5	Oxic	—	—
KLAM-21	7.2	7.2	Oxic	>10	—
KLAM-22	7.0	10.7	Oxic	>10	0.23
KLAM-23	7.4	2.5	Oxic	>10	1.3
KLAM-24	7.5	0.4	Anoxic (Mn-Fe-red)	—	0.06
KLAM-25	7.0	2.4	Mixed (Mn-Fe-red)	>10	0.05

Table A3. Oxidation-reduction classes, dissolved oxygen concentration, pH, and ratios of oxidation-reduction species of arsenic and iron, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.—Continued

[**Oxidation-reduction classes:** Fe-red, iron reducing; Mn-red, manganese reducing; Mn-Fe-red, manganese and iron reducing. **Ratio of oxidized to reduced species of iron:** $\text{As}^{+5}/\text{As}^{+3}$, ratio of the amount of arsenic in the +5 oxidation state (arsenate) to the amount in the +3 oxidation state (arsenite); $\text{Fe}^{+3}/\text{Fe}^{+2}$, ratio of the amount of iron in the +3 oxidation state (ferric) to the amount in the +2 oxidation state (ferrous). **GAMA site identification number:** KLAM, Klamath Mountains study unit; KLAM-U, Klamath Mountains study unit understanding site. **Other abbreviations:** mg/L, milligrams per liter; <, less than; >, greater than; na, not available; —, concentration too low to measure ratio]

USGS— GAMA site identification number	pH (standard units)	Dissolved oxygen (mg/L)	Oxidation- reduction class	Ratios of oxidized and reduced species of metals	
				$\text{As}^{+5}/$ As^{+3}	$\text{Fe}^{+3}/$ Fe^{+2}
Klamath Mountains study unit grid sites—Continued					
KLAM-26	6.8	1.4	Oxic	—	0.27
KLAM-27	6.2	6.1	Mixed Mn-red	—	0.17
KLAM-28	6.5	3.4	Oxic	—	<0.01
KLAM-29	6.6	11.8	Oxic	>10	0.75
KLAM-30	6.8	<0.2	Anoxic (Mn-Fe-red)	—	0.02
KLAM-31	9.4	2.6	Oxic	—	—
KLAM-32	6.9	4.2	Oxic	—	0.26
KLAM-33	7.6	0.9	Oxic	>10	1.0
KLAM-34	7.4	5.6	Oxic	—	0.70
KLAM-35	6.7	4.1	Oxic	—	—
KLAM-36	6.6	7.0	Oxic	—	0.25
KLAM-37	6.1	2.3	Oxic	—	0.48
KLAM-38	6.9	7.3	Oxic	—	<0.01
Klamath Mountains study unit understanding site					
KLAM-U-01	7.2	7.4	Oxic	>10	>10

field at all KLAM study unit grid sites (Mathany and Belitz, 2014). Redox conditions were classified on the basis of DO, nitrate, manganese, and iron concentrations using a modified version of the classification scheme of McMahon and Chapelle (2008) and (Jurgens and others, 2009). Samples were classified as oxic, anoxic, or mixed according to the TEAPs inferred from the data (table A3).

Arsenic (As) and iron (Fe) can occur as different species depending on the redox state of the groundwater. The ratio of the amount of the more oxidized species to the amount

of the more reduced species for each constituent provides information about the progress of the TEAP involving each constituent. The following ratios are reported in table A3:

- $\text{As}^{+5}/\text{As}^{+3}$, where As^{+5} is the amount of arsenic present in the more oxidized +5 oxidation state (arsenate) and As^{+3} is the amount of arsenic present in the more reduced +3 oxidation state (arsenite); and
- $\text{Fe}^{+3}/\text{Fe}^{+2}$, where Fe^{+3} is the amount of iron present in the more oxidized +3 oxidation state (ferric iron) and Fe^{+2} is the amount of iron present in the more reduced +2 oxidation state (ferrous iron).

Total concentrations of As and Fe and concentrations of As^{+3} and Fe^{+2} were reported in Mathany and Belitz (2014). The concentrations of As^{+5} and Fe^{+3} were calculated by difference. The ratio of $\text{As}^{+5}/\text{As}^{+3}$ was reported as greater than 10 if total arsenic was detected and As^{+3} was not detected, and as less than 0.01 if the total arsenic concentration equaled the As^{+3} concentration. Similarly, $\text{Fe}^{+3}/\text{Fe}^{+2}$ was reported as greater than 10 if total iron was detected and Fe^{+2} was not detected, and as less than 0.01 if the total iron concentration equaled the Fe^{+2} concentration.

Groundwater Age

Groundwater dating techniques indicate the time since the groundwater was recharged into the primary aquifer system. The techniques used in this report to estimate groundwater residence times or ‘age’ were those based on tritium (for example, Tolstikhin and Kamensky, 1969; Torgersen and others, 1979) and carbon-14 activities (for example, Vogel and Ehhalt, 1963; Plummer and others, 1993).

Tritium is a short-lived radioactive isotope of hydrogen with a half-life of 12.32 years (Lucas and Unterweger, 2000). Tritium is produced naturally in the atmosphere from the interaction of cosmogenic radiation with nitrogen (Craig and Lal, 1961) and anthropogenically by above-ground nuclear explosions and the operation of nuclear reactors. Tritium enters the hydrologic cycle following oxidation to tritiated water. Above-ground nuclear explosions resulted in a large increase in tritium values in precipitation, beginning in about 1952 and peaking in 1963 at values over 1,000 TU in the northern hemisphere (Michel, 1989). Radioactive decay over a period of 50 years would decrease tritium values of 10 TU to 0.6 TU. Tritium values in precipitation under natural conditions in the KLAM study unit in 2010 were about 2 to 3 TU (updated values from Michel, 1989). On the west coast, most of the storms are oceanic in origin, so the water from these storms is mostly from exchange with surface ocean water, which has relatively low tritium (Michel, 1989).

