Status and Understanding of Groundwater Quality in the North San Francisco Bay Groundwater Basins, 2004: California GAMA Priority Basin Project

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CALIFORNIA

GAMA

PROGRAM

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

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

Sampling priority

- Priority basins
- Low-use basins
- Areas that are outside DWR-defined groundwater basins

Study area
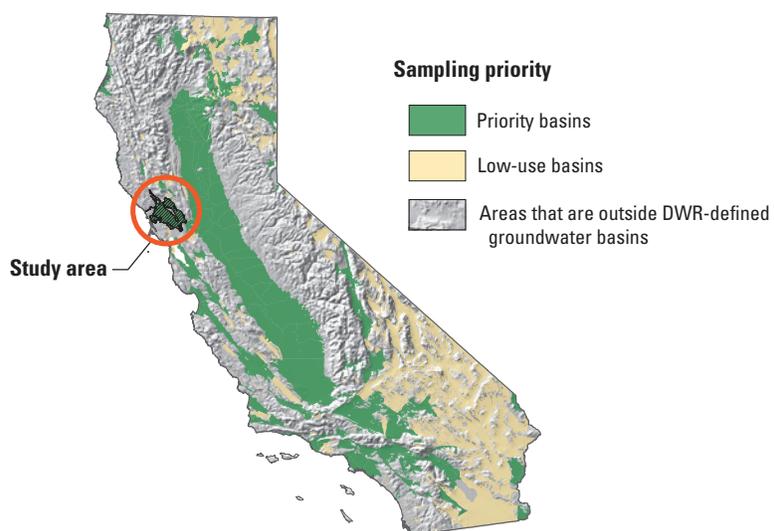
Cover photographs:

Front cover: Well in Sonoma County, California. (Photograph taken by Tyler Johnson, U.S. Geolgoical Survey.)

Back cover: Vineyard in Sonoma, California. (Photograph taken by George Bennett, U.S. Geolgical Survey.)

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

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Abbreviations and Acronyms

AB	Assembly Bill (through the California State Assembly)
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
LRL	laboratory reporting level
LSD	land-surface datum
LT-MDL	long-term method detection 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
MRL	minimum reporting level
na	no data available
nc	no significant correlation
nd	constituent not detected
ns	not sampled
NL-CA	California Department of Public Health notification level
QC	quality control
RSD5-US	U.S. Environmental Protection Agency risk-specific dose at a risk factor of 10^{-5}
SMCL-CA	California Department of Public Health secondary maximum contaminant level
SMCL-US	U.S. Environmental Protection Agency secondary maximum contaminant level
TDS	total dissolved solids
US	United States
VOL	Volcanic Highlands study area of the North San Francisco Bay study unit
VP	Valleys and Plains study area of the North San Francisco Bay study unit
VPFP	Valleys and Plains study area flow path well
WG	Wilson Grove Formation Highlands study area of the North San Francisco Bay study unit
WGFP	Wilson Grove Formation Highlands study area flow path well

Organizations

CDPH	California Department of Public Health (Department of Health Services before July 1, 2007)
CDWR	California Department of Water Resources
LLNL	Lawrence Livermore National Laboratory
NAWQA	National Water Quality Assessment (USGS)
SWRCB	State Water Resources Control Board (California)
USEPA	U.S. Environmental Protection Agency
USGS	U. S. Geological Survey

Selected chemical names

Ammonia-N	ammonia as nitrogen
DBCP	1,2-dibromo-3-chloropropane
DEHP	bis(2-ethylhexyl) phthalate
DO	dissolved oxygen
DOC	dissolved organic carbon
EDB	1,2-dibromomethane (ethylene dibromide)
NDMA	*N*-nitrosodimethylamine
PCE	tetrachloroethene
TCE	trichloroethene
1,2,3-TCP	1,2,3-trichloropropane
TDS	total dissolved solids
THM	trihalomethane
VOC	volatile organic compound

Units of Measure

a	annum (year)
cm^3 STP g^{-1}	cubic centimeters at standard temperature and pressure per gram
δ	delta notation; the ratio of a heavier isotope to the more common lighter isotope of an element, relative to a standard reference material, expressed as per mil
ft	foot (feet)
gpm	gallons per minute
in	inch
kg	kilogram
km	kilometer
km^2	square kilometer
L	liter
L/m	liters per minute
m	meter
Ma	Megaannum (million years)
mg/L	milligrams per liter (parts per million)
mi	mile
mi^2	square mile
mL	milliliter
mm	millimeter
µg/L	micrograms per liter (parts per billion)
µS/cm	microsiemens per centimeter
pCi/L	picocuries per liter
per mil	parts per thousand
pmc	percent modern carbon
ppm	parts per million

TU	tritium unit
yr	year
>	greater than
<	less than
≤	less than or equal to
—	not detected at a concentration above the LRL
%	percent

Notes

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

$$°F=(1.8×°C)+32$$

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88).

Specific conductance is given in microsiemens per centimeter at 25 degrees Celsius (μS/cm at 25 °C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter (μg/L).

Milligrams per liter is equivalent to parts per million (ppm) and micrograms per liter is equivalent to parts per billion (ppb).

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Abstract

Groundwater quality in the approximately 1,000-square-mile (2,590-square-kilometer) North San Francisco Bay study unit was investigated as part of the Priority Basin Project of the Groundwater Ambient Monitoring and Assessment (GAMA) Program. The study unit is located in northern California in Marin, Napa, and Sonoma 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 North San Francisco Bay study was designed to provide a spatially unbiased assessment of untreated groundwater quality in the primary aquifer systems. The assessment is based on water-quality and ancillary data collected by the USGS from 89 wells in 2004 and water-quality data from the California Department of Public Health (CDPH) database. The primary aquifer systems (hereinafter referred to as primary aquifers) were defined by the depth interval of the wells listed in the CDPH database for the North San Francisco Bay study unit. The quality of groundwater in shallower or deeper water-bearing zones may differ from that in the primary aquifers; shallower groundwater may be more vulnerable to surficial contamination.

The first component of this study, the status of the current quality of the groundwater resource, was assessed by using data from samples analyzed for volatile organic compounds (VOC), pesticides, and naturally occurring inorganic constituents, such as major ions and trace elements. This status assessment is intended to characterize the quality of groundwater resources within the primary aquifers of the North San Francisco Bay 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 benchmarks. A relative-concentration greater than (>) 1.0 indicates a concentration above a benchmark, and less than or equal to (≤) 1.0 indicates a concentration equal to or below a benchmark. Relative-concentrations of organic and special interest constituents were classified as "high" (relative-concentration > 1.0), "moderate" (0.1 < relative-concentration ≤ 1.0), or "low" (relative-concentration ≤ 0.1). Inorganic constituent relative-concentrations were classified as "high" (relative-concentration > 1.0), "moderate" (0.5 < relative-concentration ≤ 1.0), or "low" (relative-concentration ≤ 0.5).

Aquifer-scale proportion was used as a metric for evaluating regional-scale groundwater quality. High aquifer-scale proportion is defined as the percentage of the primary aquifers that have a relative-concentration greater than 1.0; proportion is calculated on an areal rather than a volumetric basis. Moderate and low aquifer-scale proportions were defined as the percentage of the primary aquifers that have moderate and low relative-concentrations, respectively. Two statistical approaches—grid-based and spatially-weighted—were used to evaluate aquifer-scale proportion for individual constituents and classes of constituents. Grid-based and spatially-weighted estimates were comparable in the North San Francisco Bay study unit (90-percent confidence intervals).

For inorganic constituents with human-health benchmarks, relative-concentrations were high in 14.0 percent of the primary aquifers, moderate in 35.8 percent, and low in 50.2 percent. The high aquifer-scale proportion of inorganic constituents primarily reflected high aquifer-scale proportions of arsenic (10.0 percent), boron (4.1 percent), and lead (1.6 percent). In contrast, relative-concentrations of organic constituents (one or more) were high in 1.4 percent, moderate in 4.9 percent, and low in 93.7 percent (not detected in 64.8 percent) of the primary aquifers. The high aquifer-scale proportion of organic constituents primarily reflected high aquifer-scale proportions of PCE (1.3 percent), TCE (0.1 percent), and 1,1-dichloroethene (0.1 percent). The inorganic constituents with secondary maximum contaminant levels (SMCL), manganese and iron, had relative-concentrations that were high in 40.8 percent and 24.4 percent of the primary aquifers, respectively. Of the 255 organic and special-interest constituents analyzed for, 26 constituents were detected. Two organic constituents were frequently detected (in 10 percent or more of samples), the trihalomethane chloroform and the herbicide simazine, but both were detected at low relative-concentrations.

The second component of this study, the understanding assessment, identified the natural and human factors that affect groundwater quality by evaluating land use, physical characteristics of the wells, geochemical conditions of the aquifer, and water temperature. Results from these evaluations were used to explain the occurrence and distribution of constituents in the study unit. The understanding assessment indicated that a majority of the wells that contained nitrate also had an urban or agricultural land-use classification, had a modern or mixed age classification, and had depths to their top perforations <100 ft (30 m). Geochemical data are consistent with partial denitrification of nitrate in some reducing groundwaters in the terminal and deeper parts of the flow system.

High and moderate relative-concentrations of arsenic may be attributed to reductive dissolution of manganese or iron oxides, or to desorption or inhibition of arsenic sorption under alkaline conditions. Arsenic concentrations increased with increasing depth and groundwater age in the North San Francisco Bay study unit. High to moderate relative-concentrations of boron were primarily associated with hydrothermal activity or high-salinity waters in the Napa Sonoma lowlands.

Simazine was detected in groundwater classified as modern and mixed age more often than in groundwater classified as pre-modern age, while chloroform was detected most often in groundwater classified as mixed age. Simazine and chloroform also were observed in wells that had surrounding land use classified as agricultural or land use classified as urban, and top of perforation depths less than 100 ft (30 m). Together, the occurrence of chloroform and simazine in shallow wells with modern or mixed groundwater located in urban or agricultural areas suggests that these constituents result from anthropogenic activities during the last 50 years.

Tritium, helium-isotope, and carbon-14 data were used to classify the predominant age of groundwater samples into three categories: modern (water that has entered the aquifer in the last 50 years), pre-modern (water that entered the aquifer more than 50 years to tens of thousands of years ago), and mixed (mixtures of modern- and pre-modern-age waters). Arsenic, iron, and total dissolved solids (TDS) concentrations were significantly greater in groundwater having pre-modern-age classification than modern, suggesting that these constituents accumulate with groundwater residence time.

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 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 (http://www.waterboards.ca.gov/gama). The statewide GAMA Program currently consists of three projects: the GAMA Priority Basin Project, conducted by the USGS (http://ca.water.usgs.gov/gama/); the GAMA Domestic Well Project, conducted by the SWRCB; and GAMA Special Studies, conducted by LLNL. Statewide, the Priority Basin Project focused primarily on the deeper part of the groundwater resource, and the SWRCB Domestic Well Project generally focused on the shallower aquifer systems. Shallow groundwater wells, such as private domestic and environmental monitoring wells, may be particularly at risk because of surficial contamination. As a result, concentrations of contaminants, such as VOCs and nitrate, in shallow wells can be higher than in wells screened in the deeper primary aquifers (Landon and others, 2010).

The SWRCB initiated the GAMA Program in 2000 in response to a legislative mandate (Supplemental Report of the 1999 Budget Act 1999-00 Fiscal Year). The GAMA Priority Basin Project was initiated in response to the Groundwater Quality Monitoring Act of 2001 {Sections 10780-10782.3 of the California Water Code, Assembly Bill 599} to assess and monitor the quality of groundwater in California. The GAMA Priority Basin Project is a comprehensive assessment of statewide groundwater quality designed to help better understand and identify risks to groundwater resources and to increase the availability of information about groundwater quality to the public. For the Priority Basin Project, the USGS, in collaboration with the SWRCB, developed the monitoring plan to assess groundwater basins through direct and other statistically reliable sampling approaches (Belitz and others, 2003; 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 (Kulongoski and Belitz, 2004).

The range of hydrologic, geologic, and climatic conditions that exist in California must be considered in an assessment of groundwater quality. Belitz and others (2003) partitioned the State into ten hydrogeologic provinces, each with distinctive hydrologic, geologic, and climatic characteristics (fig. 1). All of these hydrogeologic provinces contain 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 or volcanic origin. Eighty percent of California's approximately 16,000 public-supply wells are in designated groundwater basins. Groundwater basins and subbasins were prioritized for sampling on the basis of the number of public-supply wells, with secondary consideration given to municipal groundwater use, agricultural pumping, the number of historically leaking underground fuel tanks, and registered pesticide applications (Belitz, and others, 2003). The 116 priority basins and additional areas outside defined groundwater basins, were grouped into 35 study units, which include approximately 95 percent of public-supply wells in California.

Purpose and Scope

The purposes of this report are to provide a (1) *study unit description*: description of the hydrogeologic setting of the North San Francisco Bay study unit (fig. 1), hereinafter referred to as the NSF study unit, (2) *status assessment*: assessment of the status of the current quality of groundwater in the primary aquifers in the NSF study unit, and (3) *understanding assessment*: identification of the natural and human factors affecting groundwater quality and explanation of the relations between water quality and selected potential explanatory factors.

The status assessment includes analyses of water-quality data for 83 wells selected by the USGS for spatial coverage of one well per grid cell across the NSF study unit (hereinafter referred to as USGS grid wells). Most of these wells were public-supply wells, but 2 domestic and 1 irrigation well with similar perforation depth intervals to the USGS grid wells also were sampled. Samples were collected for analysis of anthropogenic constituents, such as volatile organic compounds (VOC) and pesticides, and naturally occurring inorganic constituents such as major ions and trace elements. Water-quality data from the California Department of Public Health (CDPH) database also were used to supplement data

collected by USGS for the GAMA Program. The resulting set of water-quality data from USGS grid wells and selected CDPH wells was considered to be representative of the primary aquifer systems in the NSF study unit; the primary aquifer systems (hereinafter referred to as primary aquifers) are defined by the depth interval of the wells listed in the CDPH database for the North San Francisco Bay study unit. GAMA status assessments are designed to provide a statistically robust characterization of groundwater quality in the primary aquifers at the basin-scale (Belitz and others, 2003). The statistically robust design also allows basins to be compared and results to be synthesized at regional and statewide scales.

To provide context, the water-quality data discussed in this report were compared to State and Federal drinking-water benchmarks, both regulatory and non regulatory, for treated drinking water. The assessments in this report characterize the quality of untreated groundwater resources in the primary aquifers within the study unit, not the treated drinking water delivered to consumers by water purveyors. After withdrawal from the ground, water typically is treated, disinfected, and (or) blended with other waters to maintain acceptable water quality. Benchmarks apply to treated water that is served to the consumer, not to groundwater.

The understanding assessment uses data from six wells sampled by the USGS for the purpose of understanding (hereinafter referred to as USGS understanding wells) in addition to the 83 grid wells sampled for the status assessment, to identify the natural and human factors affecting groundwater quality, and to explain the relations between water quality and selected potential explanatory factors. Potential explanatory factors examined included land use, depth, position of wells along the along the groundwater flow paths, indicators of groundwater age, geochemical conditions, and water temperature.

Water-quality data for samples collected by the USGS for the GAMA Program in the NSF study unit and details of sample collection, analysis, and quality-assurance procedures for the NSF study unit are reported by Kulongoski and others (2006). Utilizing those same data, this report describes methods used in designing the sampling network, identifying CDPH data for use in the status assessment, estimating aquifer-scale proportions of relative-concentrations, analyzing ancillary data sets, classifying groundwater age, and assessing the status and understanding of groundwater quality by statistical and graphical approaches.

Shaded relief derived from U.S. Geological Survey
National Elevation Dataset, 2006.
Albers Equal Area Conic Projection

Provinces from Belitz and others, 2003.

Figure 1.   Location of the North San Francisco Bay study unit, California, and the California hydrogeologic provinces.

Description of Study Unit: North San Francisco Bay

The NSF study unit covers approximately 1,000 square miles (mi^2) (2,590 square kilometers [km^2]) in Napa, Sonoma and Marin Counties, which have a population of nearly 500,000. The NSF study unit lies in the Northern Coast Ranges hydrogeologic province (fig. 1) and contains eight groundwater basins (fig. 2): Alexander Valley, Napa-Sonoma Valley, Santa Rosa Valley, Wilson Grove Formation Highlands, Volcanic Highlands, Lower Russian River Valley, Petaluma Valley, and the Kenwood Valley. For the purpose of this study, these groundwater basins were grouped into three study areas based primarily on geology (fig. 3): the relatively flat-lying alluvium-filled basins were combined into the Valleys and Plains study area, the Wilson Grove Formation Highlands was selected as the second study area, and the Volcanic Highlands was identified as the third study area (fig. 2). As part of the Priority Basin Project, untreated groundwater samples were collected from 96 wells and 1 spring in the NSF study unit from August 31 to November 18, 2004 (Kulongoski and others, 2006).

Valleys and Plains Study Area

The Valleys and Plains (VP) study area extends from Alexander Valley in the north to the San Pablo Bay (San Francisco Bay) in the south, and includes most of the alluvium-filled basins in the NSF study unit (fig. 2). These basins result from a series of northwest-trending structural depressions in the southern part of the Coast Ranges of northern California (Bailey and others, 1964; Fox, 1983). Mountain ranges, 1,000 to more than 4,000 ft (300 to 1,200 m) in altitude, bound the VP study area to the north, northwest, and east, and separate the Napa Valley, Sonoma Valley, and the Santa Rosa Plain. The San Pablo Bay bounds the VP study area to the south, and the North Coast Ranges and Wilson Grove Formation Highlands bound the VP study area to the west.

The VP study area covers nearly 500 mi^2 (1,295 km^2) and includes the Napa, Sonoma, Santa Rosa, Kenwood, Petaluma, and Alexander Valleys, as well as the Napa-Sonoma lowlands to the south near San Pablo Bay (fig. 2). These valleys consist of a relatively thin cover of Quaternary alluvium overlying a thick section of Neogene volcanics and sedimentary rocks, Cretaceous sedimentary rocks, Franciscan Complex sedimentary and metamorphic rocks, and Jurassic serpentinite (Bailey and others, 1964; Fox, 1983).

In these valleys, the main water bearing unit is the alluvium and Neogene sedimentary rocks that underlie and form the valley floors (fig. 3), the thickness of which increases progressively from north to south and from the periphery of the valleys towards the rivers. In most valleys, the thickness of the alluvium ranges from less than 10 ft (3 m)

to more than 300 ft (90 m). Except for small localized areas of semiconfinement, water in the alluvium is unconfined and moves under a natural hydraulic gradient that conforms in a general way to the surface topography (Faye, 1973; Farrar and others, 2006; Metzger and others, 2006). Groundwater recharge to the alluvial aquifers occurs by stream-channel infiltration beneath the major rivers and their tributaries and by direct infiltration of precipitation on alluvial fans.

Volcanic Highlands Study Area

The Volcanic Highlands (VOL) study area (fig. 2) consists of hilly to mountainous areas of Neogene volcanic deposits, which include lava flows, agglomerates, tuffs, and intercalated sediments of volcanic debris (fig. 3). These deposits, identified as the Sonoma Volcanics, were subdivided in ascending order of members into the Mark West Andesite, the Sonoma tuff, and the St. Helena Rhyolite (Osmont, 1905). These rocks have been folded, faulted, and eroded so that they now form a series of elongate ridges separating narrow alluvial valleys.

The VOL study area is approximately 390 mi^2 (1,010 km^2) of discontinuous highlands east of the Napa Valley to the Santa Rosa Valley (fig. 2). For the purpose of this study, the VOL study area was defined as the composite of the 1.16-mi^2 (3-km^2) areas surrounding identified public-supply wells, which were completed in the volcanic formations (fig. 3, 4).

Pumice tuff, tuff breccias, and redeposited stratified tuff form the most important water bearing units in the Sonoma Volcanics, and are interspersed with the andesitic and basaltic lavas that are mostly impervious and act as confining beds, which restrict the movement of groundwater (Cardwell, 1958). The thickness of the Sonoma Volcanics is not uniform. On the northeast side of Kenwood Valley, tuff and tuff-breccia deposits are up to 1,200 ft (360 m) thick and basalt flows are over 800 ft (240 m) thick.