Previous investigations have used a range of tritium values from 0.2 to 1.0 TU as thresholds for indicating presence of water that has exchanged with the atmosphere since 1952 (Michel, 1989; Plummer and others, 1993; Michel and Schroeder, 1994; Clark and Fritz, 1997; Manning and

others, 2005). For samples collected for the KLAM study unit in 2010, tritium values greater than 1 TU were defined as indicating presence of some groundwater recharged since 1952.

Carbon-14 (^{14}C) is a widely used chronometer based on the radiocarbon content of organic and inorganic carbon. Dissolved inorganic carbon species, carbonic acid, bicarbonate, and carbonate typically are used for ^{14}C dating of groundwater. ^{14}C is formed in the atmosphere by the interaction of cosmic-ray neutrons with nitrogen and, to a lesser degree, with oxygen and carbon. ^{14}C is incorporated into carbon dioxide and mixed throughout the atmosphere. The carbon dioxide enters the hydrologic cycle because it dissolves in precipitation and surface water in contact with the atmosphere. The ^{14}C content of groundwater reflects the time since groundwater was last exposed to the atmospheric ^{14}C source. ^{14}C has a half-life of 5,730 years and can be used to estimate groundwater ages ranging from 1,000 to approximately 30,000 years before present (Clark and Fritz, 1997).

^{14}C data may be reported in units of percent modern (pM) or in units of percent modern carbon (pmc). ^{14}C data for the KLAM study unit in Mathany and Belitz (2014) are given in pM units as reported by the analyzing laboratory. ^{14}C data in pM units have been normalized for carbon isotopic fractionation based on a $\delta^{13}\text{C}$ value of -25 per mil (‰). The un-normalized ^{14}C data, in pmc units, are used in this report. Data were converted from pM to pmc using following equation derived from Plummer and others (2004):

$$\text{pmC} = \frac{\text{pM} \left(1 + \frac{\delta^{13}\text{C}}{1,000} \right)^2}{0.975^2} \quad (\text{A2})$$

where

pM is the ^{14}C value, in units of pM, and
 $\delta^{13}\text{C}$ is the measured ^{13}C composition, in units of per mil.

The ^{14}C age (residence time, presented in years) is calculated based on the decrease in ^{14}C content as a result of radioactive decay since groundwater recharge, relative to an assumed initial ^{14}C content (Clark and Fritz, 1997). Groundwater ages are reported as radiocarbon ages, in years before 1950:

$$\text{radiocarbon age} = \frac{5,568}{\ln(2)} \times \ln\left(\frac{A_0}{A}\right) - \frac{D_{\text{samp}} - 1,950}{1.029} \quad (\text{A3})$$

where

$5,568$ is the Libby half-life for ^{14}C , in years,
 A_0 is the initial ^{14}C content, assumed to be 99 pmc,
 A is the measured ^{14}C content, in pmc, and
 D_{samp} is the date of sample collection, in decimal years.

Calculated radiocarbon ages in this study are referred to as “uncorrected” because they are not adjusted to consider water-rock interactions, such as exchanges with sedimentary sources of carbon (Fontes and Garnier, 1979). Estimated errors in radiocarbon ages are up to ± 20 percent. Groundwater with a ^{14}C content of greater than 88 pmc is reported as having an age of less than 1,000 years; no attempt is made to refine ^{14}C ages less than 1,000 years. Measured values of percent modern carbon can be greater than 100 pmc because the definition of the ^{14}C content in “modern” carbon does not include the excess ^{14}C produced in the atmosphere by above-ground nuclear weapons testing.

Although more sophisticated lumped parameter models used for analyzing age distributions that incorporate mixing are available (for example, Cook and Böhlke, 2000, and Jurgens and others, 2012), use of these alternative models to characterize age mixtures was beyond the scope of this report. Rather, classification into modern (recharged after 1952), mixed, and pre-modern (recharged before 1952) categories was sufficient to provide an appropriate and useful characterization for the purposes of examining groundwater quality. Tritium concentrations, uncorrected ^{14}C age, and sample age classifications are reported in [table A4](#).

48 Status and Understanding of Groundwater Quality in the Klamath Mountains Study Unit, 2010

Table A4. Tritium and carbon-14 data and groundwater age class, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[Groundwater age classes were based on tritium and carbon-14 data. Groundwater with tritium < 1 TU was defined as pre-modern, recharged before 1952. Groundwater with tritium > 1 TU and percent modern carbon (pmc) > 90 was defined as modern, recharged after 1952. Groundwater with tritium > 1 TU and pmc < 90 was defined as mixed, containing components recharged before and after 1952. **GAMA site identification number:** KLAM, Klamath Mountains study unit; KLAM-U, Klamath Mountains study unit understanding site. **Other abbreviations:** ^{14}C , carbon-14; TU, tritium units; <, less than; >, greater than]

USGS-GAMA site identification number	Tritium (TU)	Percent modern carbon (pmc)	Radiocarbon age (years)	Radiocarbon age error (uncorrected, years)	Age class
Klamath Mountains study unit grid sites					
KLAM-01	2.2	90	<1,000	na	Modern
KLAM-02	2.4	104	<1,000	na	Modern
KLAM-03	1.9	85	1,080	30	Mixed
KLAM-04	2.8	103	<1,000	na	Modern
KLAM-05	2.5	98	<1,000	na	Modern
KLAM-06	0.4	39	7,390	30	Pre-modern
KLAM-07	2.0	94	<1,000	na	Modern
KLAM-08	2.1	48	5,590	30	Mixed
KLAM-09	2.3	76	2,090	30	Mixed
KLAM-10	2.3	95	<1,000	na	Modern
KLAM-11	2.6	107	<1,000	na	Modern
KLAM-12	3.5	95	<1,000	na	Modern
KLAM-13	2.9	104	<1,000	na	Modern
KLAM-14	2.8	100	<1,000	na	Modern
KLAM-15	2.4	101	<1,000	na	Modern
KLAM-16	3.3	97	<1,000	na	Modern
KLAM-17	1.9	104	<1,000	na	Modern
KLAM-18	2.3	96	<1,000	na	Modern
KLAM-19	2.7	103	<1,000	na	Modern
KLAM-20	1.4	95	<1,000	na	Modern
KLAM-21	1.8	95	<1,000	na	Modern
KLAM-22	2.0	96	<1,000	na	Modern
KLAM-23	1.4	97	<1,000	na	Modern
KLAM-24	1.5	78	1,760	30	Mixed
KLAM-25	2.8	77	1,920	30	Mixed
KLAM-26	2.4	111	<1,000	na	Modern
KLAM-27	2.4	104	<1,000	na	Modern
KLAM-28	2.8	97	<1,000	na	Modern
KLAM-29	2.3	64	3,340	30	Mixed
KLAM-30	0.3	56	4,440	30	Pre-modern

Table A4. Tritium and carbon-14 data and groundwater age class, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.—Continued

[Groundwater age classes were based on tritium and carbon-14 data. Groundwater with tritium < 1 TU was defined as pre-modern, recharged before 1952. Groundwater with tritium > 1 TU and percent modern carbon (pmc) > 90 was defined as modern, recharged after 1952. Groundwater with tritium > 1 TU and pmc < 90 was defined as mixed, containing components recharged before and after 1952. **GAMA site identification number:** KLAM, Klamath Mountains study unit; KLAM-U, Klamath Mountains study unit understanding site. **Other abbreviations:** ^{14}C , carbon-14; TU, tritium units; <, less than; >, greater than]

USGS–GAMA site identification number	Tritium (TU)	Percent modern carbon (pmc)	Radiocarbon age (years)	Radiocarbon age error (uncorrected, years)	Age class
Klamath Mountains study unit grid sites—Continued					
KLAM-31	2.8	76	2,010	20	Mixed
KLAM-32	3.4	88	<1,000	na	Mixed
KLAM-33	1.6	47	5,850	40	Mixed
KLAM-34	2.9	71	2,460	30	Mixed
KLAM-35	2.5	97	<1,000	na	Modern
KLAM-36	3.0	105	<1,000	na	Modern
KLAM-37	2.5	101	<1,000	na	Modern
KLAM-38	2.6	102	<1,000	na	Modern
Klamath Mountains study unit understanding site					
KLAM-U-01	2.6	88	<1,000	na	Mixed

Appendix B. Grid Cells and Sites

The locations and identification numbers of grid and USGS-understanding sites are shown in [figures B1-B5](#). Additionally, cell boundaries and cell numbers are also shown.

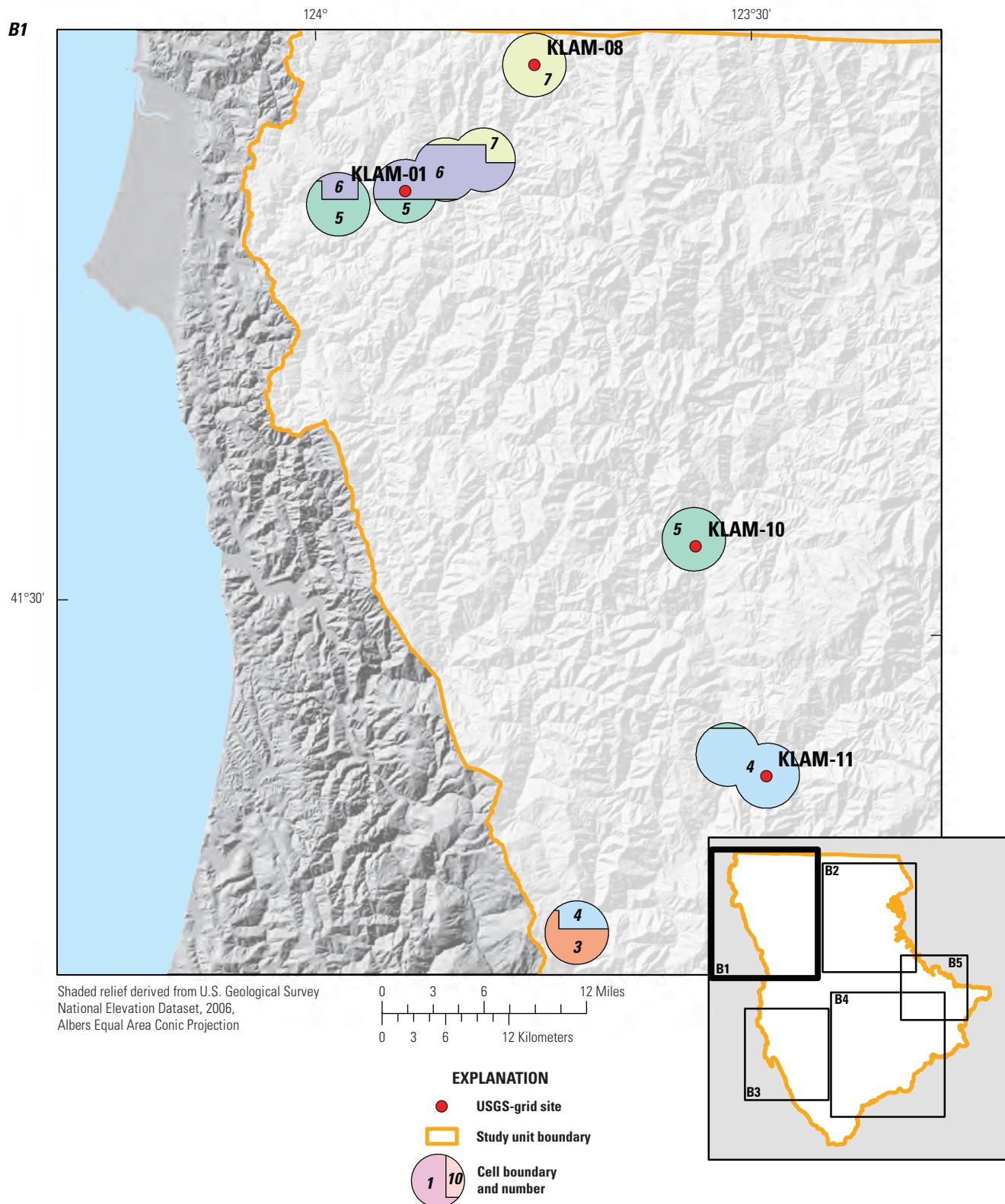


Figure B1. Identifiers and locations of cells, grid sites, and understanding sites sampled by the U.S. Geological Survey from October to December 2010, and grid sites for which data for inorganic constituents from the California Department of Public Health (CDPH) were used, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