Wilson Grove Formation Highlands Study Area

The Wilson Grove Formation Highlands (WG) study area is characterized by gently rolling hills, broad valleys, and rounded hilltops between the Santa Rosa Valley and the Pacific Ocean (fig. 2). The WG study area corresponds to the Wilson Grove Formation Highlands groundwater basin (California department of Water Resources, 2003) in Marin and Sonoma Counties of California. The WG study area covers approximately 140 mi^2 (360 km^2), and is bound to the north and south by rugged coastal mountains of up to 1,000 ft (300 m) in altitude, to the west by the Pacific Ocean, and to the east by the Santa Rosa Valley. The Wilson Grove Formation Highlands is named for the main geological unit underlying the area, the Wilson Grove Formation (Fox, 1983),
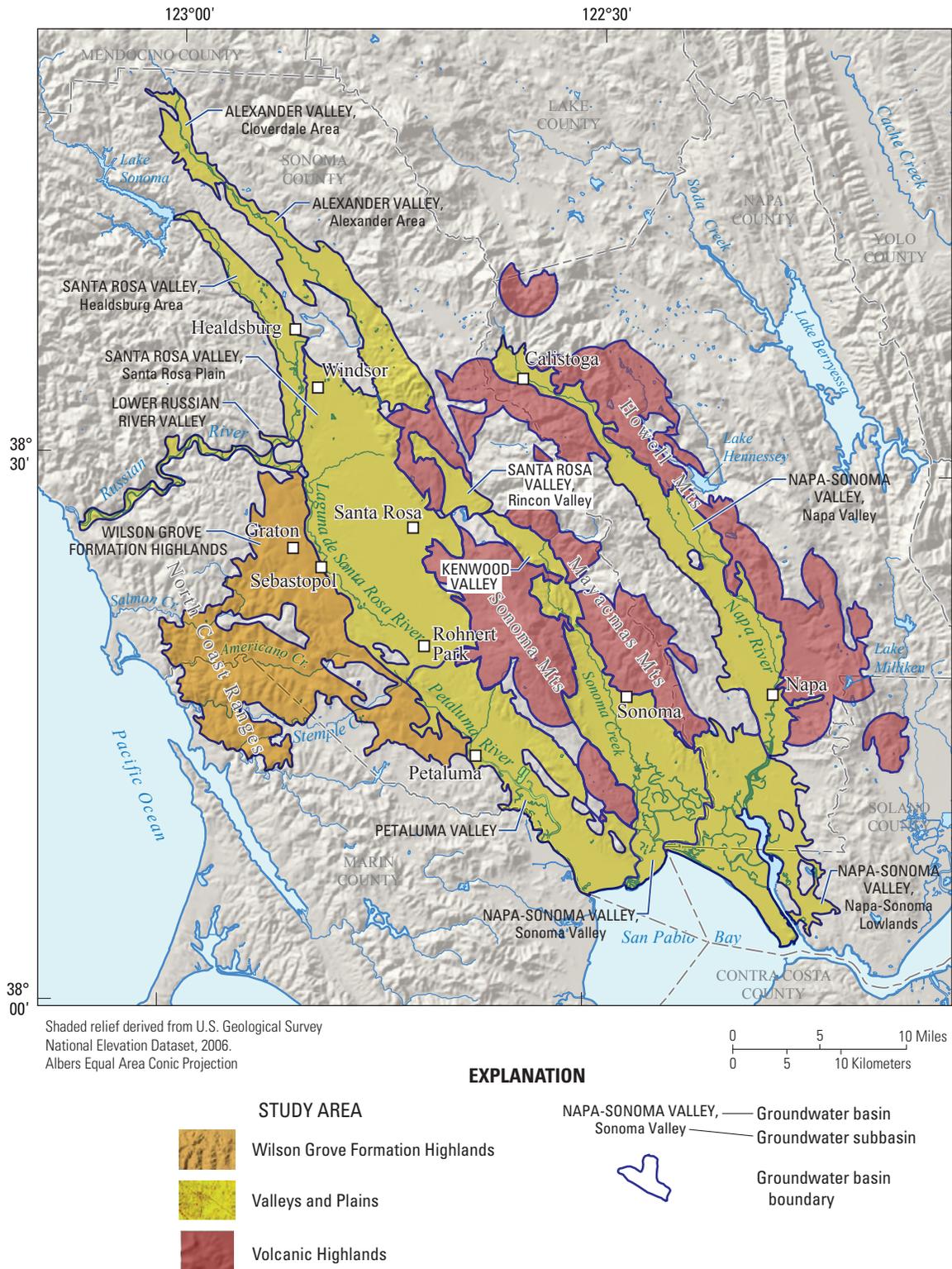
Figure 2.   Geographic features and study areas of the North San Francisco Bay study unit, California.
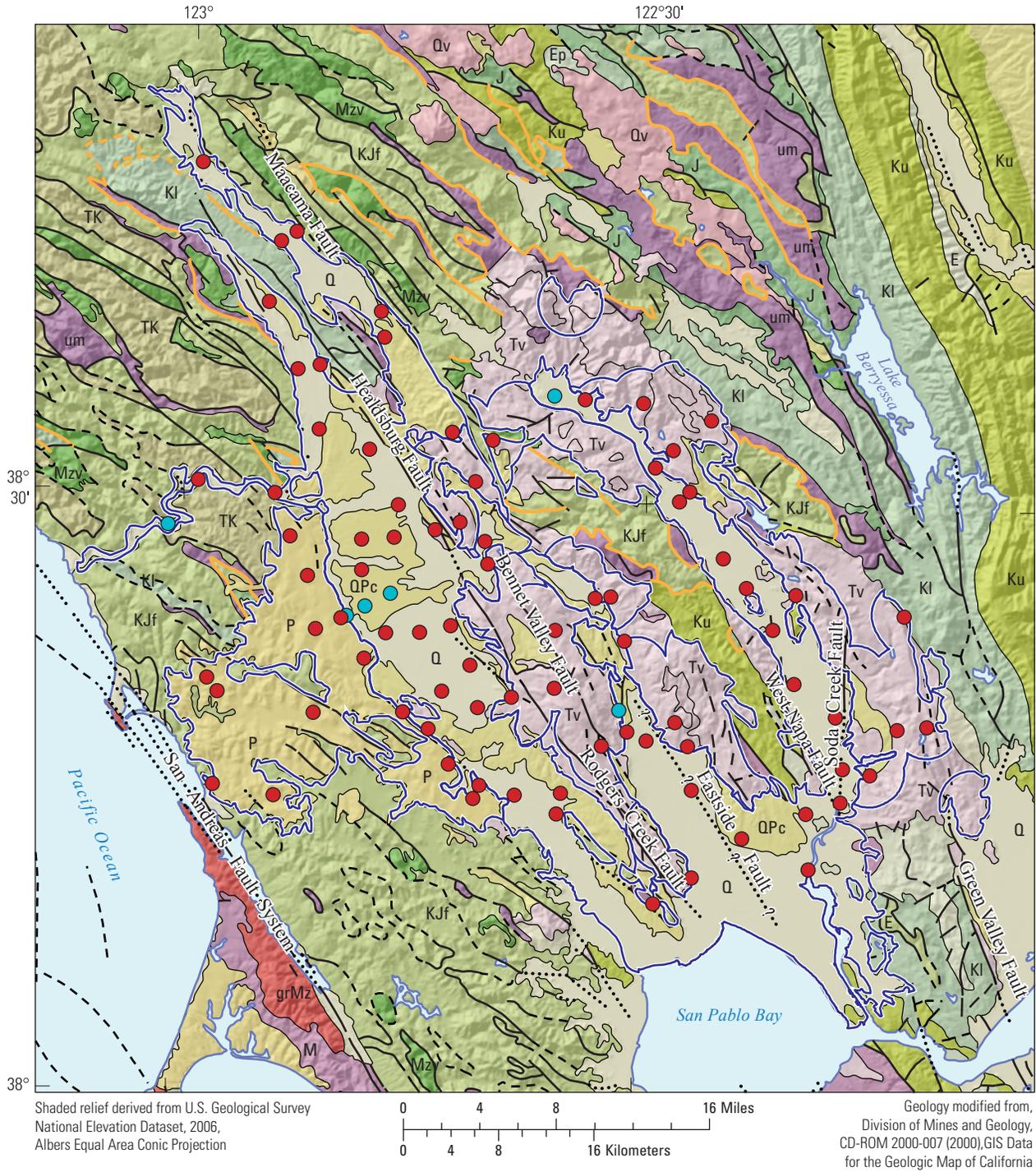
Figure 3.   Geologic map of the North San Francisco Bay study unit, California.

EXPLANATION

GEOLOGIC UNIT

Cenozoic

Sedimentary rocks

Quaternary

| Q | Recent alluvium, landslide, and sand dune deposits |

| QPc | Plio-Pleistocene and Pliocene nonmarine |

Pliocene

| P | Pliocene marine |

Miocene

| M | Miocene marine |

Eocene

| E | Eocene marine |

Paleocene

| Ep | Paleocene marine |

Volcanic rocks

Quaternary

| Qv | Volcanic flow rocks |

Tertiary

| Tv | Volcanic flow and pyroclastic rocks |

Mesozoic

Sedimentary and metasedimentary rocks

Tertiary-Cretaceous

| TK | Coastal belt rocks |

Cretaceous

| Ku | Upper Cretaceous marine |

| Kl | Lower Cretaceous marine |

| KJf | Franciscan Complex |

Jurassic

| J | Jurassic marine |

Plutonic, metavolcanic, and mixed rocks

| grMz | Granitic rocks |

| um | Ultramafic rocks |

| Mzv | Volcanic and metavolcanic |

| | Water |

—— Study unit and study area boundary

⌐⌐ ···? Fault—Dashed where approximately located, dotted where concealed, queried where uncertain

⌐ Thrust fault—Dashed where approximately located

—— Water boundary

● USGS grid well

○ USGS understanding well

Figure 3.   Continued.

and was previously described as the Merced Formation (Johnson, 1934). The marine deposits of the Wilson Grove Formation contain weakly cemented, fine grained-fossiliferous sandstones with lenses consisting of conglomerate and sandy shale, and are underlain by Franciscan Complex basement rock (fig. 3).

The Wilson Grove Formation is the main water-bearing unit because of its extent, high porosity, and moderate transmissivity (Cardwell, 1958). Most of the Wilson Grove Formation marine deposits are derived from eroded Franciscan Complex rocks and range from 300 to 2,000 ft (100 to 610 m) in total thickness.

Hydrothermal Study

The hydrothermal study characterized 7 thermal wells and 1 thermal spring. Five thermal wells were sampled in the northern Napa Valley, two thermal wells were sampled in Sonoma Valley, and one thermal spring (HOT-08) was sampled in hills composed of Cretaceous and Jurassic Franciscan Complex rocks west of Napa Valley (fig. B1*A*). The water from the wells and the spring is mainly used for recreation (mineral baths), not for drinking-water supply; therefore, these wells are not included in the status assessment of the data as they do not represent drinking-water supply. Thermal waters were considered as potential explanatory factors in the understanding assessment of water quality in the NSF study unit.

Hydrogeologic Setting of the North San Francisco Bay Study Unit

The climate in the North San Francisco Bay study unit is characterized by warm, dry summers and cool, moist winters. The National Climate Data Center station in Sonoma reports an average annual temperature of 59 ºF (15 ºC), and an average annual precipitation of 30 inches (0.76 m), while average annual precipitation to the west at Graton, California is 42 inches (1.1 m), where the average annual temperature is 57 ºF (13.9 ºC). Rain occurs primarily during the winter and early spring. However, the distribution of precipitation across the study area depends on the topography and the prevailing winds; precipitation increases concomitant with an increase in altitude.

The study areas are drained by several rivers and their principal tributaries. The Napa-Sonoma and Kenwood Valleys are drained by the Napa River and Sonoma Creek, respectively; the Petaluma Valley by the Petaluma River; the Santa Rosa, Alexander, and Lower Russian River Valleys by the Laguna de Santa Rosa and Russian Rivers; and the Wilson Grove Formation Highlands by the Americano, Stemple, and Salmon Creeks (fig. 2). The Volcanic Highlands are drained by the tributaries of the Napa, Sonoma, and Petaluma Rivers.

In the study areas, groundwater flow generally follows the topography of the basins, from high elevations towards the drainages, and down valleys towards the San Pablo Bay or the Pacific Ocean (fig. 5). Sources of groundwater recharge include percolation of precipitation, and river and stream runoff.
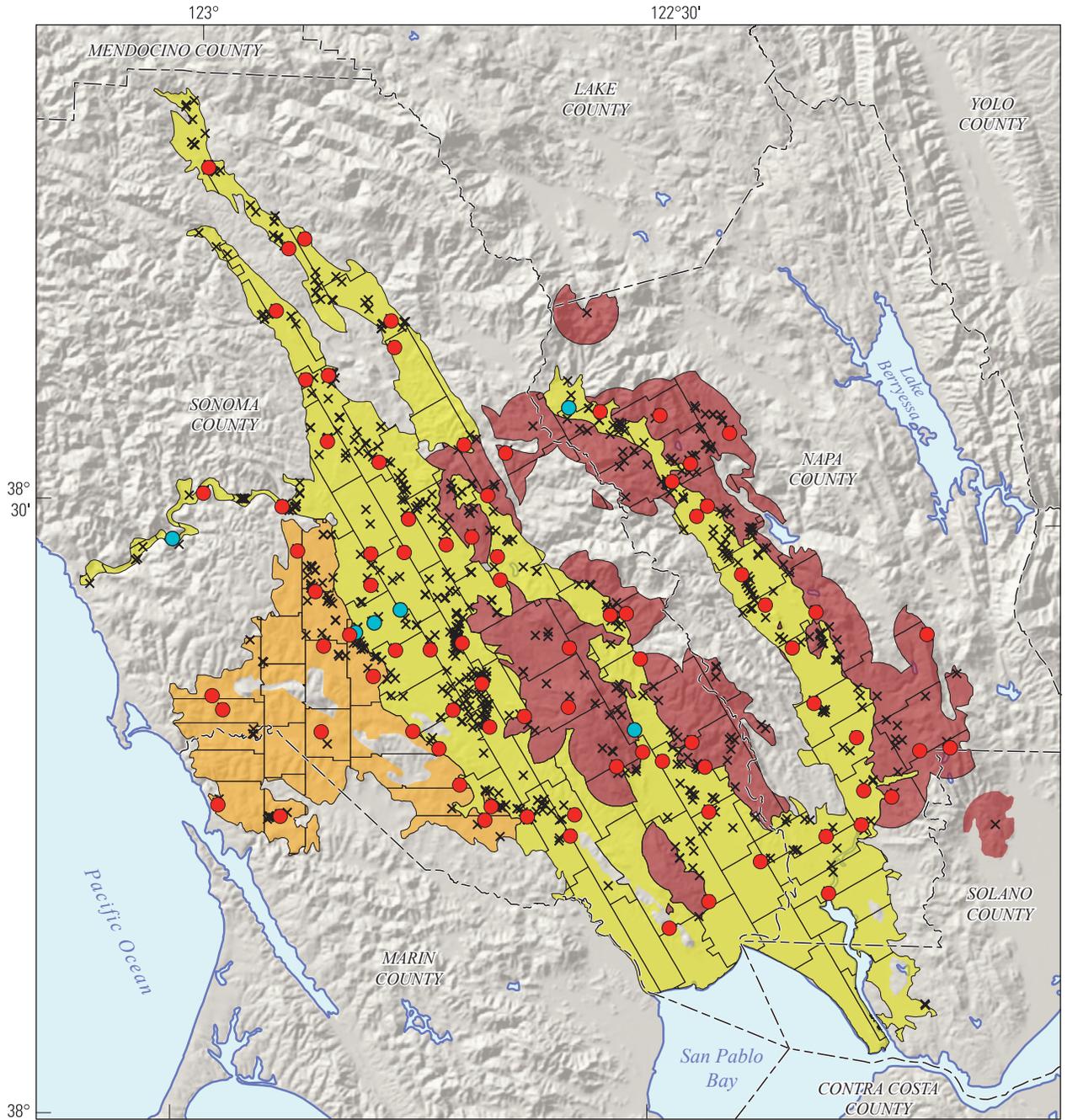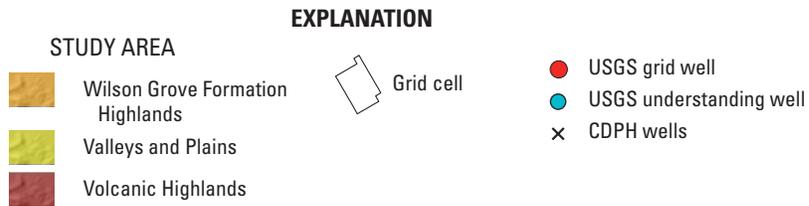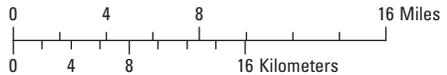
Figure 4. Locations of grid cells, California Department of Public Health (CDPH) wells, and the U.S. Geological Survey (USGS) grid and understanding wells sampled during August to December 2004 for the North San Francisco Bay study unit, California.
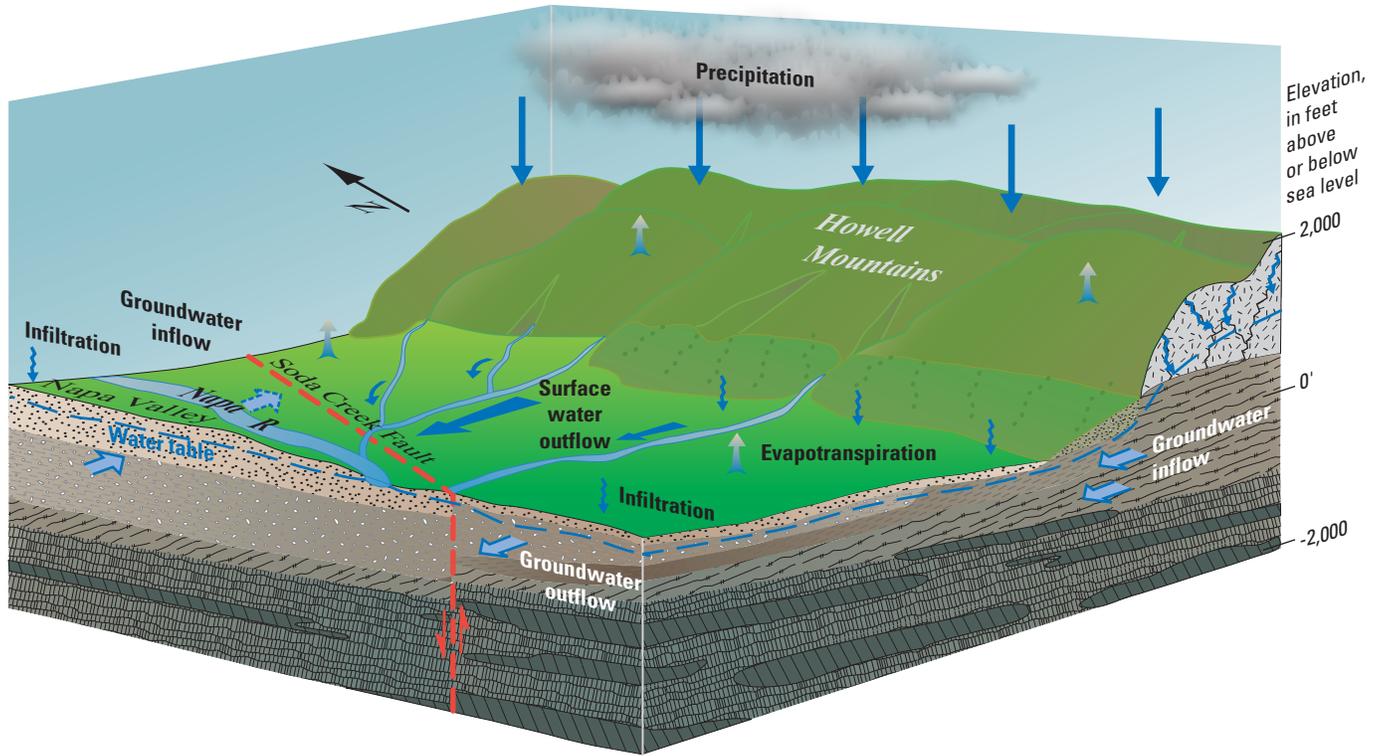
EXPLANATION
(Arrows show components of hydrologic budget)

⦚ Infiltration

⬆ Evapotranspiration

⬇ Precipitation

⬅ Direction of groundwater
movement

Figure 5. A conceptual model of the aquifer system in the Valleys and Plains valleys of the North San Francisco Bay study unit, California.

Water resources for public drinking-water supply include surface water from Lake Hennessey, Lake Milliken, Lake Mendocino, Lake Sonoma, the Sacramento River Delta, and local public-supply wells (fig. 2). The primary aquifers targeted by this study included groundwater bearing zones in which public-supply wells are completed. These wells vary in depth from 60 to 1,040 ft (18 to 316 m), depending on their location and depth of the alluvium. In the Napa and Sonoma Valleys, groundwater movement is generally from north to south towards the San Pablo Bay (fig. 2). In the Alexander Valley and the Healdsburg area of the Santa Rosa Valley, groundwater movement is generally from north to south towards the Lower Russian River Valley, at which point the flow becomes from east to west towards the Pacific Ocean.