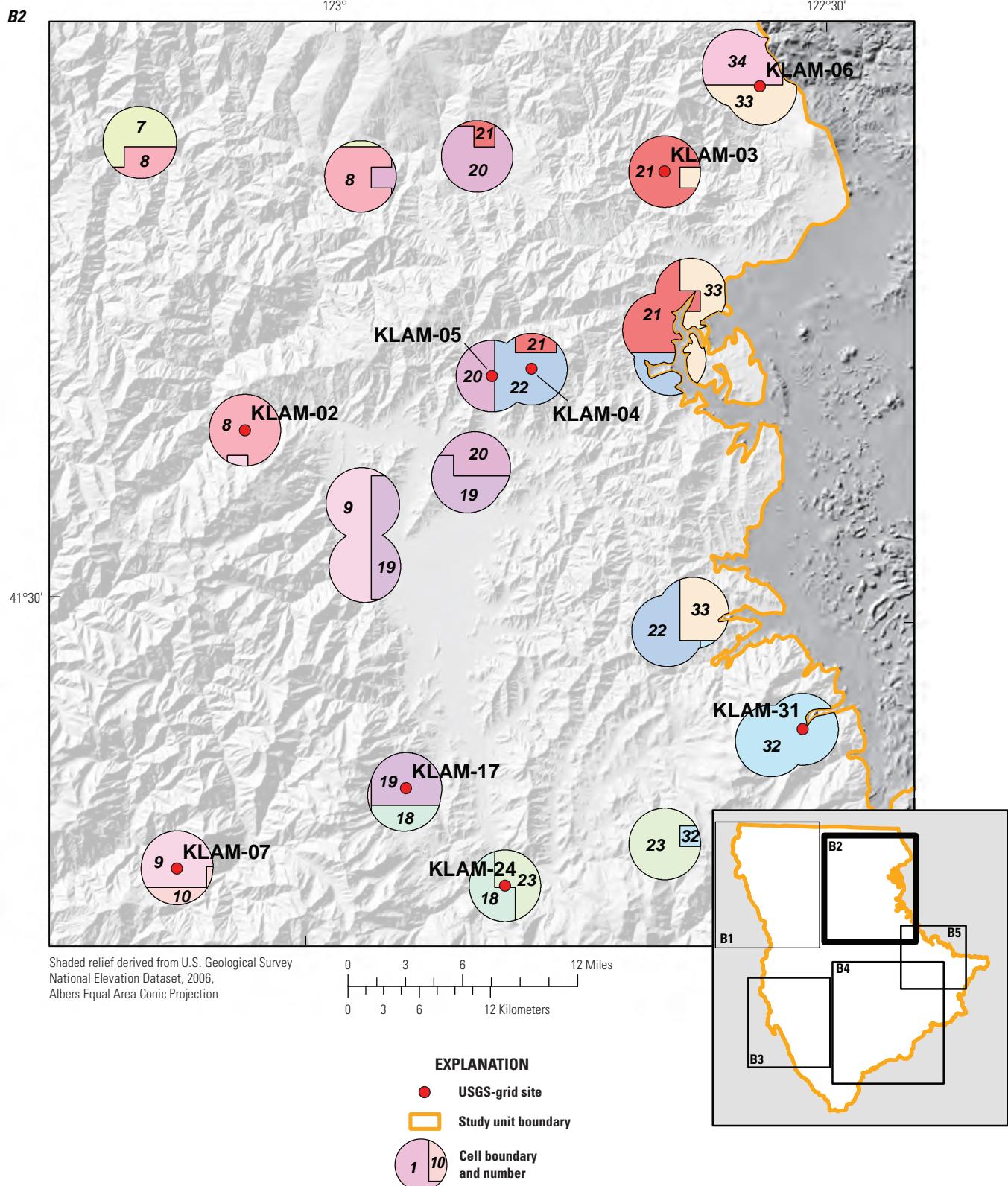


Figure B2. Identifiers and locations of cells, grid sites, and understanding sites sampled by the U.S. Geological Survey from October to December 2010, and grid sites for which data for inorganic constituents from the California Department of Public Health (CDPH) were used, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

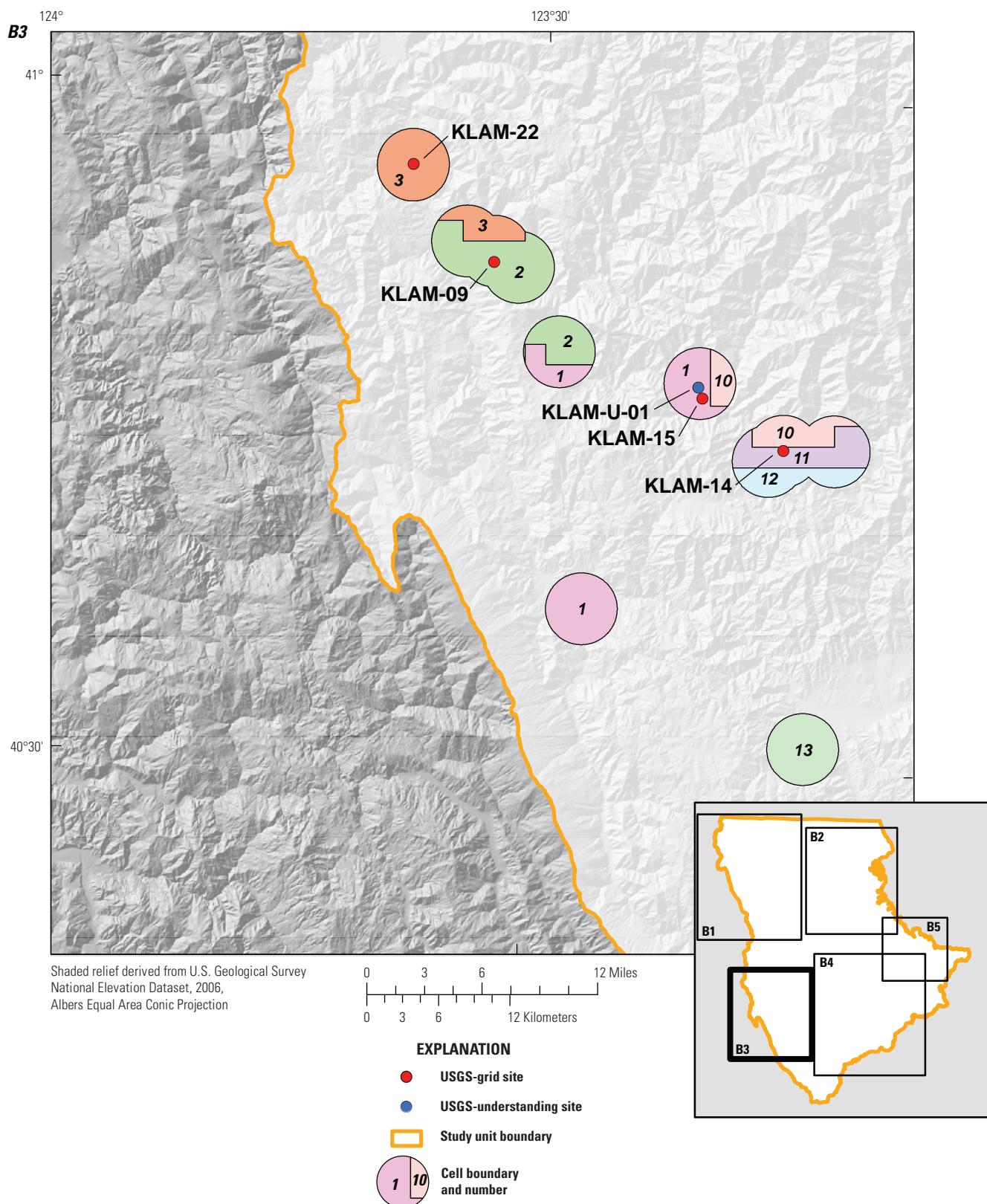


Figure B3. Identifiers and locations of cells, grid sites, and understanding sites sampled by the U.S. Geological Survey from October to December 2010, and grid sites for which data for inorganic constituents from the California Department of Public Health (CDPH) were used, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

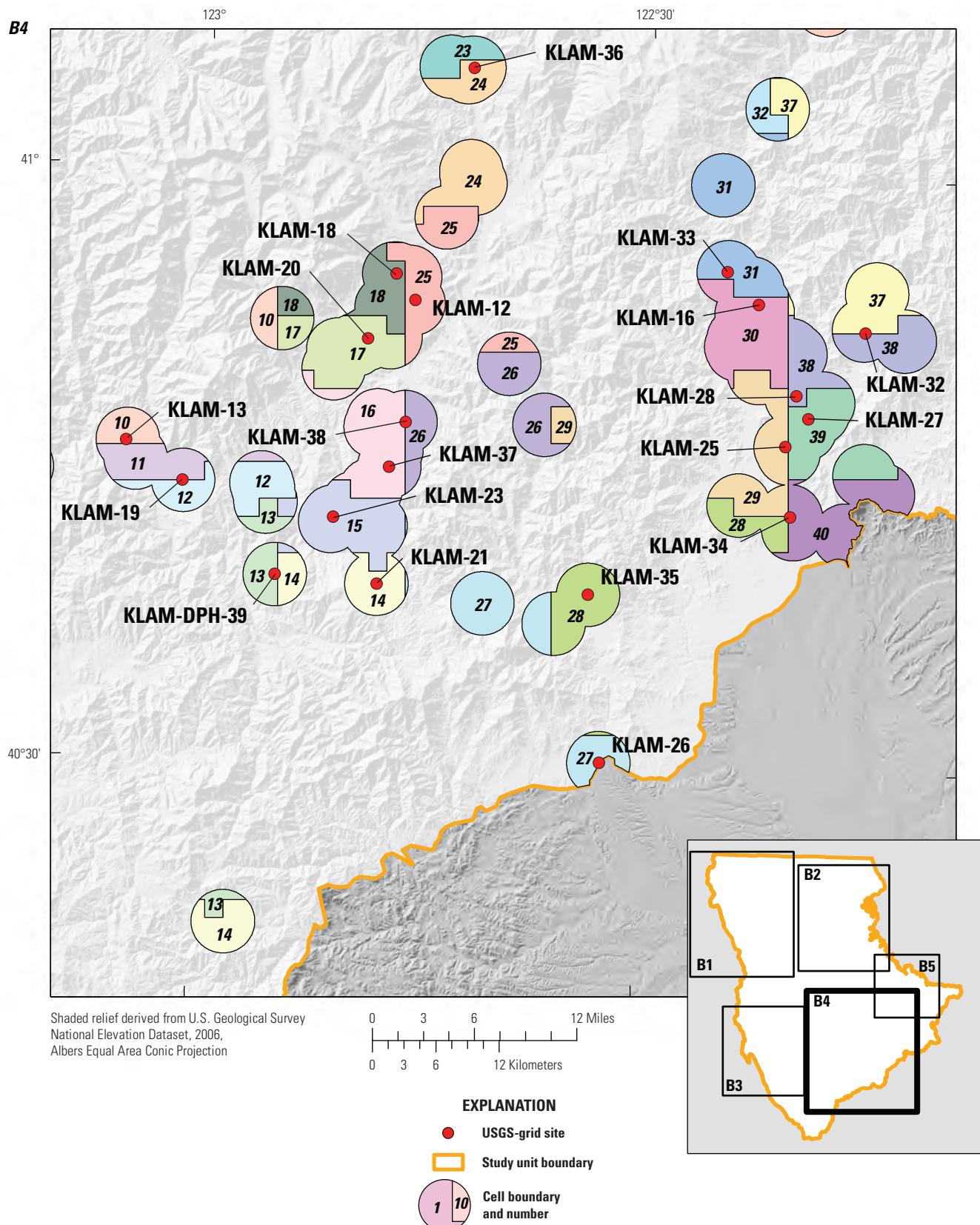


Figure B4. Identifiers and locations of cells, grid sites, and understanding sites sampled by the U.S. Geological Survey from October to December 2010, and grid sites for which data for inorganic constituents from the California Department of Public Health (CDPH) were used, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