Land use in the study unit is 55 percent natural, 31 percent agricultural, and 14 percent urban according to classifications from USGS National Land Cover Data (Vogelmann and others, 2001; Price and others, 2003) (figs. 6A, 7; Appendix E: Land-Use Classification). Most of the agricultural and urban land is in the Valleys and Plains study area, whereas most of the natural landscapes are in the Volcanic Highlands and Wilson Grove Formation Highlands study areas (figs. 6, 7). However, vineyards extend up into the Volcanic Highlands, and irrigation and pesticide application do occur in these areas. Natural lands are mostly grassland and forests, while the primary use of agricultural land is for pasture (cattle, sheep, and poultry), hay, vineyards, flowers, nurseries, and orchards (California Department of Water
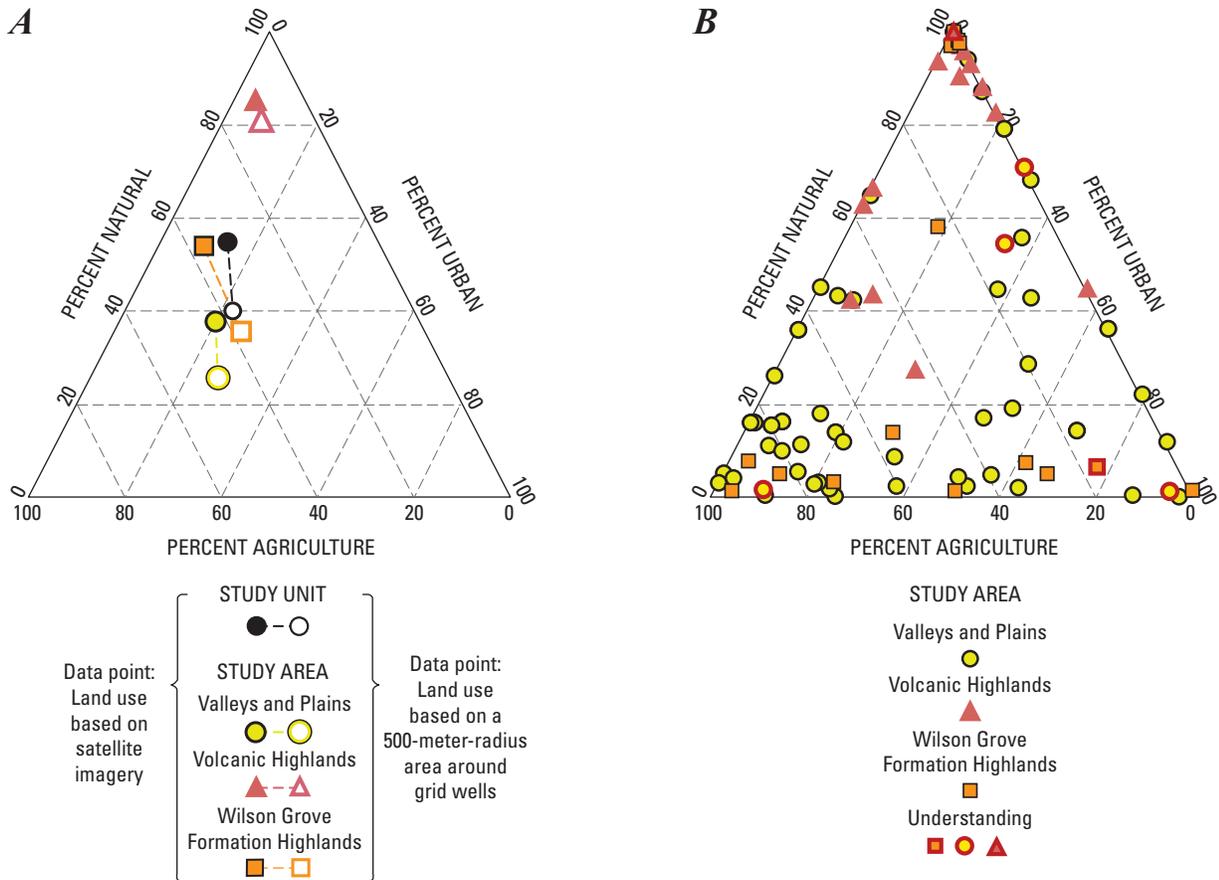
Figure 6. Percent urban, agricultural, and natural land use in *A*. the study unit and study areas, and *B*. the 500-meter-radius area surrounding wells in the North San Francisco Bay study unit, California.

Resources, 2001a,b). The largest urban areas are the cities of Santa Rosa, Petaluma, Rohnert Park, Healdsburg, Windsor, Napa, and Sonoma. Figure 6*A* shows the percentage of land use for selected categories that was calculated for the NSF study unit, each study area, and for the cumulative area within a 1,640-ft (500-m) radius around each well. Figure 6*B* shows the land-use-category percentages for the area around individual wells in the NSF study unit. Figure 7 shows the land-use classification map that is based on satellite imagery (see Appendix E: Land-Use Classification for details), and the NSF USGS grid wells.

Regional Geologic Setting

The Northern Coast Ranges of California are characterized by a strong northwest trending physiography (figs. 1, 3). The core of the Coast Ranges consists of three major rock groups: the Franciscan Complex, the Great Valley Sequence, and the Coast Range Ophiolite which together make up the basement rocks. These rocks span an age range from Jurassic to Eocene and were originally deposited in marine environments west of the continent. Subsequently

these sediments were transported toward and accreted against the North American continent. Cenozoic folding and faulting produced the topography of mountain ranges and intervening valleys present today. Basement rocks are blanketed by Cenozoic sedimentary and volcanic rocks along the Pacific coast, around San Francisco Bay, and in some of the inland valleys. The area now occupied by the Santa Rosa Plain was the continental margin during the later part of the Cenozoic and a site of sedimentary depositional transition between marine, estuarine, and terrestrial environments (Fox, 1983; Powell and others, 2004; McLaughlin and others, 2005). Similarly, the mouths of Petaluma, Sonoma, and Napa Valley were connected with the brackish waters of the San Francisco Bay and accumulated large thicknesses of bay mud associated with Pleistocene sea-level changes. All the larger inland valleys are underlain now by thick layers of sedimentary and volcanic rocks (Farrar and others, 2006). The volcanic rocks in the Clear Lake volcanic field (approximately 30 mi (48 km) north of Calistoga) and the Sonoma Volcanics also cover large parts of the Sonoma, Howell, and Mayacmas Mountains (figs. 2, 3). Most of the valleys and ridges have formed in response to northwest trending, right-lateral, strike-slip
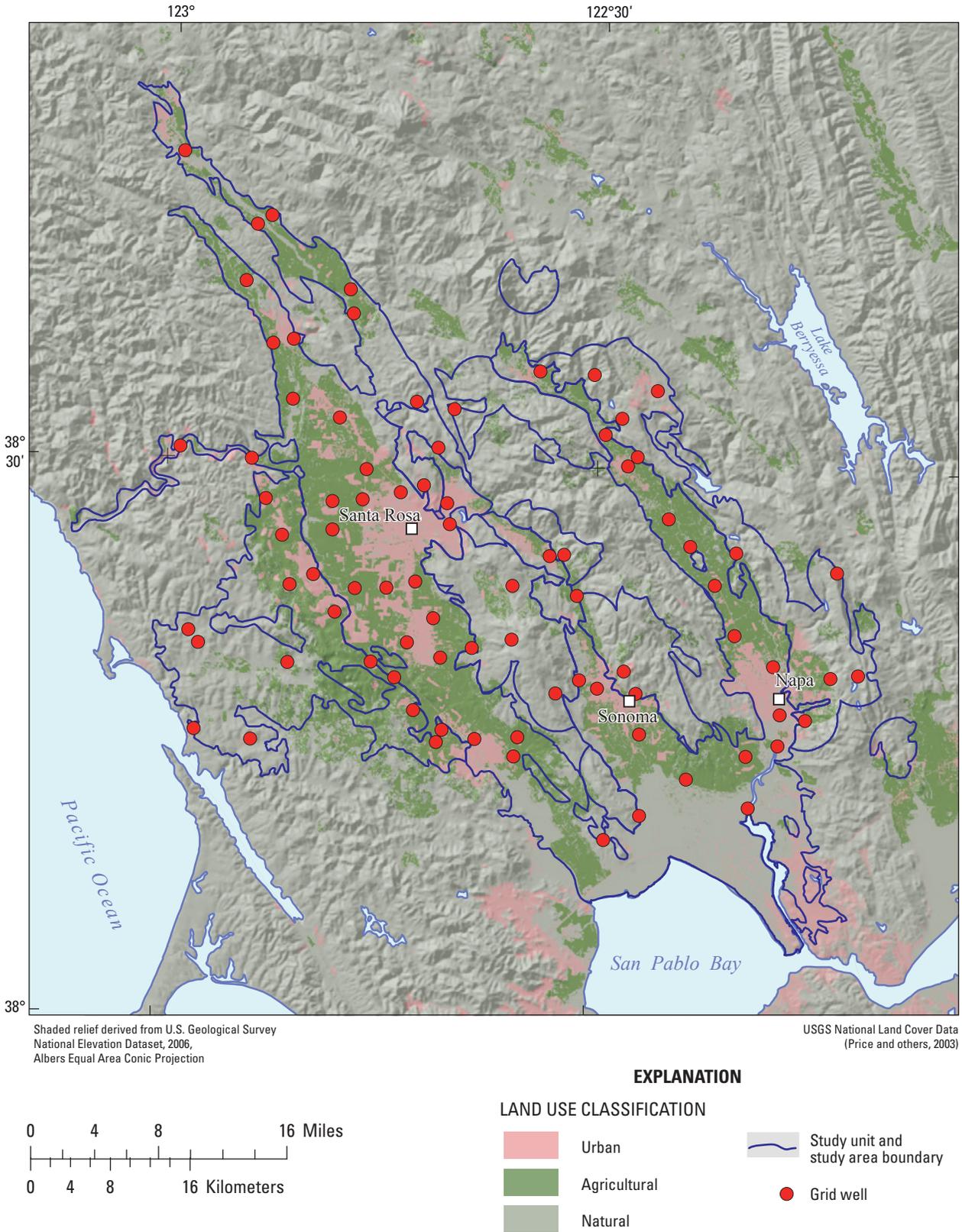
Figure 7.   Land use in the North San Francisco Bay study unit, California, and the locations of U.S. Geological Survey grid wells.

faulting and reverse faulting on west-dipping, high-angle faults that characterize a 50-mi (80-km) wide strip of coastal California north of the San Francisco Bay.

The principal mountain ranges within the study area, from the Pacific Ocean coastline to east of Napa Valley, approximately 40 mi (66 km), are the North Coast Ranges, the Sonoma Mountains, the Mayacmas Mountains, and the Howell Mountains (fig. 2). The altitude of the highlands is generally less than 2,000 ft (600 m); the altitude of most ridge lines is between 500 and 1,500 ft (150 to 460 m). The Sonoma Mountains are higher relief than the North Coast Range and rise steeply to altitudes of 1,000 to 2,000 ft (300 to 600 m) east of Santa Rosa. The Mayacmas Mountains are less steep and generally range between 500 and 1,000 ft (150 to 300 m) in altitude. The North Coast Range is made up of low rounded hills that reach altitudes of 600 to 1,200 ft (180 to 370 m). Between the mountain ranges lie three prominent sub-parallel, northwest-trending valleys: Santa Rosa Valley, Sonoma Valley, and Napa Valley.

Each of the valleys has substantial urban population centers, surrounded by large tracts of agricultural land and sparse rural populations (fig. 7). The valleys form separate watersheds, which have separate underlying groundwater flow systems. Thermal springs and wells are in parts of each of the three valleys. The thermal waters that issue from springs or are pumped from wells in each valley are derived from separate hydrothermal systems that have similar hydrogeologic settings.

Quaternary Sedimentary Deposits

Quaternary sedimentary deposits recognized and mapped within the study area include alluvial deposits, near shore marine and estuarine sediments, colluvium, and landslide deposits. The depositional environment, source materials, and age of deposits determine the composition, sorting, bedding, degree of cementation, and other characteristics of the deposits relevant to their hydraulic properties.

The alluvial sediments of Quaternary age have been mapped as distinct deposits on the basis of degree of consolidation, cementation, clast size and sorting, and geomorphic expression. Alluvial fan deposits cover more area than the other alluvial sediments in the study area. The fan, river terrace, and stream-channel deposits generally consist of heterogeneous mixtures of poorly to well sorted sand, silt, clay, gravel, cobbles, and boulders in thin to massive interfingering beds of limited lateral extent (tens to hundreds of feet), often having lenticular form. Most of the deposits near valley axes lie flat, but near valley margins, beds in wedge-shaped fan deposits dip toward the valley. Large volumes of alluvial sediment are present in all the main valleys in the study area. The alluvial sediment may be divided into older (Pleistocene) and younger (Holocene) deposits, which, to some degree, is consistent with the amount

of cementation and consolidation of the sediments (Cardwell, 1958; Kunkel and Upson, 1960). The maximum thickness of the older alluvium is about 500 ft (152 m), and the younger alluvium is generally less than 150 ft (50 m) thick.

The generally porous nature of the alluvial deposits and close proximity to modern streams allows for rapid recharge of precipitation to the groundwater system and for exchanges between groundwater and surface water in and near stream channels. Groundwater is unconfined in most places, but semiconfined conditions exist beneath thick layers of clay or silt in some areas. Early development of groundwater resources in the study area focused on the drilling of shallow wells in alluvial deposits, taking advantage of shallow depths to water, high porosities, and moderate hydraulic conductivities. However, because of the broad range of lithologic characteristics and correlative hydraulic properties of the alluvial deposits and their saturated thickness, well yields historically have ranged from dry to over 1,000 gpm (3,785 L/m). In some areas, as groundwater extraction increased, water levels declined and the alluvial deposits no longer could supply sufficient water to wells, especially for agriculture or municipal supply. The alluvial deposits are still the primary aquifers along major streams and in much of Napa Valley. Large collector wells completed in gravels along the Russian River provide thousands of gallons of water per minute for municipal supply, and smaller agricultural wells obtain yields of 100 to >1,000 gpm (378 to 3,785 L/m). In the Napa Valley, well yields from alluvial deposits generally are below 50 gpm (189 L/m), but can be as high as 400 gpm (1,514 L/m); specific yields are between 8 and 17 percent (California Department of Water Resources, 2003).

Large areas near the mouths of Petaluma, Sonoma, and Napa Valley are covered with fine-grained, poorly consolidated materials deposited in estuarine and near shore marine environments, mapped as Bay Mud. These materials were deposited near sea level in the Holocene (<10,000 years), occupy the topographically lowest parts of the valleys, and extend off-shore into the San Pablo Bay. The deposits are composed mostly of silt, clay, peat, and fine sand, with isolated accumulations of beach sand. The fine-grained texture and general lack of cementation provides high porosity (>40 percent) but low hydraulic conductivity and a specific-yield range of 3–7 percent (California Department of Water Resources, 1982). Few wells, as of 2006, are completed in the Bay Mud because of the low yields obtained from the fine-grained sediments and the poor quality, saline water contained in them.

The landslide and colluvial deposits occur as isolated patches or thin cover near the flanks of the valleys. The limited thickness or areal extent of these deposits, and their topographic position, generally above the autumnal water-table elevation, do not facilitate the development of water wells.

Faults

The most important faults in the region are the northwest trending, right-stepping, en-echelon faults that are part of the San Andreas dextral transform system active from Miocene to Holocene (McLaughlin and others, 2005). These include the Rodgers Creek, Healdsburg, Bennett Valley, Mayacma, and Green Valley Faults (fig. 3). Total slip on the Rodgers Creek Fault is up to 40 mi (65 km) (McLaughlin and others, 1996). The faults have many of the classic geomorphic features of strike-slip fault movement: scarps, benches, stratigraphic discontinuities, deflected drainages, sag ponds, and springs. The youthful geomorphic expression and seismicity along the faults of the San Andreas system attest to their active classification for earthquake hazards. The distinctive geomorphic expression of the faults is usually obscured where they strike beneath alluvium covered valleys.

The most important hydrologic impact of faults in the region is their role in developing the inland valleys. On a local scale, the faults are hydrologically important because they are planar features or zones across or within which the movement of groundwater may be inhibited or preferentially increased. Faulting breaks indurated rocks, producing zones of fractures that increase permeability and may provide preferential paths for groundwater flow. However, over time, the movement of groundwater through fractures may cause chemical weathering and cementation that reduces the permeability and converts the fault plane or zone into a groundwater barrier. Faulting in unconsolidated sediments or indurated rocks can produce zones of fine-grained fault gouge having low permeability, resulting in a groundwater barrier or zone of restricted groundwater flow. Faults may also displace rocks or sediments in such ways that formations with very different hydraulic properties are moved adjacent to one another.

Faults are thought to be important surfaces along which, in some circumstances, fluids may move vertically and allow deep waters to move to the surface or into shallow formations. This process is of special significance for the hydrothermal systems that are active in Napa, Sonoma, and Santa Rosa Valleys, where thermal springs and wells tend to be aligned with and near valley-bounding faults (Youngs and others, 1983). It has been speculated that faults in Santa Rosa Valley, form barriers to groundwater movement. However, conclusive proof of this phenomenon has not been documented by hydraulic testing (California Department of Water Resources, 1987). A more thorough discussion of the stratigraphy is included in Appendix A.

Methods

The *status assessment* provides a spatially-unbiased assessment of groundwater quality within in the primary aquifers, while the understanding assessment was designed to evaluate the natural and human factors that affect groundwater quality of the NSF study unit. This section describes the methods used for (1) defining groundwater quality, (2) assembling the datasets used for the status assessment, (3) determining which constituents warrant assessment, (4) calculating aquifer-scale proportions, and (5) statistical analyses for the understanding assessment. Methods used for compilation of data on potential explanatory factors are described in Appendix E.

The primary metric for defining groundwater quality was relative-concentration, which references concentrations of constituents measured in groundwater to regulatory and nonregulatory benchmarks used to evaluate drinking-water quality. Constituents are included or not included in the assessment on the basis of objective criteria by using these relative-concentrations. Groundwater-quality data collected by USGS–GAMA and data compiled in the CDPH database are used in the *status assessment*. Two statistical methods based on spatially-unbiased equal-area grids are used to calculate aquifer-scale proportions of low, moderate, or high relative-concentrations: the "grid-based" method uses one value per cell to represent groundwater quality and the "spatially-weighted" method uses many values per cell.

The CDPH database contains historical records from more than 25,000 wells, necessitating targeted retrievals to effectively access relevant water-quality data. For example, for the area representing the NSF study unit, the historical CDPH database contains more than 309,000 records from 790 wells. The CDPH data were used in three ways in the *status assessment*: to fill in gaps in the USGS data for the grid-based calculations of aquifer-scale proportions, to identify constituents for inclusion in the assessment, and to provide the majority of the data used in the spatially-weighted calculations of aquifer-scale proportions.

Relative-Concentrations and Water-Quality Benchmarks

Concentrations of constituents are presented as relative-concentrations in the *status assessment*:

$$\text{Relative-concentration} = \frac{\text{sample concentration}}{\text{benchmark concentration}}$$

Relative-concentrations were used because they provide context for the measured concentrations in the sample: relative-concentrations less than one indicate sample concentrations less than the benchmark, and values greater than one indicate sample concentrations 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.

Toccalino and others (2004), Toccalino and Norman (2006), and Rowe and others (2007) previously used the ratio of the measured sample concentration to the benchmark concentration (either MCLs or Health-Based Screening Levels [HBSL]) and defined this ratio as the benchmark quotient. Relative-concentrations used in this report are equivalent to the benchmark quotient reported by Toccalino and others (2004) for constituents that have MCLs. However, HBSLs were not used in this report, as they are not currently used as benchmarks by California drinking-water regulatory agencies. Relative-concentrations can only be computed for constituents with water-quality benchmarks; therefore, constituents lacking water-quality benchmarks are not included in the *status assessment*.

Regulatory and nonregulatory benchmarks apply to treated water that is served to the consumer, not to untreated groundwater. However, to provide some context for the results, concentrations of constituents measured in the untreated groundwater were compared with benchmarks established by the U.S. Environmental Protection Agency (USEPA) and CDPH (U.S. Environmental Protection Agency, 200; California Department of Health Services, 2008a,b). 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. Nonregulatory CDPH and USEPA secondary maximum contaminant levels (SMCL-CA and SMCL-US). For constituents with both recommended and upper SMCL-CA levels, the values for the upper levels were used.

3. Nonregulatory, 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).

Note that 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 is provided by Kulongoski and others (2006).

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

Category	Relative-concentrations of organic constituents	Relative-concentrations of inorganic constituents
High	>1	>1
Moderate	>0.1 and $\leq$1	>0.5 and $\leq$1
Low	$\leq$0.1	$\leq$0.5

The boundary between moderate and low relative-concentrations was set at 0.1 for organic and special interest constituents for consistency with other studies and reporting requirements (Toccalino and others, 2004; U.S. Environmental Protection Agency, 1998). For inorganic constituents, the boundary between moderate and low relative-concentrations was set at 0.5. A larger boundary value was used because in the NSF study unit and elsewhere in California (Landon and others, 2010), the naturally occurring inorganic constituents tend to be more prevalent in groundwater. While more complex classifications could be devised based upon the properties and sources of individual constituents, use of a single moderate/low boundary value for each of the two major groups of constituents provided a consistent objective criterion for distinguishing constituents occurring at moderate rather than low concentrations.

Datasets for Status Assessment

U.S. Geological Survey Grid Wells

The primary data used for the grid-based calculations of aquifer-scale proportions of relative-concentrations were data from wells sampled by USGS–GAMA. Detailed descriptions of the methods used to identify wells for sampling are given in Kulongoski and others (2006). Briefly, each study area was divided into 10-mi^2 (~25 km^2) equal-area grid cells, and in each cell, one well was randomly selected to represent the cell (Scott, 1990). Wells were selected from the population of wells in State-wide databases maintained by the CDPH and the USGS. The NSF study unit contained a total of 100 grid cells, and the USGS sampled wells in 83 of those cells (USGS grid wells). Of the 83 USGS grid wells, 80 were listed in the CDPH database; the other 3 were irrigation or domestic wells perforated at depths similar to the depths of CDPH wells in the cell. USGS grid wells were named with an alphanumeric GAMA ID consisting of a prefix identifying the study area and a number indicating the order of sample collection (fig. B1; table B1). The following prefixes were used to indicate study area: VOL, Volcanic Highlands study area, VP, Valleys and Plains study area, and WG, Wilson Grove Formation Highlands study area. In this report, the well VOL-04 was reclassified as an understanding well because it occupied the same cell as well VOL-20.

Samples collected from USGS grid wells were analyzed for 270 to 342 constituents (table 1). Water quality indicators (field parameters), volatile organic compounds, pesticides, NDMA, perchlorate, 1,2,3-TCP, noble gases, and selected isotopes used as hydrologic tracers were analyzed in samples from all wells. Major and minor ions, trace elements, nutrients, and redox species were analyzed in samples from many wells, and radiochemical constituents, and carbon isotopes were analyzed in samples from some wells. The collection, analysis, and quality-control data for the analytes listed in table 1 are described by Kulongoski and others (2006). However, further quality assurance and quality controls (QA/QC) were applied to the data. Data for constituents detected in the blank samples were screened below the concentration equal to the constituent's highest blank sample detection plus one half of the constituent's laboratory reporting level.

California Department of Public Health Grid Wells

The three study areas were divided into 100 grid cells, out of which 17 cells did not have a USGS grid well; 54 cells had a USGS grid well but no USGS data for major ions, trace elements, nutrients, and radiochemical constituents; and 11 cells had a USGS grid well but incomplete USGS data for nutrient and radiochemical constituents. The CDPH database was queried to provide these missing inorganic and radiochemical data. CDPH wells with data for the most recent three years available at the time of sampling (8/30/01 through 9/1/04) were considered. If a well had more than one analysis for a constituent in the three year interval, the most recent data were selected.