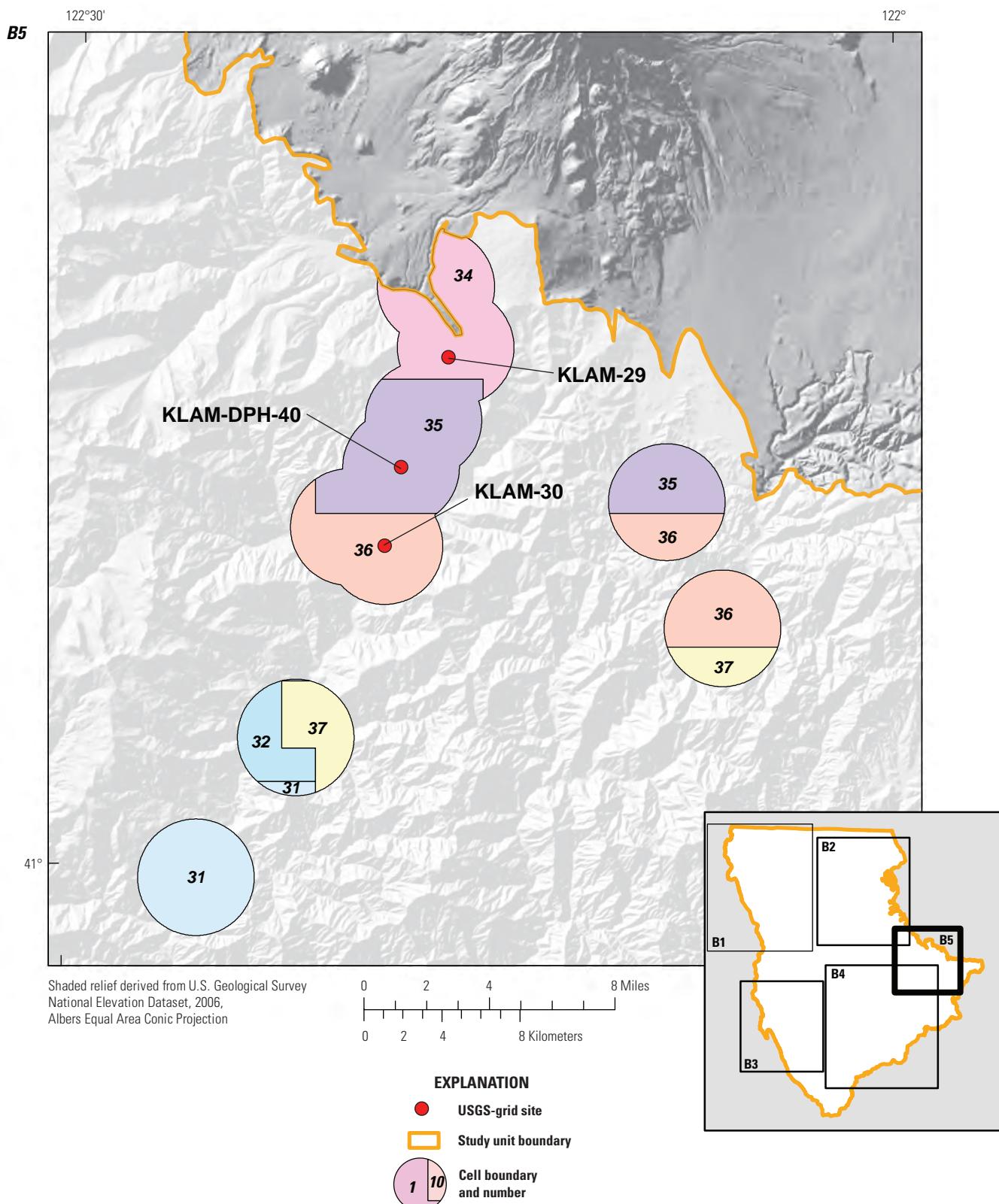


Figure B5. Identifiers and locations of cells, grid sites, and understanding sites sampled by the U.S. Geological Survey from October to December 2010, and grid sites for which data for inorganic constituents from the California Department of Public Health (CDPH) were used, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Appendix C. Calculation of Aquifer-Scale Proportions

The methods used to calculate aquifer-scale proportions using the grid-based and spatially weighted approaches are described in this appendix.

Grid-Based Calculation

In the grid-based approach, one value in each grid cell, a “grid site,” was randomly selected to represent the primary aquifer system (Belitz and others, 2010). For organic constituents, the one value in each grid cell was obtained from the samples analyzed by USGS–GAMA from 38 grid sites. For inorganic constituents, one value in each grid cell was obtained from the samples analyzed by USGS–GAMA from 38 of the grid sites, and data were obtained from the CDPH water-quality database for 2 additional grid cells not sampled by USGS–GAMA (table C1). Confidence intervals for grid-based aquifer proportions were computed using the Jeffreys interval for the binomial distribution (Brown and others, 2001). The Jeffreys interval is only one of a small number of formulas that can be used to calculate a confidence interval for a proportion within a statistical population. Its use here is based on an analysis and comparison of other intervals by Belitz and others (2010); they concluded that the Jeffreys interval was ideal due to its narrower confidence window and better one-sided coverage probability. The grid-based estimate is designed to be spatially unbiased; however, the grid-based approach may not identify constituents that exist at high or moderate concentrations in small proportions of the primary aquifer system.

Spatially Weighted Calculation

The spatially weighted approach used data from the 38 grid sites and 1 understanding site sampled and analyzed by USGS–GAMA in 2010 and data compiled in the CDPH water-quality database for samples collected between December 1, 2007, and December 31, 2010. The most recent analyses were used for each constituent at each site. The spatially weighted approach uses all the sites in each cell to calculate the high, moderate, and low relative-concentrations for the cell.