The decision tree used to identify suitable data from CDPH wells is described in Appendix B. Briefly, the first choice was to use CDPH data from the same well sampled by the USGS (USGS grid well). In this case, "DG" was added to the well's GAMA ID to signify that it was a well sampled by the USGS but also used CDPH data (fig. B1; table B1). If the DG well did not have all of the needed data, a second well in the cell was randomly selected from the subset of CDPH wells with data and a new identification with "DPH" and a new number was assigned to that well (fig. B1; table B1). The combination of the USGS grid wells and the DG- and DPH-CDPH-grid wells, produced a grid-well network covering 91 of the 100 grid cells in the NSF study unit (table B1). The remaining 9 cells had no accessible wells.

Note that the CDPH database generally did not contain data for all of the missing inorganic constituents at every CDPH grid well; therefore, the number of wells used for the grid-based assessment was different for different inorganic constituents (table 2). Although other organizations also collect water-quality data, the CDPH data is the only statewide database of groundwater-chemistry data available for comprehensive analysis.

CDPH data were not used to supplement USGS grid well data for VOCs, pesticides, or perchlorate for the *status assessment*. A larger number of VOCs and pesticide compounds are analyzed for the USGS–GAMA Program than are available from CDPH. USGS–GAMA collected data for 88 VOCs plus 114 pesticides and pesticide degradates at every well in the NSF study unit (table 1). In addition, method detection limits for USGS–GAMA analyses of organic constituents were typically one to two orders of magnitude lower than the reporting limits for analyses compiled by CDPH (table 3). Data for these constituents were collected by USGS–GAMA at all 83 USGS grid wells sampled.

Additional Data Used for Spatially-Weighted Calculation

The spatially-weighted calculations of aquifer-scale proportions of relative-concentrations used data from the USGS grid wells, additional wells sampled by USGS–GAMA, and all wells in the CDPH database having water-quality data during the three-year interval August 30, 2001 to September 1, 2004. For wells with both USGS and CDPH data, only the USGS data were used.

Six additional wells were sampled by the USGS to increase the sampling density in several areas to better understand specific groundwater-quality issues in the study unit (fig. B1*A*). These "USGS-understanding" wells were numbered with prefixes modified from those used for the USGS grid wells (VPFP-01, -02, -03, -04, and VOL-04, and WGFP-01) (fig. B1*A,* table B1). Seven hydrothermal wells and one hydrothermal spring also were sampled but were not included in this water-quality assessment because they were not used for drinking-water supply. The hydrothermal data is used for comparison purposes in Appendix F.

Table 1. Analyte groups and number of constituents and wells sampled for each analytical schedule in the North San Francisco Bay study unit, California, August to December, 2004.

[1,2,3-TCP, 1,2,3-trichloropropane; NDMA, *N*-nitrosodimethylamine; USGS, U.S. Geological Survey. µg/L, microgram per liter]

	Basic	Intermediate	Hydrothermal	Expanded
Analytical schedule				
Total number of wells	56	11	8	22
Number of grid wells sampled	54	10	0	19
Number of understanding wells sampled	2	1	8	3
Analyte class	Number of constituents			
Water-quality indicators (field parameters)				
Specific conductance and temperature	2	2	2	2
Dissolved oxygen and pH			1	2
Field alkalinity, bicarbonate, and carbonate				3
Turbidity				1
Organic constituents				
Volatile organic compounds (VOC) and gasoline additives [1]	88	88	0	88
Pesticides and pesticide degradates	61	61	0	61
Polar pesticides and degradates	53	53	0	53
Potential waste-water indicators [2]	50	50	0	50
Dissolved organic carbon				1
Constituents of special interest				
Perchlorate, NDMA, and low-level 1,2,3-TCP [3]	3	3	0	3
Inorganic constituents				
Major and minor ions, silica, total dissolved solids (TDS), and trace elements		36	36	36
Nutrients				5
Arsenic and iron species			6	6
Chromium species	3	3	3	3
Isotopes				
Stable isotopes of hydrogen and oxygen	2	2	2	2
Carbon-13 and carbon-14				2
Radioactivity and dissolved gases				
Tritium [4]	1	1	1	1
Noble gases and tritium [5]	7	7	7	7
Dissolved gases (carbon dioxide, argon, methane, nitrogen, oxygen)			5	5
Radon and radium isotopes				3
Gross alpha and beta radioactivity				4
Microbial constituents				
Total coliforms, colifage (somatic and F-specific), *E*. coli				4
Total	270	306	63	342

[1] Includes nine constituents classified as fumigants or fumigant synthesis byproducts.

[2] Does not include 13 constituents in common with VOCs and pesticides.

[3] 1,2,3-TCP was analyzed as a constituent of special interest with a method reporting level of 0.005 µg/L and on the USGS VOC schedule 2020, which has a laboratory reporting level of 0.12 µg/L.

[4] Analyzed at U.S. Geological Survey Tritium Laboratory, Menlo Park, California.

[5] Analyzed at Lawrence Livermore National Laboratory, Livermore, California.

Table 2. Inorganic constituents and associated benchmark information, and the number of grid wells with USGS–GAMA data and California Department of Public Health (CDPH) data, for each constituent, North San Francisco Bay study unit, California.

[MCL-US, U.S. Environmental Protection Agency (USEPA) maximum contaminant level; MCL-CA, CDPH maximum contaminant level; SMCL-CA, CDPH secondary maximum contaminant level; NL-CA, CDPH notification level; AL-US, USEPA action level; HAL-US, USEPA lifetime health advisory; USGS, U.S. Geological Survey. µg/L, microgram per liter; mg/L, milligram per liter; pCi/L, picocurie per liter]

Constituent type	Constituent	Benchmark type	Benchmark value	Units	Number of grid wells with USGS-GAMA data	Number of grid wells with CDPH data
Nutrient	Ammonia, as nitrogen	HAL-US	30	mg/L	22	0
Nutrient	Nitrate plus nitrite, as nitrogen	MCL-US	10	mg/L	22	63
Nutrient	Nitrite, as nitrogen	MCL-US	1	mg/L	22	54
Trace element	Aluminum	MCL-CA	1,000	µg/L	31	49
Trace element	Antimony	MCL-US	6	µg/L	31	49
Trace element	Arsenic	MCL-US	10	µg/L	31	49
Trace element	Barium	MCL-CA	1,000	µg/L	31	49
Trace element	Beryllium	MCL-US	4	µg/L	31	49
Trace element	Boron	NL-CA	1,000	µg/L	31	43
Trace element	Cadmium	MCL-US	5	µg/L	31	49
Trace element	Chromium	MCL-CA	50	µg/L	32	22
Trace element	Copper	AL-US	1,300	µg/L	31	39
Trace element	Iron	SMCL-CA	300	µg/L	32	47
Trace element	Lead	AL-US	15	µg/L	31	32
Trace element	Manganese	SMCL-CA	50	µg/L	31	45
Trace element	Mercury	MCL-US	2	µg/L	23	49
Trace element	Molybdenum	HAL-US	40	µg/L	31	1
Trace element	Nickel	MCL-CA	100	µg/L	31	49
Trace element	Selenium	MCL-US	50	µg/L	31	49
Trace element	Silver	SMCL-CA	100	µg/L	31	46
Trace element	Strontium	HAL-US	4,000	µg/L	31	0
Trace element	Thallium	MCL-US	2	µg/L	31	49
Trace element	Uranium	MCL-US	30	µg/L	31	0
Trace element	Vanadium	NL-CA	50	µg/L	31	44
Trace element	Zinc	SMCL-US	5,000	µg/L	31	38
Minor ion	Fluoride	MCL-CA	2	mg/L	28	49
Major ion	Chloride	SMCL-CA	500	mg/L	32	39
Major ion	Sulfate	SMCL-CA	500	mg/L	32	38
Major ion	Total dissolved solids (TDS)	SMCL-CA	1,000	mg/L	32	38
Radioactive	Gross-alpha radioactivity, 30 day count	MCL-US	15	pCi/L	21	31
Radioactive	Gross-beta radioactivity, 30 day count	MCL-CA	50	pCi/L	21	1
Radioactive	Radium-226	MCL-US	5	pCi/L	21	0
Radioactive	Radium-228	MCL-US	5	pCi/L	2	7
Radioactive	Radon-222	MCL-US	4,000	pCi/L	21	2

Table 3.   Comparison of the number of compounds, and median laboratory reporting levels or method detection limits, by type of constituent for data reported in the California Department of Public Health database and data collected by the U.S. Geological Survey for the North San Francisco Bay study unit, California, August to December, 2004.

[CDPH, California Department of Public Health; MDL, method detection limit; LRL, laboratory reporting level; mg/L, milligram per liter; µg/L, microgram per liter; pCi/L, picocurie per liter; SSMDC, sample-specific minimum detectable concentration; ns, not sampled]

Constituent type	CDPH		USGS GAMA		Median unit
	Number of compounds	Median MDL	Number of compounds	Median LRL	
Volatile organic compounds and gasoline additives (including fumigants)	61	0.5	88	0.06	µg/L
Pesticides plus degrades	27	2	114	0.019	µg/L
Nutrients, major and minor ions	4	0.4	17	0.06	mg/L
Trace elements	20	8	25	0.12	µg/L
Radioactive constituents (SSMDC)[1]	5	1	8	0.05	pCi/L
Perchlorate	1	4	1	0.5	µg/L
N-Nitrosodimethylamine (NDMA)	ns	ns	1	0.002	µg/L

[1] Value reported in GAMA column is the median SSMDC for eight radioactive constituents collected and analyzed by GAMA.

Identification of Constituents for Status Assessment

Up to 342 constituents were analyzed in samples from NSF study unit wells; however, only a subset of these constituents is discussed in this report. Three criteria were used to identify constituents for inclusion:

1. Constituents present at high or moderate relative-concentrations in the CDPH database within the 3-year interval,

2. Constituents present at high or moderate relative-concentrations in the USGS grid wells or USGS-understanding wells or,

3. Organic constituents having study unit detection frequencies greater than 10 percent in the USGS grid well dataset.

These criteria identified 11 organic constituents and 15 inorganic constituents for inclusion in the *status assessment* (table 4). An additional 15 organic constituents and 35 inorganic constituents were detected by USGS–GAMA, and are not included in the *status assessment* because they either have no established benchmarks, or were only detected at low relative-concentrations (table 5). Constituents discussed in the *understanding assessment* had high relative-concentration in >2 percent of the primary aquifers or were detected in >10 percent of the USGS grid well dataset. The remaining constituents that were not detected by USGS–GAMA in the NSF study unit are listed in Kulongoski and others (2006).

The CDPH database also was used to identify constituents that have been reported at high relative-concentrations historically, but not currently. The historical period was defined as from the earliest record maintained in the CDPH electronic database to August 29, 2001 (May 16, 1974, through August 29, 2001).

Constituents may be historically high, but not currently high, due to improvement of groundwater quality with time or abandonment of wells with high concentrations. Historically high constituents that do not otherwise meet the criteria for inclusion in the *status assessment* are not considered representative of potential groundwater-quality concerns in the study unit from 2001 to 2004. For the NSF study unit, there were nine historically high constituents (table 6).

Calculation of Aquifer-Scale Proportions

The *status assessment* is intended to characterize the quality of groundwater resources within the primary aquifers of the NSF study unit. The primary aquifers are defined by the depth intervals over which wells listed in the CDPH database are perforated. The use of the term "primary aquifers" does not imply that there exists a discrete aquifer unit. In most groundwater basins, municipal and community supply wells generally are perforated at greater depths than are domestic wells (for example, Farrar and others, 2006). Thus, because domestic wells are not listed in the CDPH database, the primary aquifer generally corresponds to the portion of the aquifer system tapped by municipal and community supply wells. A majority of the wells used in the *status assessment* are listed in the CDPH databases, and are therefore classified as municipal and community drinking-water supply wells. However, to the extent that domestic wells are perforated over the same depth intervals as the CDPH wells, the assessments presented in this report may also be applicable to the portions of the aquifer systems used for domestic drinking-water supplies.

Table 4. Aquifer proportions from grid-based and spatially-weighted methods for constituents (1) for which high relative-concentrations were reported in the California Department of Public Health (CDPH) database during August 30, 2001, to September 1, 2004, or (2) that had moderate or high relative-concentrations in samples collected from grid wells during August to December 2004, North San Francisco Bay study unit, California.

[Grid-based aquifer-scale proportions for organic constituents are based on samples collected by the U.S. Geological Survey from 83 grid wells during August to December, 2004. Spatially-weighted aquifer-scale proportions for organic constituents are based on CDPH data for August 30, 2001, to September 1, 2004, combined with grid-well and understanding-well data. High, concentrations greater than benchmark; moderate, concentrations less than benchmark and greater than or equal to 0.1 of benchmark for organic constituents or 0.5 of benchmark for inorganic constituents; low, concentrations less than 0.1 of benchmark for organic constituents or 0.5 of benchmark for inorganic constituents. AL–US, U.S. Environmental Protection Agency (USEPA) action level; HAL–US, USEPA lifetime health advisory; MCL–US, USEPA maximum contaminant level; MCL–CA, CDPH maximum contaminant level; NL–CA, CDPH notification level; SMCL–CA, CDPH secondary maximum contaminant level; mg/L, milligram per liter; µg/L, microgram per liter; ns, not sampled; pCi/L, picocurie per liter; %, percent]

| Constituent | Benchmark | | | Raw detection frequency [1] | | | Spatially-weighted aquifer-scale proportion [1] | | | Grid-based aquifer-scale proportion | | | 90% confidence interval for grid-based high proportion [2] | |
	Type	Value	Unit	Number of wells	Percent Moderate	High	Number of cells	Proportion, in percent Moderate	High	Number of cells	Proportion, in percent Moderate	High	Limit, in percent Lower	Upper
Trace element														
Aluminum	MCL-CA	1,000	µg/L	406	0.5	0.7	81	0.4	0.6	80	0.0	0.0	0.0	2.0
Antimony	MCL-US	6	µg/L	404	0.0	0.7	81	0.0	0.7	80	0.0	0.0	0.0	2.0
Arsenic	MCL-US	10	µg/L	407	21.6	10.3	81	24.1	12.2	80	25.0	10.0	5.7	16.9
Boron	NL-CA	1,000	µg/L	288	3.1	3.5	77	4.7	3.6	74	5.4	4.1	1.6	9.7
Lead	AL-US	15	µg/L	274	1.8	2.2	71	1.5	1.8	63	1.6	1.6	0.4	6.8
Mercury	MCL-US	2	µg/L	401	1.0	0.0	80	1.1	0.0	72	1.4	0.0	0.0	2.2
Molybdenum	HAL-US	40	µg/L	35	2.9	0.0	33	3.0	0.0	32	3.1	0.0	0.0	4.9
Nickel	MCL-CA	100	µg/L	406	0.0	0.2	80	0.0	0.2	80	0.0	0.0	0.0	2.0
Trace element with a SMCL														
Iron	SMCL-CA	300	µg/L	342	8.8	18.7	80	7.9	26.3	78	9.0	24.4	17.3	33.1
Manganese	SMCL-CA	50	µg/L	336	8.6	34.5	79	8.6	40.9	76	7.9	40.8	32.0	50.2
Radioactive constituent														
Gross-alpha radioactivity, 72 hour count [3]	MCL-US	15	pCi/L	194	0.0	[3]0	55	0.0	0.0	51	0.0	0.0	0.0	3.1
Nutrient														
Nitrate plus nitrite, as nitrogen	MCL-US	10	mg/L	549	2.7	0.5	85	3.2	0.4	76	2.6	0.0	0.0	2.1
Major and minor element														
Chloride	SMCL-CA	500	mg/L	275	0.0	0.4	73	0.0	0.7	71	0.0	0.0	0.0	2.3
Fluoride	MCL-CA	2	mg/L	397	0.3	1.5	82	0.1	1.2	77	0.0	0.0	0.0	2.1
Total dissolved solids (TDS)	SMCL-CA	1,000	mg/L	273	4.4	0.4	71	5.0	0.7	70	7.1	1.2	0.0	2.3

Table 4. Aquifer proportions from grid-based and spatially-weighted methods for constituents (1) for which high relative-concentrations were reported in the California Department of Public Health (CDPH) database during August 30, 2001, to September 1, 2004, or (2) that had moderate or high relative-concentrations in samples collected from grid wells during August to December 2004, North San Francisco Bay study unit, California.—Continued

[Grid-based aquifer-scale proportions for organic constituents are based on samples collected by the U.S. Geological Survey from 83 grid wells during August to December, 2004. Spatially-weighted aquifer-scale proportions are based on CDPH data for August 30, 2001, to September 1, 2004, combined with grid-well and understanding-well data. High, concentrations greater than benchmark; moderate, concentrations less than benchmark and greater than or equal to 0.1 of benchmark for organic constituents; low, concentrations less than 0.1 of benchmark for organic constituents or 0.5 of benchmark for inorganic constituents. AL-US, U.S. Environmental Protection Agency (USEPA) action level; HAL-US, USEPA lifetime health advisory; MCL-US, USEPA maximum contaminant level; MCL-CA, CDPH maximum contaminant level; NL-CA, CDPH notification level; SMCL-CA, CDPH secondary maximum contaminant level; mg/L, milligram per liter; µg/L, microgram per liter; ns, not sampled; pCi/L, picocurie per liter; %, percent]

Constituent	Benchmark			Raw detection frequency[1]			Spatially-weighted aquifer-scale proportion[1]			Grid-based aquifer-scale proportion			90% confidence interval for grid-based high proportion[2]	
	Type	Value	Unit	Number of wells	Percent Moderate	Percent High	Number of cells	Proportion, in percent Moderate	Proportion, in percent High	Number of cells	Proportion, in percent Moderate	Proportion, in percent High	Limit, in percent Lower	Limit, in percent Upper
Solvent														
1,2-Dichloroethane[3]	MCL-CA	0.5	µg/L	304	0.0	[3]0.0	87	0.0	0.0	83	0.0	0.0	0.0	1.9
Tetrachloroethene (PCE)	MCL-US	5	µg/L	307	0.7	0.7	87	0.4	1.3	83	0.0	0.0	0.0	1.9
Trichloroethene (TCE)	MCL-US	5	µg/L	312	1.6	0.6	87	2.1	0.1	83	0.0	0.0	0.0	1.9
Other VOC														
1,1-Dichloroethene	MCL-CA	6	µg/L	302	0.0	0.3	87	0	0.1	83	0.0	0.0	0.0	1.9
Bis(2-ethylhexyl) phthalate (DEHP)[3]	MCL-CA	4	µg/L	62	0.0	[3]0	62	0	0.0	ns	ns	ns	ns	ns
Benzene	MCL-US	1	µg/L	305	0.7	0.0	87	1.7	0.0	83	1.2	0.0	0.0	1.9
Toluene[3]	MCL-US	150	µg/L	309	0.0	[3]0	87	0	0.0	83	0.0	0.0	0.0	1.9
1,2-Dibromo-3-chloropropane (DBCP)[3]	MCL-US	0.2	µg/L	160	0.0	[3]0	84	0	0.0	83	0.0	0.0	0.0	1.9
1,2-Dibromoethane (EDB)[3]	MCL-US	0.05	µg/L	235	0.0	[3]0	84	0	0.0	83	0.0	0.0	0.0	1.9
Herbicides														
Simazine	MCL-CA	4	µg/L	418	0.0	0.0	86	0.0	0.0	81	0.0	0.0	0.0	2.0
Insecticide														
Diazinon	HAL-US	1	µg/L	175	0.6	0.0	84	1.2	0.0	83	1.2	0.0	0.0	1.9

[1] Based on the most recent data for each CDPH well during the period August 30, 2001 to September 1, 2004, combined with GAMA grid- and understanding-well data.

[2] Based on the Jeffrey's interval for the binomial distribution (Brown and others, 2001).

[3] The high value was reported in the CDPH database between August 30, 2001 to September 1, 2004, but the high value was not the most recently reported value used for calculating aquifer-scale proportion.

Table 5. Number of constituents analyzed and detected with associated benchmarks in each constituent class, North San Francisco Bay study unit, California, August to December 2004.

[AL, U.S. Environmental Protection Agency (USEPA) action level; CDPH, California Department of Public Health; HAL, USEPA lifetime health advisory; MCL, USEPA or CDPH maximum contaminant level; NL, CDPH notification level; RSD5, USEPA risk specific dose at 10^{-5}; SMCL, USEPA or CDPH secondary maximum contaminant level; VOC, volatile organic compound]

Organic constituent class

Benchmark type	Sum of organic and special interest compounds		VOC and gasoline additives (excluding fumigants)		Fumigants		Pesticides and degradates		Polar pesticides and degradates		Potential wastewater indicator compounds		Special interest compounds	
	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected
MCL	50	15	29	13	4	0	3	2	9	0	4	0	1	0
HAL	33	2	6	0	1	0	14	2	9	0	2	0	1	0
NL	17	1	15	0	0	0	0	0	0	0	1	1	1	0
RSD5	7	0	2	0	2	0	3	0	0	0	0	0	0	0
AL	0	0	0	0	0	0	0	0	0	0	0	0	0	0
SMCL	0	0	0	0	0	0	0	0	0	0	0	0	0	0
None	148	8	27	0	2	0	41	1	35	2	43	5	0	0
Total:	255	26	79	13	9	0	61	5	53	2	50	6	3	0

Inorganic constituent class

Benchmark type	Sum of inorganic constituents		Major and minor ions		Nutrients		Trace elements		Radioactive constituents	
	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected
MCL	23	23	1	1	2	2	12	12	8	8
HAL	4	4	0	0	1	1	3	3	0	0
NL	2	2	0	0	0	0	2	2	0	0
RSD5	0	0	0	0	0	0	0	0	0	0
AL	2	2	0	0	0	0	2	2	0	0
SMCL	6	6	3	3	0	0	3	3	0	0
None	13	13	7	7	3	3	3	3	0	0
Total	50	50	11	11	6	6	25	25	8	8

	Analyzed	Detected
Organic and inorganic constituents combined	305	76

Table 6.   Constituents with historically high concentrations recorded in the California Department of Public Health (CDPH) database.