For each constituent, the high aquifer-scale proportion was calculated by (1) computing the proportion of wells having high relative concentrations in each grid cell and then (2) averaging the grid cell values computed in step 1 (Isaaks and Srivastava, 1989):

$$P_{SU} = \frac{\sum \frac{W_{high}}{W_{total}}}{C} \quad (C1)$$

Table C1. California Department of Public Health (CDPH) data used for the grid-based calculations of aquifer-scale proportions, Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

[CDPH data are from the most recent analysis for each constituent during the period December 1, 2007, through December 31, 2010. In the CDPH database, non-detections are reported as zero (0) for some samples. **Units:** mg/L, milligrams per liter; µg/L, micrograms per liter. **Other abbreviations:** na, not available]

USGS–GAMA site identification number	KLAM-DPH-39	KLAM-DPH-40
Date sampled	12/21/2009	10/20/2009
Cell	13	35
Trace elements (µg/L)		
Antimony	0	na
Arsenic	0	na
Barium	570	na
Beryllium	0	na
Cadmium	0	na
Chromium	0	na
Copper	0	na
Fluoride ¹	0	na
Lead	0	na
Mercury	0	na
Selenium	0	na
Thallium	0	na
Nutrients (mg/L)		
Nitrate, as nitrogen	0	0
Nitrite, as nitrogen	0	na

¹ Concentrations of fluoride are presented in milligrams per liter (mg/L).

where

- P_{SU} is the aquifer-scale proportion for the study unit,
- C is the number of cells with data for the constituent,
- W_{total} is the number of wells in a given cell, and
- W_{high} is the number of wells in a given cell with high relative-concentrations for the constituent.

The same procedure was used to calculate the proportions of moderate and low relative-concentrations. The resulting proportions were spatially unbiased (Isaaks and Srivastava, 1989).

Appendix D. Comparison of CDPH and USGS–GAMA Data

Although the ultimate contribution of CDPH data to the KLAM study unit was limited, the CDPH and USGS–GAMA data were compared to assess the validity of combining data for inorganic constituents from these different sources. Concentrations of inorganic constituents (alkalinity, calcium, magnesium, potassium, sodium, chloride, sulfate, and TDS), which generally are prevalent at concentrations substantially above reporting levels, were compared for each site using data from both sources. Four sites had alkalinity data from the USGS–database and the CDPH water-quality database, two sites had data for calcium, magnesium, and sodium from both databases, and only one site had chloride, sulfate, and TDS data from both databases. Wilcoxon signed-rank tests of paired analyses for these eight constituents indicated no significant differences between USGS–GAMA and CDPH data for these constituents. Differences between the paired datasets were very minor, and most sample pairs plotted very close to a 1:1 line (fig. D1). These plots indicated that the USGS–GAMA and CDPH inorganic data were comparable.

Major-ion data for grid sites with sufficient data (USGS and CDPH data) were plotted on a trilinear diagram (Piper, 1944) along with all CDPH major-ion data to determine whether the groundwater types in grid sites were similar to groundwater types observed in the study unit. Trilinear 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 (fig. D2). Trilinear diagrams often are used to define groundwater type (Hem, 1985). All major-ion data in the CDPH water-quality database with a cation/anion imbalance of less than 10 percent were retrieved

and plotted on the trilinear diagrams for comparison with USGS–grid site data.

The ranges of water types for USGS–grid sites and other sites from the CDPH water-quality database were generally similar (fig. D2). In both datasets, samples from most sites showed no single cation accounting for more than 60 percent of the total cations, and bicarbonate accounted for more than 80 percent of the total anions. Waters in these sites are described as *mixed cation–bicarbonate* type waters. Only a few sites from either dataset appeared dissimilar to the *mixed cation–bicarbonate* type observed in a majority of the sites. Four sites in the USGS–GAMA grid dataset had magnesium concentrations representing more than 60 percent of the cation total, which was not seen in any of the CDPH sites. These four sites could be classified as *magnesium–bicarbonate* type waters. One USGS–GAMA grid site had a *sodium–chloride* type water (sodium and chloride representing greater than 60 percent of the cation and anion totals, respectively), which was not seen in the CDPH dataset. With the exception of the USGS–GAMA grid sites which had *magnesium–bicarbonate* type waters and the USGS–GAMA grid site with the *sodium–chloride* type water, the range and relative abundances of major cations and anions in a majority of USGS–GAMA grid sites were similar to the range of those in CDPH sites. Because relatively few CDPH sites are in the KLAM study unit and CDPH sites don't always have the complete suite of constituents necessary for the determination of water type, the water types identified using the CDPH dataset may not be as complete as in other USGS–GAMA study units which had larger CDPH datasets.