[High concentration, above human-health benchmark; AL-US, U.S. Environmental Protection Agency (USEPA) action level; MCL-CA, CDPH maximum contaminant level; MCL-US; USEPA maximum contaminant level; NL-CA, CDPH notification level; µg/L, microgram per liter; pCi/L, picocurie per liter]

Constituent	Benchmark		Unit	Date of most recent high concentration	Number of historically high wells [1]	Number of wells [1]
	Type	Value				
Trace element						
Cadmium	MCL-US	5	µg/L	6/28/1988	1	532
Chromium	MCL-CA	50	µg/L	8/13/1987	1	513
Copper	AL-US	1,300	µg/L	8/25/1999	1	449
Thallium	MCL-US	2	µg/L	8/11/1999	1	496
Radioactive constituent						
Radium-226	MCL-US	5	pCi/L	10/10/1996	2	18
Trihalomethane						
Chloroform	MCL-US	[2] 80	µg/L	8/30/1993	2	518
Solvent						
1,1-Dichloroethane	MCL-CA	5	µg/L	11/24/1987	1	518
Dichloromethane (methylene chloride)	MCL-US	5	µg/L	11/2/1989	2	517
Constituent of special interest						
Perchlorate	MCL-CA	6	µg/L	6/14/2000	1	53

[1] Based on historical CDPH well data for May, 16, 1974–August 29, 2001.

[2] The MCL-US benchmark for trihalomethanes is the sum of the concentrations of chloroform, bromoform, bromodichloromethane, and dibromochloromethane.

Two statistical approaches, grid-based and spatially-weighted, were applied to evaluate the proportions of the primary aquifers in the NSF 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 meeting the criteria for inclusion in the *status assessment*, and for classes of constituents. Classes of constituents with health-based benchmarks included trace elements, radioactive constituents, nutrients, major and minor elements, solvents, other VOCs, herbicides, and insecticides. Aquifer-scale proportions were also calculated for the following constituents having aesthetic (SMCL) thresholds: total dissolved solids, chloride, manganese, and iron.

The grid-based calculation uses the grid-well dataset assembled from the USGS grid and CDPH grid wells. For each constituent, the high aquifer-scale proportion was calculated by dividing the number of cells represented by a high value for that constituent by the total number of grid cells with data for that constituent. The moderate and low aquifer-scale proportions were calculated similarly. Confidence intervals for the high aquifer-scale proportions were computed using the Jeffrey's interval for the binomial distribution (Brown and others, 2001). The grid-based estimate is spatially unbiased. However, the grid-based approach may not detect constituents that are present at high concentrations in small proportions of the primary aquifers. For calculation of high aquifer-scale proportion for a class of constituents, cells were considered high if any of the constituents had a high value. Cells were considered moderate if any of the constituents had a moderate value, but none had a high value.

The spatially-weighted calculation uses the dataset assembled from all of the CDPH and USGS wells. For each constituent, the high aquifer-scale proportion was calculated by computing the proportion of "high" wells in each cell and then averaging the proportions for all the cells (Isaaks and Srivastava, 1989). The moderate aquifer-scale proportion was calculated similarly. Confidence intervals for spatially-weighted detection frequencies of high concentrations are not described in this report. For calculation of high aquifer-scale proportion for a class of constituents, wells were considered high if any of the constituents had a high value. Wells were considered moderate if any of the constituents had a moderate value, but not a high value.

In addition, for each constituent, the detection frequencies of high and moderate values for individual constituents were calculated using the same dataset as used for the spatially-weighted calculations. However, raw detection frequencies are not spatially unbiased because the wells in the CDPH database are not uniformly distributed (fig. 4). For example, if a constituent were present at high concentrations in a small region of the aquifer that had a high density of wells, 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 D for details of statistical methods).

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

- If the grid-base high aquifer-scale proportion was zero and the spatially-weighted proportion was greater than zero, then the spatially-weighted result was used. This situation can arise when the concentration of a constituent is high in a small fraction of the primary aquifers.

- If the grid-based high aquifer-scale proportion was nonzero and the spatially-weighted proportion was outside the 90-percent confidence interval (based on the Jeffrey's interval for the binomial distribution), then the spatially-weighted proportion was used.

The grid-based moderate and low proportions were used in most cases because the reporting limits for many organic constituents and some inorganic constituents in the CDPH database were higher than the boundary between the moderate and low categories. However, if the grid-based moderate proportion was zero and the spatially-weighted proportion was greater than zero, then the spatially-weighed value was used as a minimum estimate for the moderate proportion.

Understanding-Assessment Methods

The potential explanatory factors—land use, well depth, depth to the tops of the well perforations, normalized position along flow path, classified groundwater age, and geochemical-condition (see Appendix E for more details)—were analyzed in relation to constituents of interest for the understanding assessment in order to establish context for physical and chemical processes within the groundwater system. Statistical tests were used to identify significant correlations between the constituents of interest and potential explanatory factors. The strongest correlations for understanding factors influencing water quality are shown in figures.

The wells selected for the understanding assessment were USGS grid and CDPH grid wells and USGS-understanding wells. CDPH DPH wells were not used in the understanding assessment because carbon isotope, tritium, dissolved oxygen, and some well construction data were not available. Correlations between explanatory factors and groundwater constituents were tested using either the set of grid plus understanding wells or grid wells only. Because the USGS-understanding wells were not randomly selected on a spatially distributed grid, these wells were excluded from analyses of relations of water quality to areally-distributed factors (land use) to avoid areal-clustering bias. However, six USGS-understanding wells were selected for analyses of relations between constituents and the vertically-distributed explanatory factors (depth, groundwater-age classification, and geochemical conditions). TDS was measured directly or calculated from specific conductance (see Appendix C).

Statistical Analysis

Nonparametric statistical methods were used to test the significance of correlations between water-quality variables and potential explanatory factors. Nonparametric statistics are robust techniques that are generally not affected by outliers and do not require that the data follow any particular distribution (Helsel and Hirsch, 2002). The significance level (p) used to test hypotheses for this report was compared to a threshold value (α) of 5 percent ($\alpha = 0.05$) to evaluate whether the relation was statistically significant ($p < \alpha$). Correlations were investigated using Spearman's method to calculate the rank-order correlation coefficient (ρ) between continuous variables. The values of ρ can range from +1.0 (perfect positive correlation) to 0.0 (no correlation) to –1.0 (perfect negative correlation).

The Wilcoxon rank-sum test was used to evaluate the correlation between water quality and categorical explanatory factors: for example, groundwater age (modern, mixed, or pre-modern), redox conditions (oxic, mixed, or anoxic/suboxic), and land-use classification (natural, agricultural, urban, or mixed). The Wilcoxon rank-sum test can be used to compare two independent populations (data groups or categories) to determine whether one population contains larger values than the other (Helsel and Hirsch, 2002). The null hypothesis for the Wilcoxon rank sum test is that there is no significant difference between the values of the two independent data groups being tested. The Wilcoxon rank sum test was used for multiple comparisons of two independent groups rather than the multiple-stage Kruskal-Wallis test for identifying differences between three or more groups, although a set of Wilcoxon rank sum tests is more likely to falsely indicate a significant difference between groups than the Kruskal-Wallis test (Helsel and Hirsch, 2002). However, given the potentially large and variable number of differences to be evaluated, the Wilcoxon rank sum test was selected as a consistent and practical direct test of differences. Because of the small sample size, the exact distribution with continuity correction also was applied.

Potential Explanatory Factors

Land Use

Land use around USGS grid wells (radius of 1,640 ft [500 m]) in the NSF study unit was dominated by natural landscape (40 percent of the area) and agricultural land (38 percent of the area). Only 22 percent of the area was urban land (fig. 6A). Land classified as natural also made up the greatest percentage of the total land area (taking into account the entire area of the study unit rather than just the area around grid wells)(figs. 6A, 7). In the WG study area, 27 percent of the land within 1,640 ft (500 m) of grid wells was urban, but in the whole study areas, only 10 percent was urban (fig. 6A). The higher percentage of urbanized land surrounding the grid wells reflects the co-location of public-supply wells and population density. The area surrounding grid wells, particularly for the WG study area, may reflect greater urban influence than might be expected on the basis of the average land use of the study area (fig. 7).

Well Depth

Well construction information was available for 73 of the 83 grid wells sampled in the NSF study unit. Grid wells had depths ranging from 60 to 864 ft (18 to 263 m) below land surface; the median was 317 ft (97 m) (fig. 8; table B1). Depths to the tops of the perforations ranged from 20 to 690 ft (6 to 210 m) with a median of 95 ft (29 m). The perforation length was up to 560 ft (171 m) with a median of 155 ft (47 m). The wide range in construction depths reflects the geological differences between the VP, VOL, and WG study areas. The understanding wells, 5 out of 6 of which were public supply wells, have ranges in well depth and depth to top of perforations (fig. 8) very similar to those of the grid wells.

Normalized Position of Wells along Flowpaths

Wells were sampled along three river valleys—the Napa, the Sonoma, and the Russian River systems—in order to assess the effects that position of wells along flow paths had on groundwater quality ("Normalized position of wells along flow paths" in Appendix E; table B1). This study examined the change in concentrations of major and minor ions, and trace elements as a function of the normalized position of wells along groundwater flowpaths. Types of wells considered for these flow paths were grid, understanding, and CDPH-other wells. There were 13 wells with designated position along the Napa flow-path, 7 wells along the Sonoma flow-path, and 12 wells along the Russian River (Alexander Valley to the Lower Russian River Valley) flow-path (fig. 9).

Age Classification

Groundwater samples were assigned age classifications on the basis of the tritium, carbon-14, and helium-4 content of the samples (Appendix E: "Groundwater Age Classification"). Age classifications were assigned to 87 USGS grid- and understanding-well groundwater samples; 14 were classified as modern, 23 were mixed, and 50 were pre-modern age (table E2). Samples from 10 wells could not be classified because the age-tracer data was incomplete or did not meet quality-assurance checks.

Median groundwater ages generally increased with depth to the top of the well perforations (fig. 10A). The depth to the top perforations was significantly shallower in wells having modern age distributions compared to pre-modern age distributions (fig. 10A). The well depths of wells classified as modern were significantly shallower than those of wells classified as mixed or pre-modern (table B1, E2, fig. 10B). Water in five of the eleven wells perforated entirely within the upper 100 ft (30 m) of the aquifer was modern age, while water in most wells with perforations ≥100 ft (30 m) below land surface was pre-modern (fig. 10C). Water in wells with the top perforations <100 ft (30 m) and the bottom perforations ≥100 ft (30 m) was mostly of mixed age.

Geochemical Condition and Water Temperature

An abridged classification of oxidation-reduction (redox) conditions adapted from the framework presented by McMahon and Chapelle (2008) for 56 wells sampled by the USGS–GAMA Priority Basin Project is given in Appendix E; table E1. The classification "indeterminate" was added to the framework for groundwater samples that did not have sufficient data available to be classified as oxic, anoxic/suboxic, or mixed anoxic/oxic. Groundwater was anoxic/suboxic (suboxic to anoxic) in 44 percent of the wells, mixed anoxic/oxic in 24 percent of the wells, and oxic in 32 percent of the wells.

Correlations between Explanatory Factors

Apparent correlations between explanatory factors and a water-quality constituent could actually reflect correlations between two or more explanatory factors. Therefore, it is important to identify statistically significant correlations between explanatory factors (table 7).

Percent agricultural land use is significantly correlated (negatively) with normalized position along the flowpath (table 7). This correlation reflects agricultural land-use dominating in the proximal sections of the valleys (fig. 7).
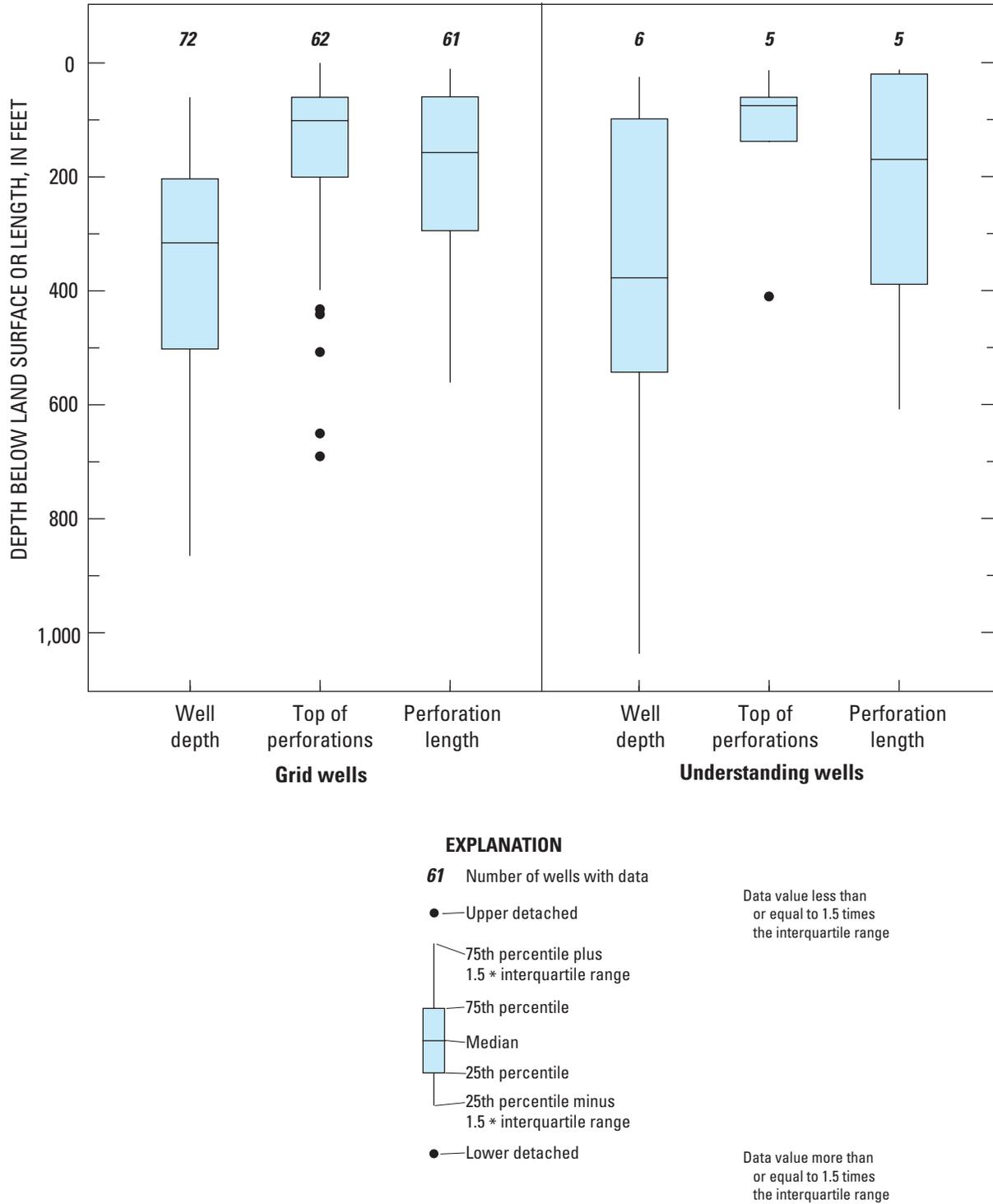
Figure 8.   Construction characteristics for grid wells and understanding wells, North San Francisco Bay study unit, California.
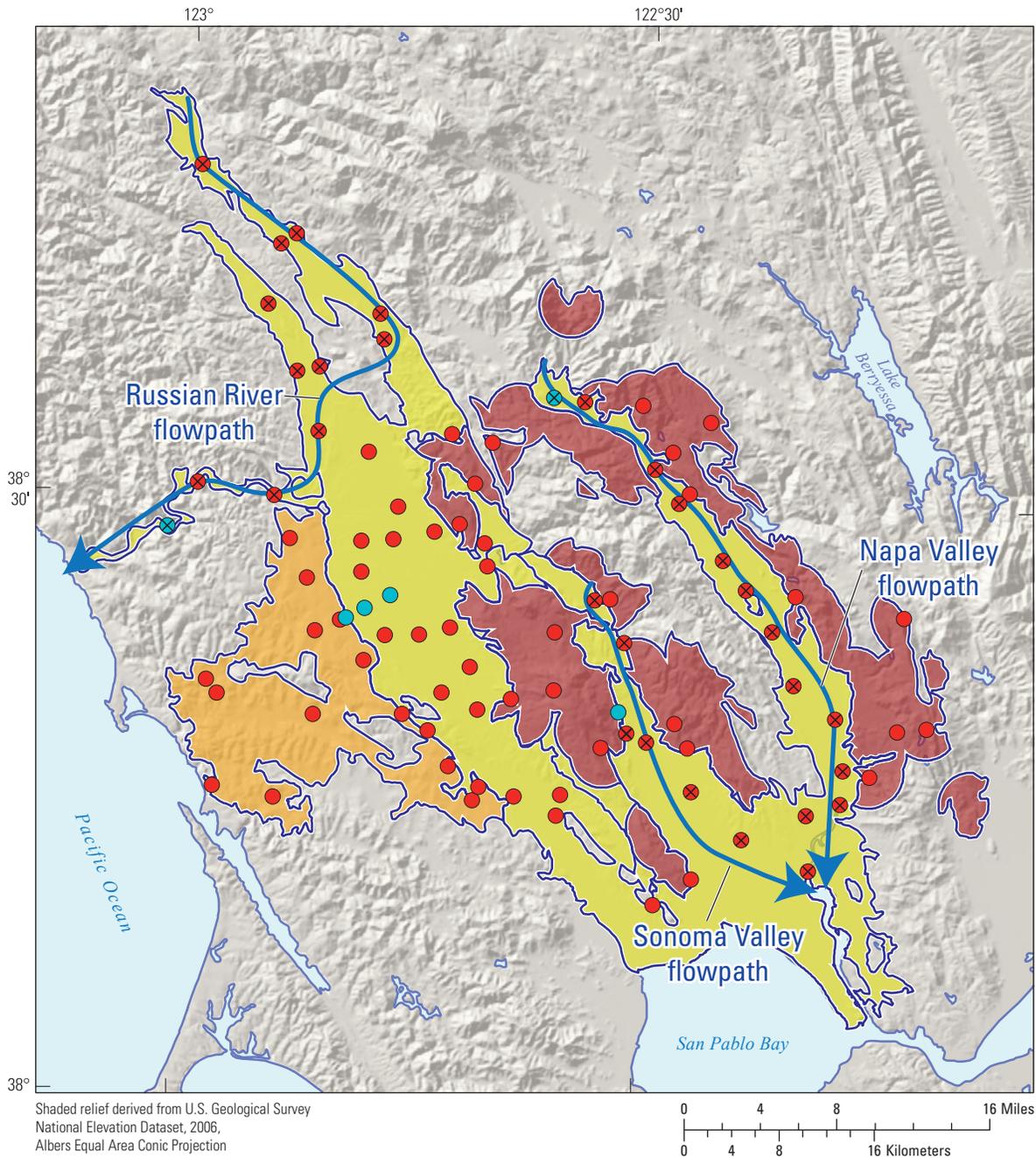
Figure 9.   Normalized position of wells along a flowpath in the North San Francisco Bay study unit, California.
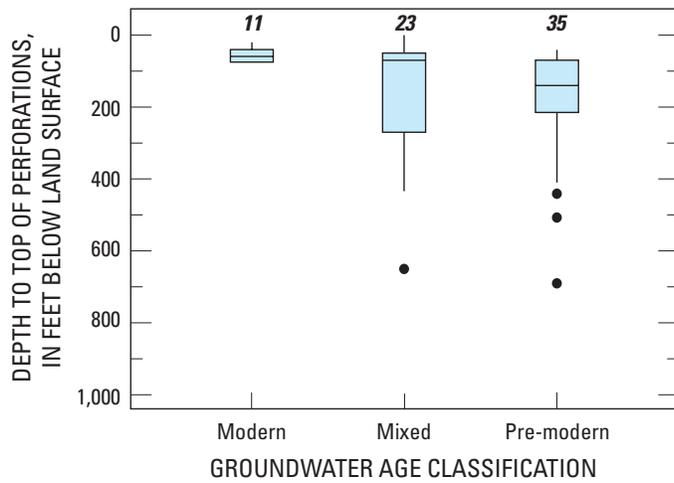
A

B
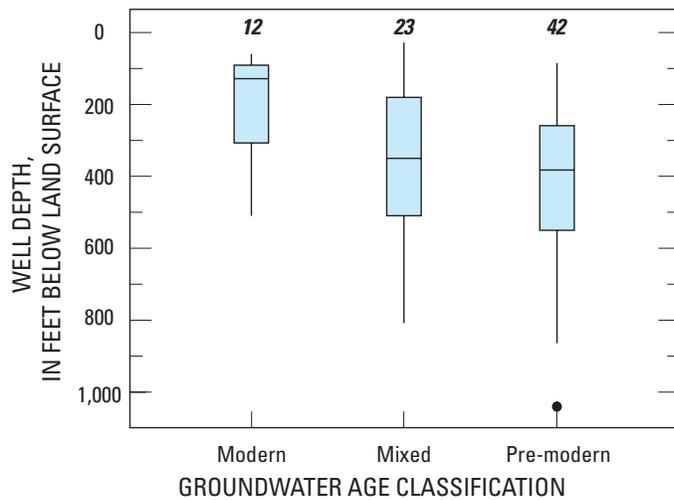
C
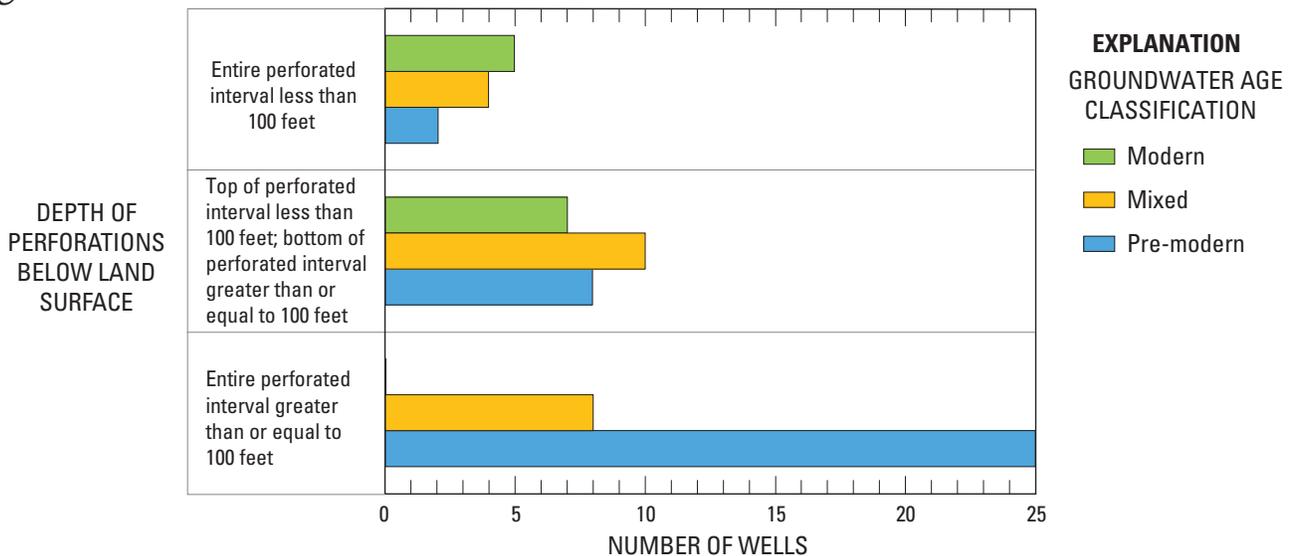
Figure 10.   The relation of classified groundwater age to *A*. depth to top of perforations below land surface, *B*. well depth below land surface, and *C*. age classification in relation to the depth of well perforations, North San Francisco Bay study unit, California.

Table 7. Results of nonparametric analysis (Spearman's method) of correlations between selected potential explanatory factors, North San Francisco Bay study unit, Callifornia.

[ρ, Spearman's correlation statistic; significant positive correlation and significant negative correlations shown. nc, no significant correlation]

Type of well analyzed	Explanatory factor	Normalized position along flowpath	Depth to top of perforations	Depth of well	Dissolved oxygen concentration	pH
		ρ: Spearman's correlation statistic				
Grid wells	Percent urban land use	nc	nc	nc	nc	nc
Grid wells	Percent agricultural land use	−0.37	nc	nc	nc	nc
Grid wells	Percent natural land use	nc	nc	nc	nc	nc
Grid wells	Normalized position along flowpath	■	0.56	nc	−0.50	0.43
Grid and understanding wells [1]	Depth to top of perforations	0.62	■		nc	0.34
Grid and understanding wells [1]	Depth of well	nc	0.68	■		nc
Grid and understanding wells [1]	Dissolved oxygen concentration	−0.50	nc	nc	■	
Grid and understanding wells [1]	pH	0.42	0.34	nc	−0.64	■

[1]Understanding wells do not include hydrothermal wells or spring data.

Depth to the top of the perforations is significantly correlated (positively) with normalized position along the flowpath, which may reflect deeper perforations in wells towards the terminal end of the valleys (table 7). Depth to the top perforations is significantly correlated (positively) with well depth also. Depth to the top perforations is significantly correlated (positively) with pH also, suggesting that higher pH in water is found deeper in the primary aquifers.

Figure 11 presents a cross section of well perforations and well redox classification plotted as normalized position of wells along the flowpath on the x-axis, and depth of the perforation interval on the y-axis. This figure was derived from data for all of the flow-path wells plotted on a single composite flow path (see Appendix E for details). Shallow groundwater in the upgradient part of the flowpath is oxic trending towards less oxic water deeper in the aquifer and farther along the flowpath. The distal (downgradient) part of the normalized flowpath has mainly anoxic/suboxic and mixed conditions. The range of geochemical conditions may reflect natural spatial variability and mixing of water with variable reduction-oxidation characteristics of water in wells that have long perforated intervals.

The pH ranged from 4.1 to 9.4 in the USGS grid wells, USGS-understanding wells, and CDPH-other wells (fig. 12A). The relationship between pH and well depth is shown in figure 12B. Two trends are apparent. The pH of groundwater classified as pre-modern is generally higher (median = 7.4; n = 34) than modern groundwater (median = 6.9; n = 10). Second, groundwater classified as pre-modern tends to be from deeper wells, and groundwater classified as modern tends to be from shallower wells. The higher pH water (pH > 7.4) was classified as predominantly pre-modern age and most was from wells deeper than 200 ft (64 m) (fig. 12B), while the lower pH groundwater was characterized as shallow and of modern or mixed age.

Dissolved oxygen is significantly correlated (negatively) with pH, reflecting the decrease in oxygen in waters with reducing conditions (table 7). Concentrations of DO were significantly correlated (negatively) with normalized position of wells along flowpaths, consistent with the visual patterns evident in figure 11. Wilcoxon tests indicated significantly higher DO in wells classified as having water of modern ages, as compared with wells having water of pre-modern ages (table 8).

The pH is significantly correlated (positively) with normalized position along flowpath and depth to top of perforations (table 7), suggesting that the ion balance changes so that groundwater is less acidic in the distal part of the valleys and in deep aquifers. Wilcoxon tests indicated significantly lower pH in wells classified as having modern and mixed ages compared to pre-modern ages (table 8). Groundwater found deeper in the aquifer, or in the distal parts of a flow path, generally has longer residence times than groundwater from shallow or proximal sites.

Implications of correlations between explanatory variables are discussed later in the report as part of the analysis of factors affecting individual constituents.
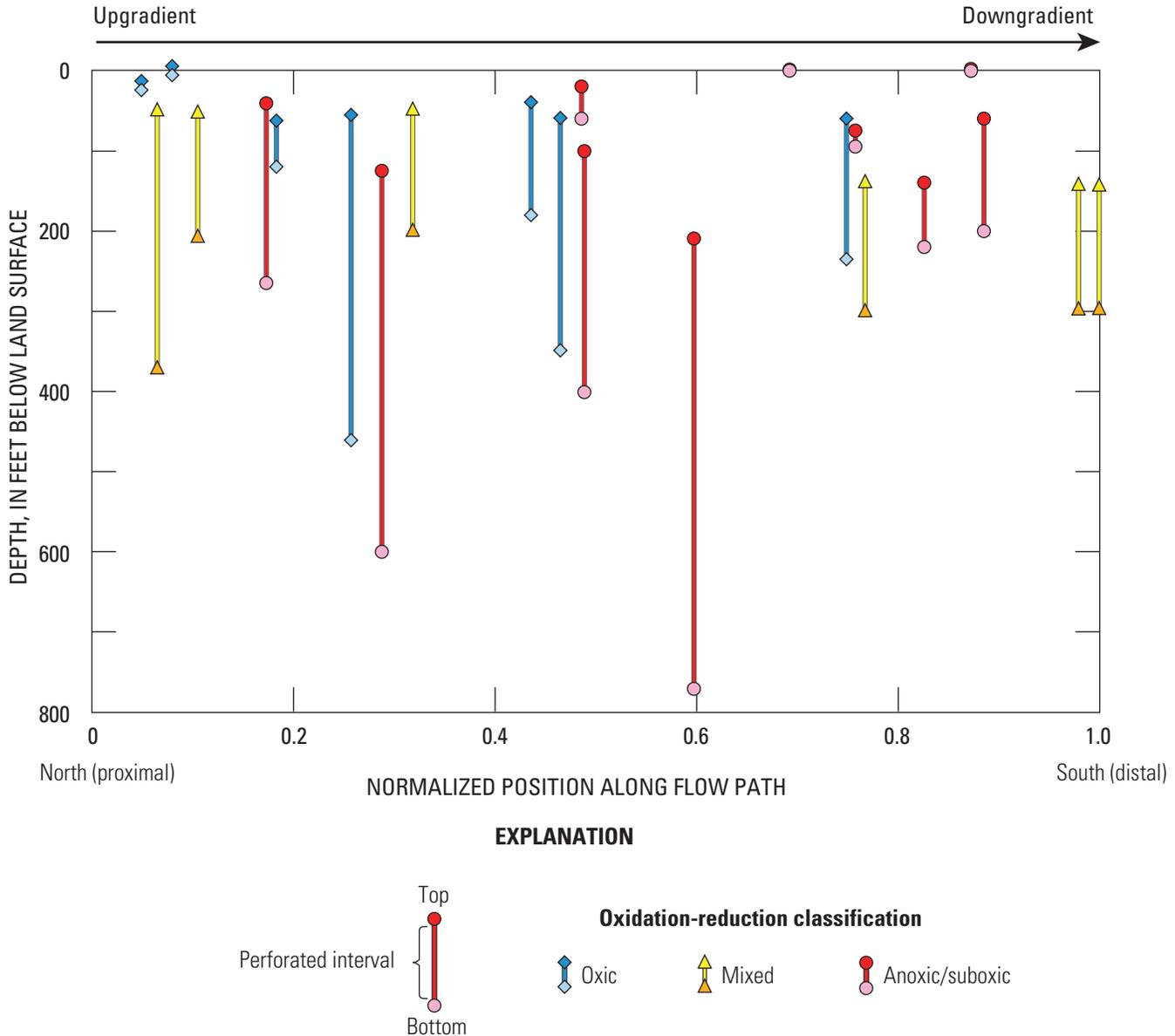
Figure 11. The relation of oxidation-reduction condition to normalized position of wells along a flowpath, and depth of perforated interval of wells, North San Francisco Bay study unit, California.

Status and Understanding of Water Quality

The *status assessment* was designed to identify the constituents or classes of constituents most likely to be water quality concerns by virtue of their high concentrations or their prevalence. Approximately 28,000 individual analytical results were included in the assessment of groundwater quality for the NSF study unit. The *status assessment* applies only to constituents having regulatory or nonregulatory health-based or aesthetic/technical- based benchmarks established by the USEPA or the CDPH (as of 2009). The spatially-distributed, randomized approach to well selection and data analysis yields a view of groundwater quality in which all areas of the public-supply aquifers are weighted equally; regions with a high density of groundwater use or with high density of potential contaminants were not preferentially sampled. The understanding assessment identifies the natural and human factors affecting water quality in the NSF study unit, and focuses on the constituents identified as significant in the status assessment.
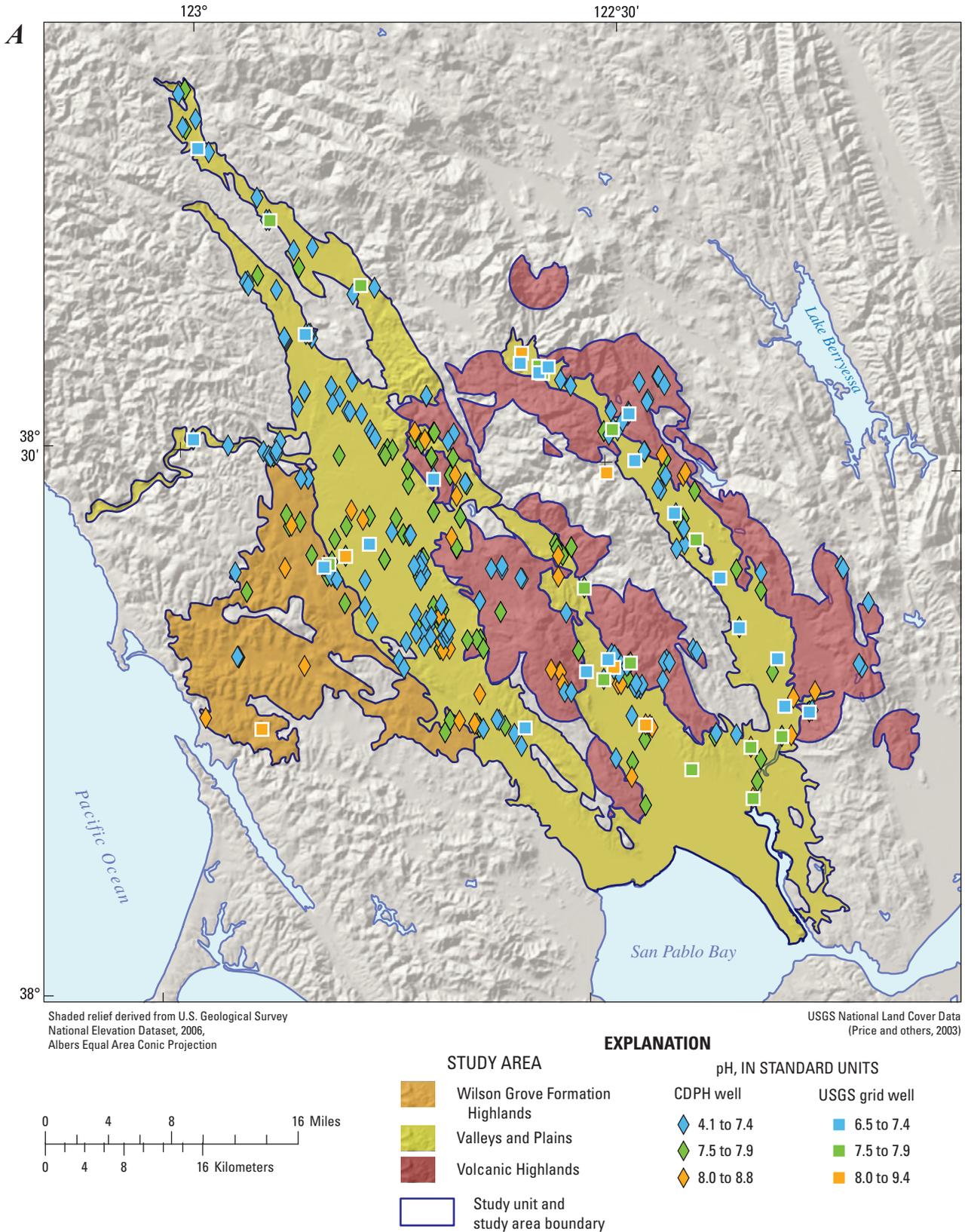
Figure 12A. pH levels in U.S. Geological Survey (USGS) grid wells, USGS-understanding wells, and California Department of Public Health (CDPH) wells, North San Francisco Bay study unit, California.
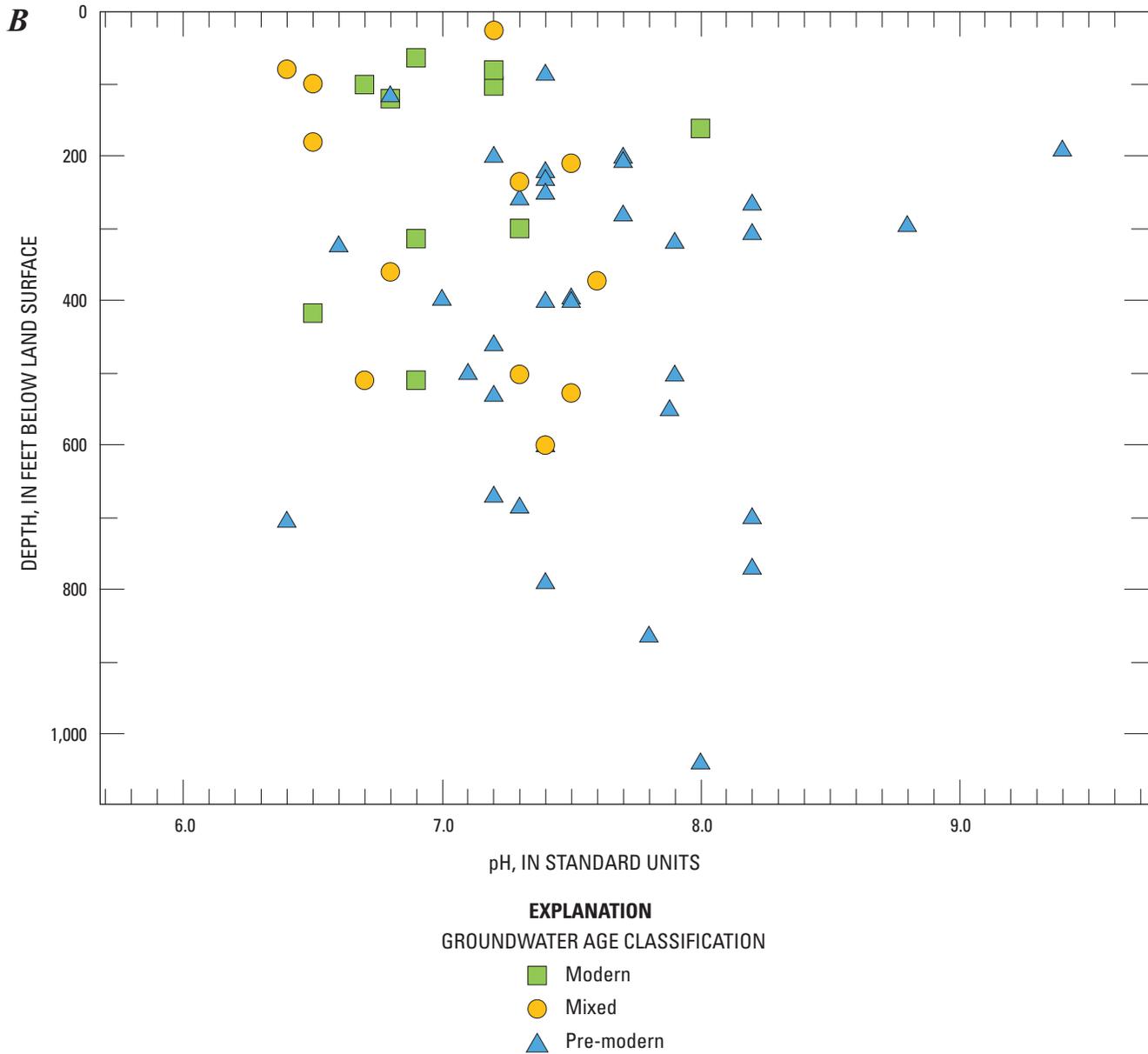
Figure 12*B*.   pH as a function of well depth and groundwater age classification, North San Francisco Bay study unit, California.

The following discussion of the *status and understanding assessment* results is divided into inorganic and organic constituents. The assessment begins with a survey of how many constituents were detected at any concentration compared to the number analyzed, and a graphical summary of the relative-concentrations of constituents detected in the grid wells. Results then are presented for the subset of constituents that met criteria for inclusion based on concentration, or for organic constituents, prevalence.

Spatially-weighted high aquifer-scale proportions fell within the 90-percent confidence intervals for their respective grid-based aquifer-scale high proportions for all of the 15 constituents listed on table 4, providing evidence that the grid-based approach yields statistically equivalent results to the spatially-weighted approach.

Table 8. Results of Wilcoxon rank sum tests on grid-well data used to determine significant differences between constituent values grouped by explanatory factor classes, North San Francisco Bay study unit, California.

[Wilcoxon rank sum tests with exact distribution and continuity correction; Z, test statistic for Wilcoxon test; significantly positive Z value (first classification is larger than second); significantly negative Z value (first classification is smaller than the second); nc, no significant correlation; PCE, tetrachloroethene; TCE, trichloroethene]

Selected water-quality constituents	Groundwater age classification			Geochemical conditions classifications			Land-use classifications					
	Modern age compared with mixed age	Mixed age compared with pre-modern age	Modern age compared with pre-modern age	Oxic conditions compared with mixed conditions	Mixed conditions compared with anoxic/suboxic conditions	Oxic conditions compared with anoxic/suboxic conditions	Natural compared with agricultural land use	Natural compared with mixed land use	Natural compared with urban land use	Agricultural compared with mixed land use	Agricultural compared with urban land use	Urban compared with mixed land use
						Z: Test statistic for Wilcoxon test						
Arsenic	nc	nc	−2.38	nc	nc	nc	nc	nc	nc	nc	nc	nc
Boron	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
Iron	nc	nc	−2.20	−3.62	nc	nc	nc	nc	nc	nc	nc	nc
Lead	nc	nc	nc	2.49	nc	nc	nc	nc	nc	nc	nc	nc
Manganese	−2.04	nc	−2.34	−2.23	nc	nc	nc	nc	nc	nc	nc	nc
Total dissolved solids	nc	nc	−2.59	nc	nc	nc	nc	nc	nc	nc	nc	nc
Dissolved oxygen	nc	nc	2.12	nc	2.69	4.30	nc	nc	nc	nc	nc	nc
pH	nc	−2.51	−3.03	−2.05	nc	−2.82	nc	nc	nc	nc	nc	nc
Nitrate plus nitrite, as nitrogen	nc	3.67	3.31	nc	2.86	2.98	nc	nc	nc	nc	nc	2.25
Chloroform	nc	2.33	nc	nc	2.06	2.06	nc	−2.56	−2.04	nc	nc	nc
Solvents, sum of concentrations (PCE + TCE + 1,1-dichloro-ethane)	nc	nc	2.68	nc	nc	nc	nc	nc	nc	nc	nc	nc
Simazine	2.68	2.34	5.04	nc	nc	nc	nc	nc	nc	nc	nc	nc

Inorganic Constituents

Inorganic constituents generally occur naturally in groundwater, although their concentrations may be influenced by human as well as natural factors. All 50 inorganic constituents analyzed by the USGS–GAMA were detected in the NSF study unit, of which 31 had regulatory or nonregulatory health-based benchmarks, 6 had nonregulatory aesthetic/technical-based benchmarks, and 13 had no established benchmarks (table 5). The inorganic constituents detected at high relative-concentrations in one or more grid wells were arsenic, boron, lead, iron, manganese, and total dissolved solids (table 4). The maximum relative-concentration (sample concentration divided by the benchmark concentration) for each constituent is indicated in figure 13.