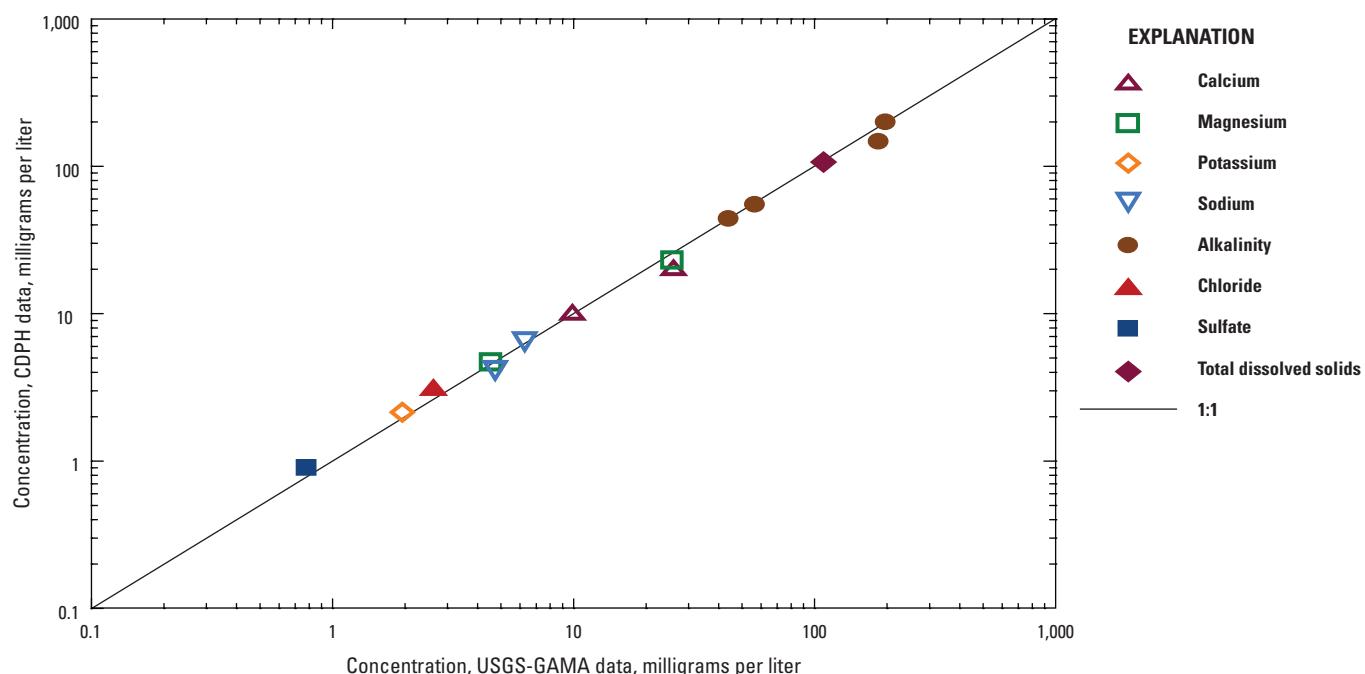


Figure D1. Paired inorganic concentrations from USGS–grid sites and the most recent available analysis in the CDPH water-quality database for the same site in the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

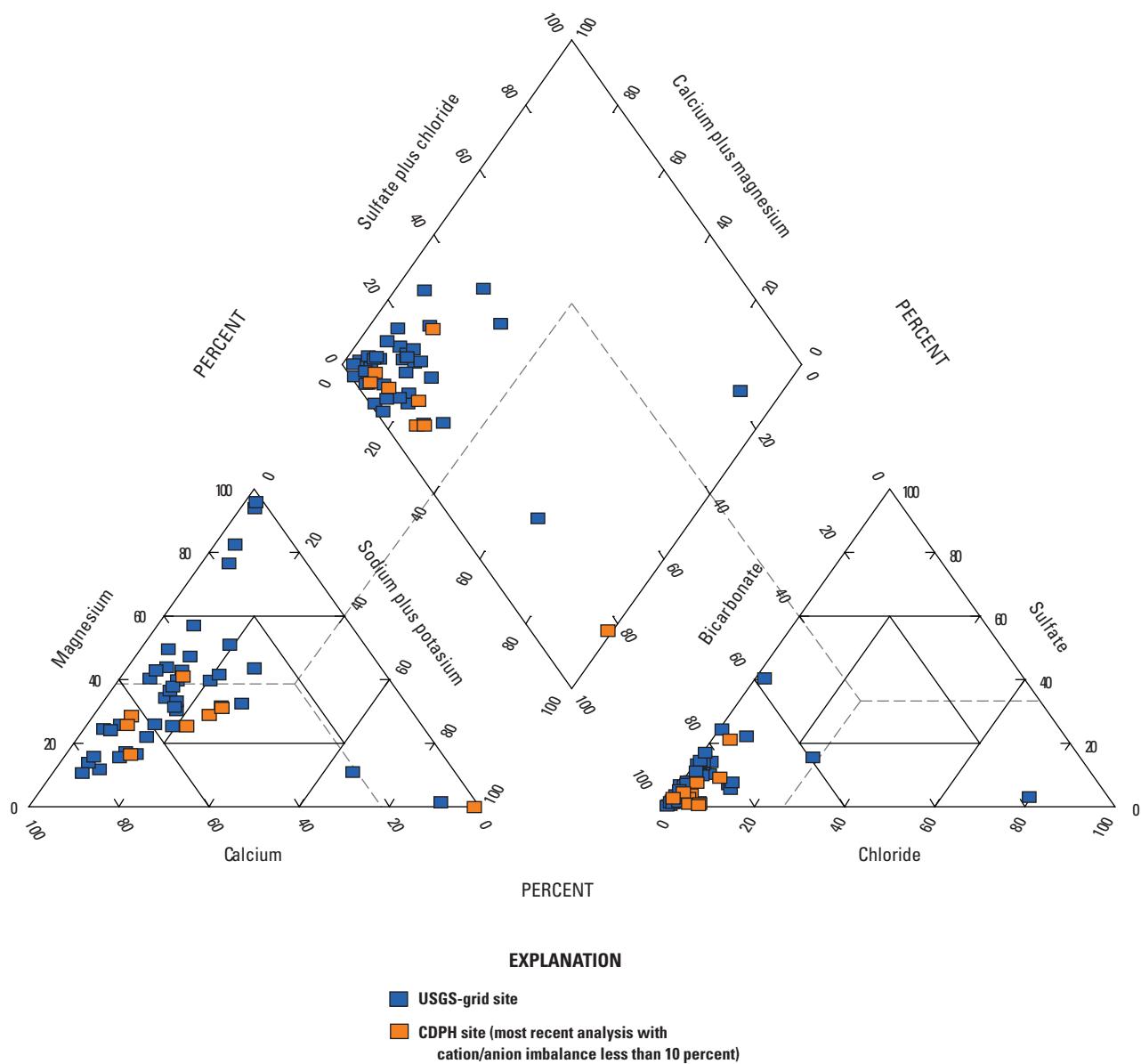


Figure D2. Piper diagram showing USGS-grid sites and all sites in the CDPH water-quality database that had major-ion data with acceptable cation/anion balances during the 3-year interval used in the status assessment for the Klamath Mountains study unit, 2010, California GAMA Priority Basin Project.

Publishing support provided by the U.S. Geological Survey
Science Publishing Network, Sacramento, Tacoma, and Raleigh Publishing Service Centers

For more information concerning the research in this report, contact the

Director, California Water Science Center
U.S. Geological Survey
6000 J Street, Placer Hall
Sacramento, California 95819
<http://ca.water.usgs.gov>