Nine inorganic constituents, the trace elements arsenic, boron, lead, mercury, molybdenum, iron and manganese; the nutrient nitrate (as nitrogen); and TDS, met the selection criterion of having maximum relative-concentrations greater than 0.5 in the grid-based aquifer proportions (fig. 13; table 4). Inorganic constituents, as a group (nutrients, trace elements, and radioactive constituents), had high proportions in 14.0 percent of the primary aquifers, moderate proportions in 35.8 percent, and low proportions in 50.2 percent (table 9). High aquifer proportion equals the percentage (%) of grid wells with high relative-concentrations, and therefore the percentage (%) of the primary aquifers with high values.

Trace Elements

Trace elements, as a class, had high relative-concentrations (for one or more constituents) in 13.6 percent of the primary aquifers, moderate values in 33.3 percent, and low values in 53.1 percent (table 9). High relative-concentrations of trace elements reflected high relative-concentrations of arsenic (10.0 percent), boron (4.1 percent), and lead (1.6 percent) (table 4).

Figure 14 shows maximum relative-concentrations of inorganic constituents in grid wells. To illustrate the spatial distributions of inorganic constituents, figures 15A–F are maps showing arsenic, boron, lead, nitrate, manganese, iron, and TDS data for USGS grid wells and CDPH wells from the period August 30, 2001 to September 1, 2004.

Table 4 lists the percentage of the primary aquifers with high and moderate relative-concentrations for the individual constituents. Ten percent of the primary aquifers had high relative-concentrations of arsenic and 25 percent had moderate relative-concentrations (table 4). High and moderate relative-concentrations of arsenic occurred in all three study areas (figs. 14, 15A). 4.1 percent of the primary aquifers had high relative-concentrations of boron and 5.4 percent had moderate relative-concentrations. Lead was detected at a high

relative-concentration in one grid well (1.6 percent of the primary aquifers) and at a moderate relative-concentration in one grid well (1.6 percent of the primary aquifers), both located in the Valley and Plains study area (figs. 14, 15C). Mercury had high relative-concentration in 0 percent of the primary aquifers and moderate relative-concentrations in 1.4 percent. Molybdenum had high relative-concentration in 0 percent of the primary aquifers and moderate values in 3.1 percent.

Three trace elements—aluminum, antimony, and nickel—had spatially-weighted high relative-concentrations in 0.6 percent, 0.7 percent, and 0.2 percent of the primary aquifers, respectively, as compared to 0 percent for these elements for the grid-based approach (table 4). The spatially-weighted approach includes data from a larger number of wells than the grid-based approach, and therefore is more likely to include constituents present at high concentrations in small proportions of the primary aquifers.

The trace elements cadmium, chromium, copper, and thallium had high relative-concentrations in at least one well reported in the CDPH database before 2001 but not during the current period of study (table 6), and these high values represented historic values rather than current values.

Among constituents with SMCLs, iron had a high relative-concentration in 24.4 percent and a moderate relative-concentration in 9.0 percent of the primary aquifers (table 4, fig. 14). High relative-concentrations of iron were in a greater percentage of the VP study area (20 percent) than in the VOL study area (5 percent) or the WG study area (0 percent). Manganese had a high relative-concentration in 40.8 percent and a moderate relative-concentration in 7.9 percent of the primary aquifers. High relative-concentrations of manganese were in a greater percentage of the VP study area (43 percent) than in the VOL study area (11 percent) or the WG study area (0 percent).

Understanding Assessment for Arsenic

Arsenic is a naturally occurring semi-metallic trace element. Potential sources of arsenic to groundwater are both natural and anthropogenic. Natural sources include the dissolution of arsenic-rich minerals, such as arsenian pyrite, a common constituent of shales, and apatite, a common constituent of phosphorites. Arsenic can also be used as a wood preservative, in glass production, in paints, dyes, metals, drugs, soaps, and semiconductors, and in mining copper and gold (Welch and others, 2000). Arsenic solubility increases with increasing water temperature, such that hydrothermal fluids often have higher arsenic concentrations (Ballantyne and Moore, 1988; Webster and Nordstrom, 2003), as do older groundwaters that have had extended exposure to arsenic bearing minerals.
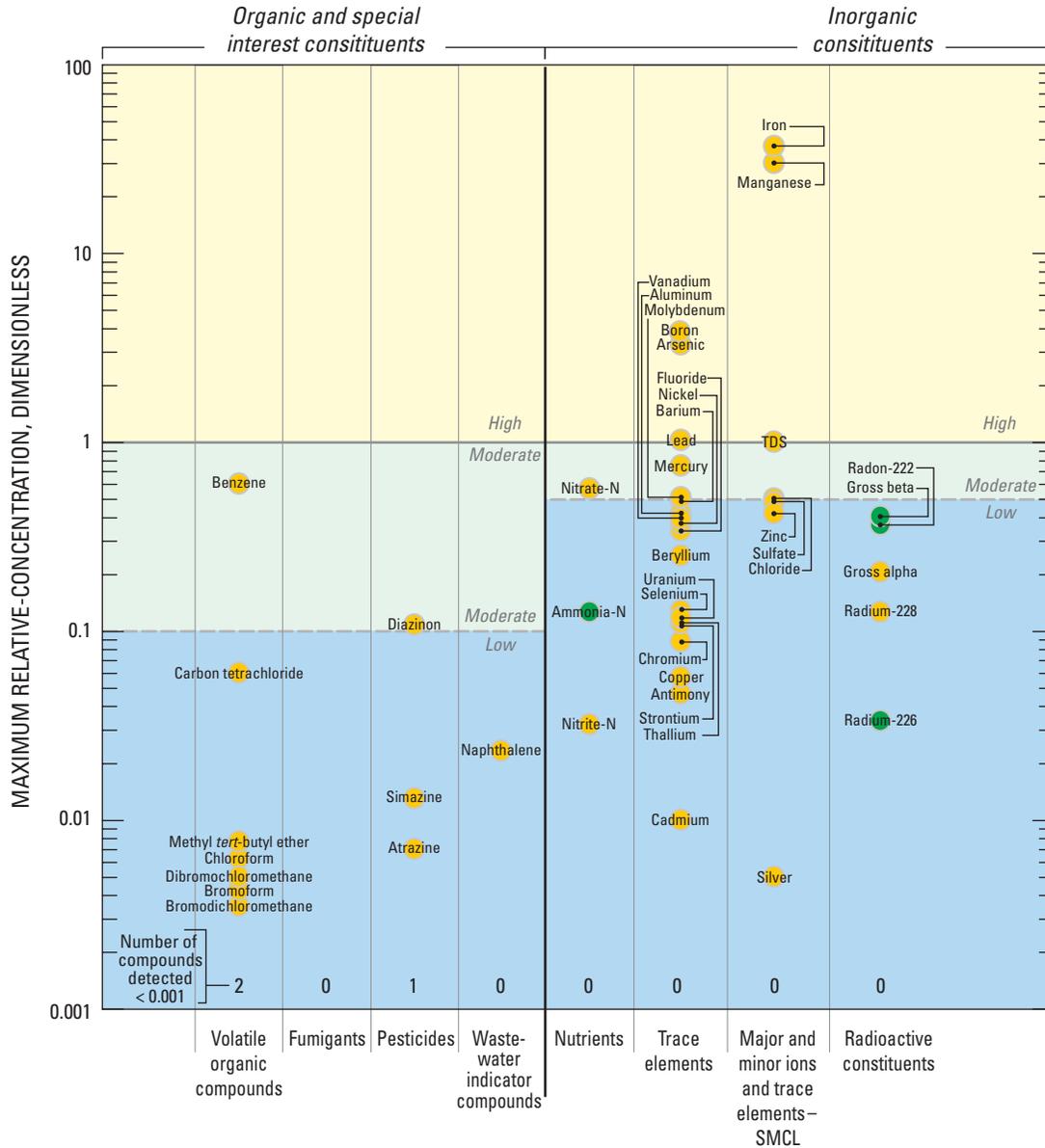
Figure 13. Maximum relative-concentration of constituents, by constituent type, detected in grid wells in the North San Francisco Bay study unit, California. N, nitrogen; TDS, total dissolved solids; SMCL, secondary maximum contaminant level.

Table 9.   Aquifer-scale proportions for constituent classes, North San Francisco Bay study unit, California.

[High, concentrations greater than benchmark; moderate, concentrations less than benchmark and greater than or equal to 0.1 of benchmark for organic constituents or 0.5 of benchmark for inorganic constituents; low, concentrations less than 0.1 of benchmark for organic constituents or 0.5 of benchmark for inorganic constituents. SMCL, secondary maximum contaminant level; VOC, volatile organic compound. Values are grid based except where footnoted]

Constituent class	Not detected	Aquifer proportion, in percent		
		Low	Moderate	High
Inorganic constituents with human-health benchmark				
Trace elements	0.0	53.1	33.3	13.6
Radioactive	0.0	100.0	0.0	0.0
Nutrients	0.0	97.0	2.6	[1] 0.4
Major and minor elements	0.0	98.7	[1] 0.1	[1] 1.2
Total for inorganic constituents with human-health benchmarks	0.0	50.2	35.8	[1] 14.0
Inorganic constituents with aesthetic benchmark				
Total dissolved solids (SMCL)	0.0	91.7	7.1	1.2
Iron and manganese (SMCL)	0.0	39.8	17.9	42.3
Chloride (SMCL)	0.0	99.3	0.0	[1] 0.7
Organic constituents with human-health benchmark				
Solvents	84.1	12.0	[1] 2.5	[1] 1.4
Other VOC	93.9	4.8	1.2	[1] 0.1
Herbicides	88.0	12.0	0.0	0.0
Insecticide	98.8	0.0	1.2	0.0
Total for organic constituents with human-health benchmarks	64.8	28.9	[1] 4.9	[1] 1.4
Constituents of special interest				
Perchlorate and *N*-nitrosodimethylamine (NDMA)	100.0	0.0	0.0	0.0

[1] Spatially-weighted value.

Arsenic mobilization and distribution in groundwater is influenced by the oxidation-reduction (redox) and pH conditions of the groundwater system. Arsenic is stable in two oxidation states in the environment: arsenite (As^{+3}) and arsenate (As^{+5}). Over a wide pH range and under oxic conditions, arsenate (As^{+5}) is predicted to be the predominant species, whereas under more reducing (anoxic) conditions, arsenite (As^{+3}) would likely be predominant (Welch and others, 1988). Laboratory reaction experiments by Islam and others (2004) indicate that arsenite was the dominant arsenic species resulting from reductive dissolution of iron oxides by microbial activity and the addition of organic carbon, even though the solid-phase arsenic was in the form of arsenate.

Previous investigations (Belitz and others, 2003) and reviews of arsenic (for example, Welch and others, 2000, 2006; Frankenberger, 2002; Ravenscroft and others, 2009) have attributed elevated arsenic concentrations in groundwater to two mechanisms: the release of arsenic from dissolution of iron or manganese oxides under iron- or manganese-reducing conditions, and the desorption of arsenic from aquifer sediments, or inhibition of arsenic sorption to aquifer sediments, as a result of alkaline groundwater conditions (pH values greater than 8.0).

Evidence for the first mechanism, release of arsenic under reducing conditions, in NSF groundwaters includes the association of high and moderate concentrations of arsenic with groundwater having manganese- or iron-reducing conditions, and the occurrence of arsenite as the predominant arsenic species in these groundwaters. Concentrations of arsenic were >10 µg/L (high relative-concentration) in 8 wells; trace element and pH data were available for 5 of these wells (fig. 16*B*). Two of the 5 wells having arsenic concentrations >10 µg/L had pH ≤7.5, manganese concentrations >100 µg/L (manganese-reducing conditions), and iron concentrations >100 µg/L (iron-reducing conditions). Eight of the 20 wells that had moderate relative-concentrations of arsenic (5 to 10 µg/L) had manganese concentrations >50 µg/L, and 7 of these wells had iron concentrations >100 µg/L, suggesting that reductive dissolution of iron and manganese oxides may account for the high and moderate concentrations of arsenic in these wells.
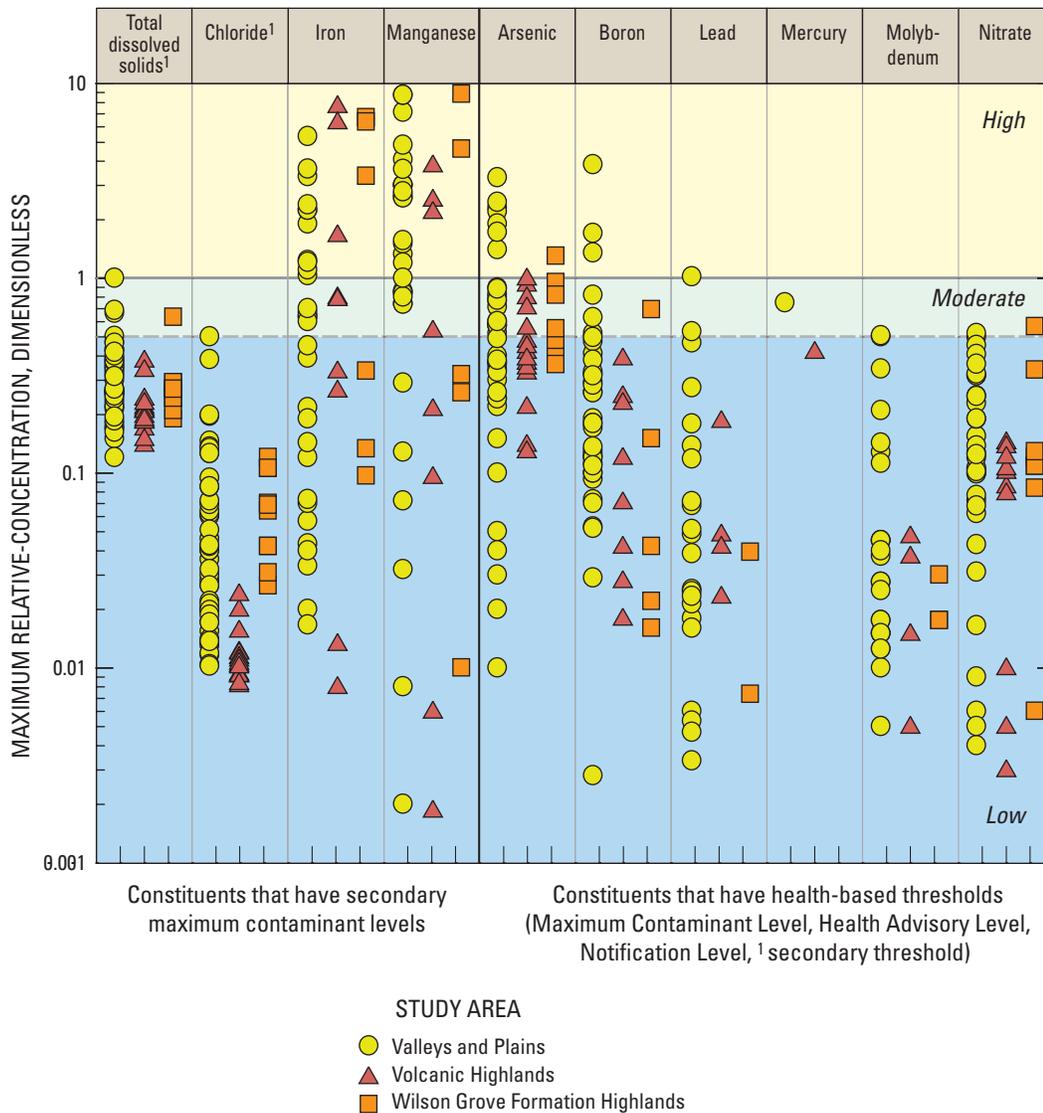
Figure 14. Maximum relative-concentrations of selected trace elements, nutrients, and major and minor ions in grid wells, North San Francisco Bay study unit, California.

Arsenic speciation data was collected at 15 wells (Kulongoski and others, 2006, table 17). Arsenite (As^{+3}) was the dominant arsenic species in four wells that had iron concentrations >100 µg/L; arsenate (As^{+5}) was the dominant arsenic species in the other 11 wells, which had iron concentrations <100 µg/L. The presence of arsenite as the dominant dissolved arsenic species in iron-reduced water in the NSF is consistent with arsenic mobilization under reducing conditions.

Evidence for the second mechanism, desorption of arsenic from aquifer sediments or inhibition of arsenic sorption to aquifer sediments with increasing pH, in 15 out of 25 wells that had high and moderate relative-concentrations of arsenic, includes pH conditions ≥7.4, manganese concentrations <100 µg/L, and iron concentrations <100 µg/L. The pH in 2 of the wells was >8.0, indicating that alkaline conditions may contribute to high concentrations of arsenic in these wells. Under oxic conditions, it is expected that dissolved arsenate would be the dominant species in groundwater (Islam and others, 2004) and arsenate would be the dominant species in most of the NSF groundwater with iron concentrations <100 µg/L.

Figure 15. Relative-concentrations of selected inorganic constituents in U.S. Geological Survey (USGS) grid and USGS-understanding wells and California Department of Public Health (CDPH) wells (data from the period August 30, 2001, to September 1, 2004), North San Francisco Bay study unit, California: *A.* arsenic, *B.* boron, *C.* lead, *D.* nitrate plus nitrite, as nitrogen, *E.* manganese, *F.* iron, and *G.* total dissolved solids.

Figure 15. Continued.

C

Shaded relief derived from U.S. Geological Survey
National Elevation Dataset, 2006,
Albers Equal Area Conic Projection

EXPLANATION

STUDY AREA

Wilson Grove Formation Highlands

Valleys and Plains

Volcanic Highlands

LEAD, IN MICROGRAMS PER LITER

CDPH well		Relative-concentration	USGS grid well	
🔵	0.0–7.5	Low	🟦	0.0–7.5
🟢	7.6–15.0	Moderate	🟩	7.6–15.0
🟠	15.1–55.0	High	🟧	15.1–15.3

Figure 15.   Continued.

Figure 15. Continued.

Figure 15. Continued.

Figure 15.   Continued.

Figure 15.   Continued.

Figure 16. Arsenic concentration related to *A.* classifications of groundwater age and *B.* well depth, manganese and iron concentrations, and pH in grid and understanding wells sampled for the North San Francisco Bay study unit, California.

Ten percent of the primary aquifers had high relative-concentrations of arsenic and 25 percent had moderate relative-concentrations (table 4). Arsenic distribution was not significantly correlated to either redox classification or pH conditions of groundwater in the NSF study unit (tables 8, 10). This result suggests that several factors, or a combination thereof, are influencing arsenic concentrations in groundwater. Arsenic concentrations were significantly higher in samples having a groundwater age classified as pre-modern, than in samples classified as having modern ages (table 8, fig. 16A). This suggests that groundwater accumulates arsenic over time from longer exposure to arsenic-bearing minerals. Arsenic was positively correlated with groundwater temperature. The higher arsenic concentrations in warmer groundwater may result from the increase in solubility of arsenic with increasing water temperature or from mixing with the deeper hydrothermal system. The negative correlation of arsenic with percent natural land use likely reflects other factors (table 10).

In the North San Francisco Bay study unit, nearly all of the samples with high arsenic relative-concentrations were from wells in the Valleys and Plains study area (fig. 15A). Areas containing groundwaters that have high arsenic concentrations are grouped into four areas: the Santa Rosa Valley, the southern Napa Valley, the Calistoga area, and the Agua Caliente (Sonoma) area (fig. 2). The locations of elevated concentrations of arsenic in the Santa Rosa Valley and southern Napa Valley (fig.15A) correspond to areas that have manganese- (or iron-) reducing (anoxic) conditions (figs. 15E and 15F) and likely result from the release of arsenic during reductive dissolution of iron or manganese oxides.

The elevated concentrations of arsenic in the Calistoga and Agua Caliente hydrothermal areas most likely result from shallow groundwater mixing with deep thermal waters. Deep thermal waters have high temperatures and high pH values. High temperatures will cause arsenic (and boron) to leach from nearly any rock (Webster and Nordstrom, 2003), whereas alkaline conditions facilitate the desorption of arsenic and inhibit the sorption of arsenic to aquifer sediments. The increase in arsenic solubility caused by an increase in water temperature, and the desorption or inhibition of sorption of arsenic under alkaline conditions results in the higher arsenic concentrations in groundwater from the Calistoga and Agua Caliente hydrothermal areas. A more comprehensive investigation of the hydrothermal system in the NSF study unit is being prepared and will lead to a separate publication.

Understanding Assessment for Boron

Boron is a naturally occurring metalloid that occurs in many minerals. Natural sources of boron include igneous rocks, such as granite and pegmatite (as the mineral tourmaline), and evaporite minerals, such as borax, kernite, and colemanite (Hem, 1970; Reimann and Caritat, 1998). Borax, a boron-containing evaporate mineral that is mined in California, is used as a cleaning agent and therefore may be present in sewage and industrial wastes. Seawater contains 4.5 mg/L of boron (Summerhayes and Thorpe, 1996), and boron is associated with thermal springs (Hem, 1970; Kulongoski and others, 2006). Boron also is used to produce semiconductors, insecticides, preservatives, and chemical reagents.

Boron speciation in groundwater is dependent on pH, salinity, and specific cation content. The neutral form of boron, $B(OH)_3$, is predominant at pH <9.2, while the anionic form, $B(OH)_4^-$, is predominant at pH >9.2 (Dotsika and others, 2006). Boron is highly mobile because no mineral has a low enough solubility to provide an upper limit to its concentration range. However, boron concentration in groundwater is limited by mixing of thermal water with nonthermal waters.

Boron had high relative-concentrations in 4.1 percent of the primary aquifers and was detected at 3 VP wells at high relative-concentration, and at 4 wells (3 VP and 1 WG) at moderate relative concentrations (fig. 15B). Boron distribution was not significantly correlated to redox classification or pH (tables 8, 10), nor did it correlate to land use or groundwater age classifications.

In the northern Alexander Valley, higher concentrations of boron may result from the infiltration of waters from Hot Creek, which drains the Geysers geothermal area near Middletown north of Calistoga. Similarly, northern Napa Valley has higher boron concentrations, which may result from shallow groundwater mixing with the deeper hydrothermal system that provides thermal waters to numerous spas and the "Old Faithful Geyser" in Calistoga. In the Sonoma and Napa-Sonoma lowlands, higher boron concentrations may result from the mixing of shallow groundwater with the discharge from hot springs in Sonoma and Agua Caliente, or with high salinity connate water from the dissolution of evaporites.

Table 10. Results of non-parametric (Spearman's method) analysis for correlations between selected water-quality constituents and potential explanatory factors, North San Franciso Bay study unit, California.

[AL-US, U.S. Environmental Protection Agency (USEPA) action level; CDPH, California Department of Public Health; MCL-US, USEPA maximum contaminant level; N, nitrogen; NL-CA, CDPH notification level; SMCL-CA, CDPH secondary maximum contaminant level; TDS, total dissolved solids. nc, no significant correlation; ρ, Spearman's correlation statistic]

Selected water-quality constituent	Benchmark type	High proportion, in percent	Potential explanatory factors [1]									
			Data analyzed: grid and understanding wells							Data analyzed: grid wells		
			Depth to top of perforations	Well depth	Dissolved oxygen	pH	Groundwater temperature	Normalized position along flowpath	Altitude of land surface at well	Percent urban land use [2]	Percent agricultural land use [2]	Percent natural land use [2]
			ρ: Spearman's correlation statistic							ρ: Spearman's correlation statistic		
Inorganic constituent												
Arsenic [3]	MCL-US	10.0	nc	nc	nc	nc	0.24	nc	nc	nc	nc	−0.23
Boron [3]	NL-CA	4.1	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
Iron [3]	SMCL-CA	24.4	nc	nc	−0.40	nc	nc	nc	nc	nc	nc	nc
Lead	AL-US	1.6	nc	nc	0.38	−0.25	nc	nc	nc	nc	nc	nc
Manganese [3]	SMCL-CA	40.8	nc	nc	nc	nc	nc	nc	nc	nc	nc	nc
TDS	SMCL-CA	0.7	nc	nc	nc	0.43	nc	nc	−0.39	nc	nc	nc
Nitrate plus nitrite (as N)	MCL-US	0.4	nc	nc	0.63	nc	−0.40	nc	nc	nc	nc	−0.24
Organic constituent												
Chloroform [4]	MCL-US	0.0	nc	nc	nc	−0.28	−0.23	nc	nc	nc	nc	nc
Simazine [4]	MCL-US	0.0	−0.38	−0.49	nc	−0.33	−0.29	nc	nc	nc	nc	nc

[1] Excluding hydrothermal wells and spring.

[2] Within a circle with a radius of 500 meters centered around hydrothermic well and spring data.

[3] Constituents with greater than 2 percent high aquifer proportion.

[4] Single constituents with detection frequency greater than 10 percent of grid wells.

Understanding Assessment for Manganese and Iron

Potential natural sources of manganese and iron to groundwater include the dissolution of igneous and metamorphic rocks as well as the dissolution of various secondary minerals (Hem, 1970). Rocks that contain significant amounts of manganese and iron have a relatively high composition of the minerals olivine, pyroxene, and amphibole. Potential anthropogenic sources of iron and manganese to groundwater include effluents associated with the steel and mining industries (Reimann and Caritat, 1998), and soil amendments, in the form of manganese and iron sulfates, that are added to deficient soils in order to stimulant crop growth. Distributions of iron and manganese concentrations are strongly influenced by redox conditions in the aquifer. In sediments, the oxyhydroxides of manganese and iron are common as coatings on mineral surfaces and as suspended particles (Sparks, 1995). These oxyhydroxides are stable in oxygenated systems at neutral pH. However, under anoxic conditions, the process of reductive dissolution of these minerals affects the mobility of manganese and iron in aquifer systems (Sparks, 1995).

In the NSF study unit, concentrations of manganese were significantly correlated (negatively) with oxic compared with mixed conditions (table 8). Iron was significantly correlated (negatively) with DO (table 10) and with oxic compared with mixed redox conditions (table 8). Most high and moderate relative-concentrations of iron and manganese were in the VP study area, particularly the Santa Rosa Valley and the southern Napa Valley (figs. 2, 14, 15E, 15F), reflecting the natural distribution of iron- and manganese reducing conditions that result from reductive dissolution of iron and manganese oxides in the aquifer sediments.

Radioactive Constituents

The activities of radioactive constituents generally were low in the NSF study unit (table 4). Gross alpha radio-activity above the MCL-US of 15 pCi/L was detected in 1 well out of 194 during the current period of study, however, it was not the most recent value used to calculate aquifer-scale proportion. Activities of radium-226 were detected above the MCL-US (5 pCi/L) in two wells in 1996, before the current period of study, and were considered to be historical values (table 6).

Nutrients

Nutrients had high relative-concentrations in 0.4 percent of the primary aquifers and moderate in 2.6 percent (table 9) resulting from the detection of nitrate plus nitrite (table 4). Moderate relative-concentrations of nitrate plus nitrite primarily occur in the VP and WG study areas (fig.15D).

Understanding Assessment for Nitrate plus Nitrite

Although nitrate plus nitrite was not measured at high relative-concentrations in more than 2 percent of the primary aquifers, it is a constituent that is important to water quality and is discussed in this section. Nitrogen in groundwater occurs in the forms of dissolved nitrate and nitrite. Certain bacteria and algae naturally convert nitrogen from the atmosphere to nitrate, which is an important nutrient for plants. Nitrate is present in precipitation also, and is produced by desert plants (Hem, 1970). Anthropogenic sources of nitrate include its application as a fertilizer for agriculture, and livestock, when in concentrated numbers, produce nitrogenous waste that can leach into groundwater. Septic systems may also introduce nitrogenous waste into groundwater. In addition, nitrate may be associated with uranium mining and processing (Hem, 1970).

Nitrate plus nitrite concentrations were significantly greater in groundwater of modern age compared with pre-modern age, and mixed age compared with pre-modern age. Nitrate plus nitrite concentrations were significantly greater in wells with oxic conditions compared with anoxic/suboxic conditions, and mixed conditions compared with anoxic/suboxic conditions and in wells classified as urban compared with mixed land use (table 8, fig. 17). Nitrate plus nitrite was significantly correlated positively with dissolved oxygen and correlated negatively with groundwater temperature and percent natural land use (table 10). Some of the explanatory variables related to nitrate plus nitrite, such as dissolved oxygen and groundwater age, are generally related to each other (table 8), such that older water tends to have lower dissolved oxygen and higher pH and water temperature. The negative correlation between nitrate plus nitrite and natural land use (table 10) suggests that higher concentrations of nitrate plus nitrite are likely from anthropogenic sources.

Only one well had a moderate nitrate plus nitrite (as nitrogen) relative-concentration (>5 mg/L as nitrogen). This well had an urban/agricultural land-use classification, a 170-ft depth (52 m) to the top of the perforations, and a pre-modern age classification (fig. 17). Similarly, ten of the eleven samples that had the highest nitrate plus nitrite (as nitrogen) concentrations were from areas classified as urban/agricultural land. Nine of those samples were classified as modern or mixed age and were from wells that had depths to the top perforations <100 ft (30 m). In summary, most of the wells in which nitrate plus nitrite was detected were in areas where land was classified as urban or agricultural, had a depth to the top perforations <100 ft (30 m), and had groundwater primarily classified as modern or mixed age.
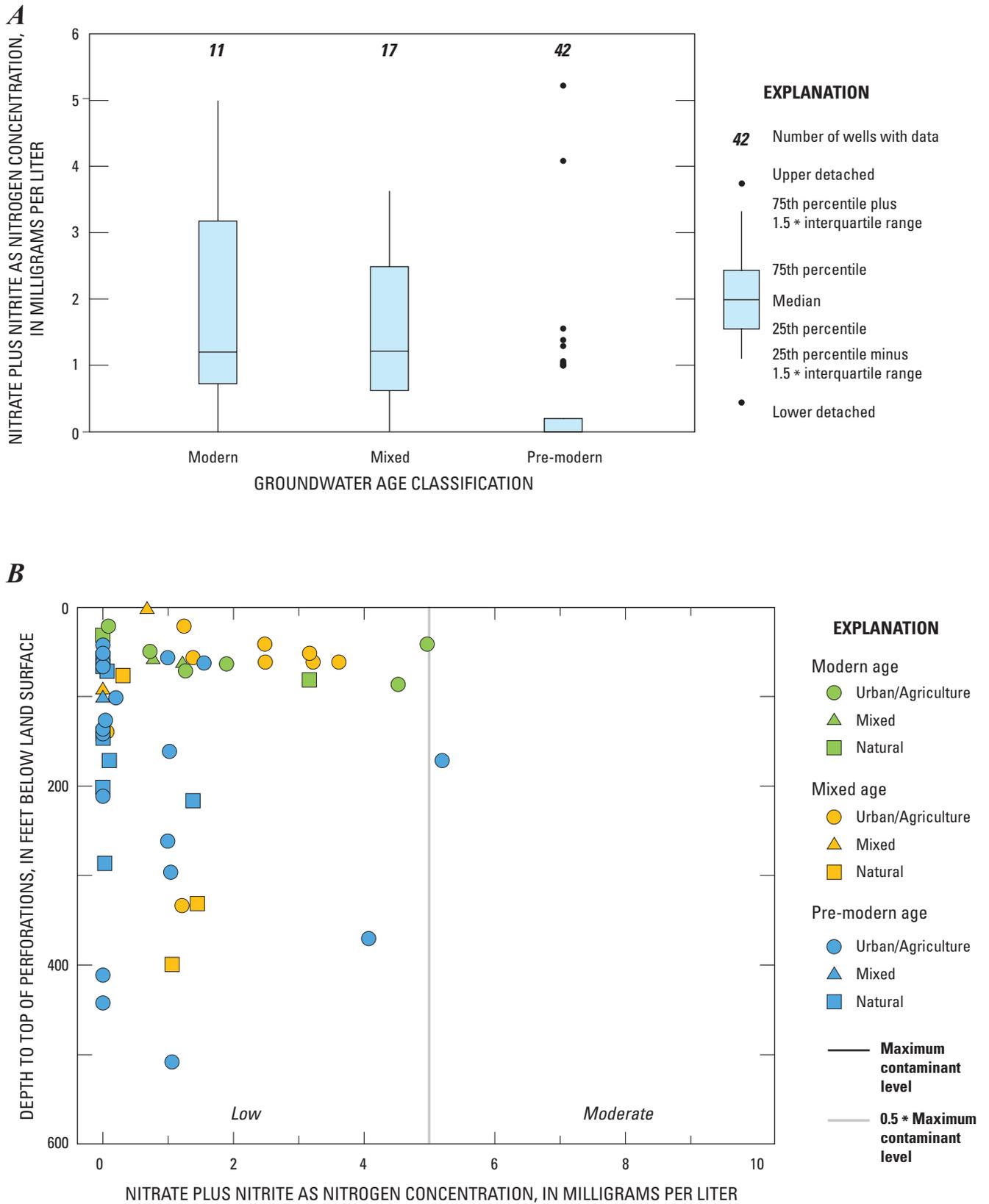
Figure 17. Nitrate plus nitrite, as nitrogen, concentrations related *A.* to classifications of groundwater age, *B.* to land use, age classification of groundwater, and depth to the top of perforations, and *C.* to dissolved oxygen concentrations in grid and understanding wells sampled for the North San Francisco Bay study unit, California.

C
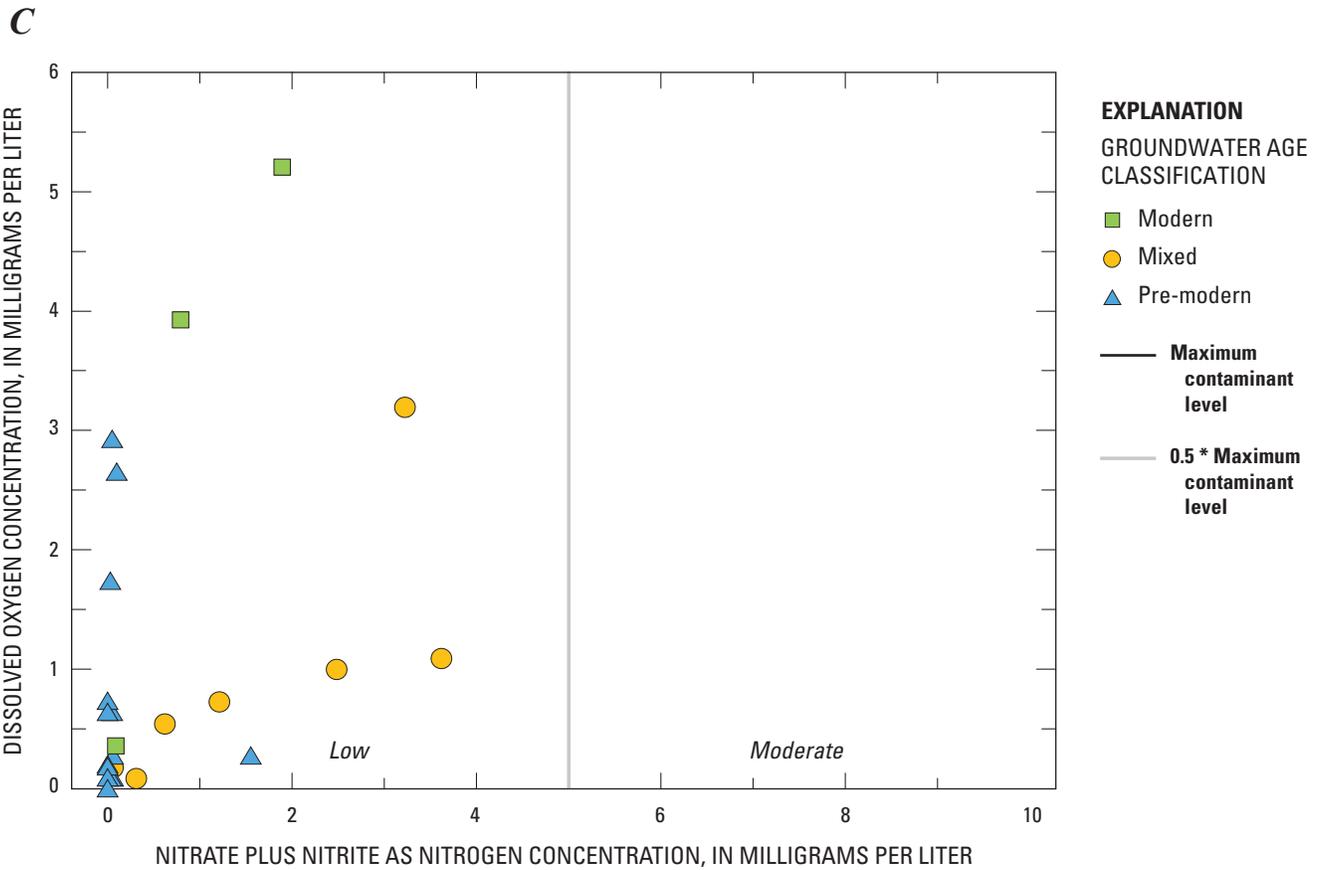
Figure 17.   Continued.

Under the anoxic conditions observed in some NSF wells, denitrification likely reduces nitrate in groundwaters, particularly in the deeper parts of the flow system. Denitrification of nitrate to dissolved nitrogen gas (N_2) in reducing groundwater has been reported in numerous studies (for example, Vogel and others, 1981; Kendall, 1998). Excess N_2 (Kulongoski and others, 2006, table 21) was measured in four groundwater samples in the VP study area, three of which were from groundwaters classified as anoxic/suboxic. These three samples had nitrate concentrations <0.06 mg/L. The fourth groundwater sample was oxic and had a nitrate plus nitrite (as nitrogen) concentration equal to 3.22 mg/L (Kulongoski and others, 2006, table 14). Data from the three samples are consistent with denitrification of nitrate in these wells.

Major and Minor Ions

The major ions chloride and sulfate, and TDS have upper SMCL-CA benchmarks based on aesthetic properties. The minor ion fluoride has an MCL-US, and the remaining seven major and minor ions do not have benchmarks.

TDS had high proportion of 1.2 percent of the primary aquifers, and moderate proportion of 7.1 percent (table 4). Chloride had aquifer high proportion of 0.7 percent, and fluoride had high proportion of 1.2 percent and moderate proportion of 0.1 percent.

Understanding Assessment for TDS

Although TDS was not measured at high relative-concentrations in more than 2 percent of the primary aquifers, it is a constituent that is important to water quality and is discussed in this section. The anion chloride is a major component of TDS, and its distribution, for the most part, reflects that of TDS. Natural sources of TDS include mixing of groundwater with deep saline groundwater (connate water), seawater intrusion from San Pablo Bay, concentration of salts by evaporation in discharge areas, and (or) rock/water interactions. Potential anthropogenic sources of TDS to groundwater in the NSF study unit include agricultural and urban irrigation evaporation, disposal of waste water and industrial effluent, and leaking water and sewer pipes.

In the NSF study unit, TDS had a significant positive correlation with pH and a negative correlation with the altitude of the well or altitude of land surface (table 10). TDS had a significant negative correlation with modern compared with pre-modern groundwater age (table 8), suggesting that dissolved solid concentrations are lower in younger groundwater. The median concentration of TDS in modern, mixed, and pre-modern groundwater were 220, 246, and 281 mg/L, respectively. Figure 18 compares the TDS and the altitude of land surface for NSF wells as a function of the normalized position of the wells along the flowpath (proximal, medial, or terminal). Concentrations of TDS in wells generally increased as the positions changed from proximal to medial to terminal (fig. 18). Evaporative enrichment of TDS as a result of irrigation practices was excluded as a cause for the increase in TDS along the flow paths because the groundwater samples from the NSF study unit follow the meteoric water-line relationship $\delta D = 8 * \delta^{18}O + 10$, and no deviation indicative of evaporation is observed (Kulongoski and others, 2006).

The high concentrations of TDS in wells VP-44, VP-36, and VP-28 most likely resulted from shallower groundwater mixing with deep saline (connate) water (Farrar and others, 2006) in the Napa Sonoma lowlands (fig. 2). These wells have distinctive chemistry, including the highest concentrations of several inorganic constituents measured in the NSF study; chloride (191 mg/L), sodium (270 mg/L), bromide (1.44 mg/L), iodide (1.1 mg/L), and sulfate (239 mg/L) (Kulongoski and others, 2006). Concentrations of iodide greater than the seawater value (0.06 mg/L; Hem, 1970) suggest that connate water is the source of the salinity to these wells.

Organic Constituents

The organic compounds are organized by constituent class, including three classes of volatile organic compounds (VOC) and two classes of pesticides. VOCs may be in paints, solvents, fuels, and refrigerants; they can be byproducts of water disinfection and are characterized by their volatile nature, or tendency to evaporate. In this report, VOCs are classified into three categories: trihalomethanes, solvents, and other VOCs (including gasoline additives and fumigants). Pesticides are used to control weeds, insects, or fungi in agricultural, urban, and suburban settings. In this report, pesticides are classified as either herbicides or insecticides.

Organic constituents were not detected at high relative-concentrations in grid wells; however, the gasoline additive benzene, and the insecticide diazinon were both detected at moderate relative-concentrations. Only 26 of the 255 organic compounds analyzed were detected, and most of these organic constituents (18 of the 26) have human-health benchmarks (table 7).

According to the spatially-weighted method, the proportion of the aquifer that had high relative-concentrations of organic constituents with human-health benchmarks was 1.4 percent (table 9), resulting from the high relative-concentrations of the solvents tetrachloroethene (PCE) (1.3 percent) and trichloroethene (TCE) (0.1 percent), and the organic synthesis reagent 1,1-dichloroethene (0.1 percent) (table 4). The proportion of the aquifer having moderate relative-concentrations of organic constituents was 4.9 percent (table 9).

Organic constituents were found in 41 percent of the 83 grid wells in the NSF study unit. The maximum relative-concentrations of two organic constituents, benzene and diazinon, were greater than 0.1 (figs. 19, 20). Two additional compounds, chloroform and simazine were detected in 10 percent or more of the primary aquifers. All concentrations of organic constituents in samples from grid and understanding wells were below human-health benchmarks.

VOCs were detected in 19 percent of the 83 grid wells representing the primary aquifers. Of the 10 VOCs detected, 9 were detected only at low relative-concentrations (fig. 19). One VOC, benzene, was detected at moderate relative-concentration in one sample. The trihalomethane (THM) chloroform was the only VOC detected in more than 10 percent of the grid wells.

Pesticides or pesticide degradates were detected in 16 percent of the 83 grid wells representing the primary aquifers. Of the 114 pesticides and pesticide degradates analyzed, 7 were detected; 4 were parent compounds with benchmarks, one was a parent compound without a benchmark, and two were degradates without benchmarks. All concentrations of pesticides were below human-health benchmarks. One pesticide, diazinon, was detected at moderate relative-concentration in one sample (fig. 20). The insecticide simazine was the only pesticide detected in 10 percent of the grid wells, (fig. 20). The individual constituents that were not detected and the wells sampled in the NSF study unit are listed in the report by Kulongoski and others (2006).
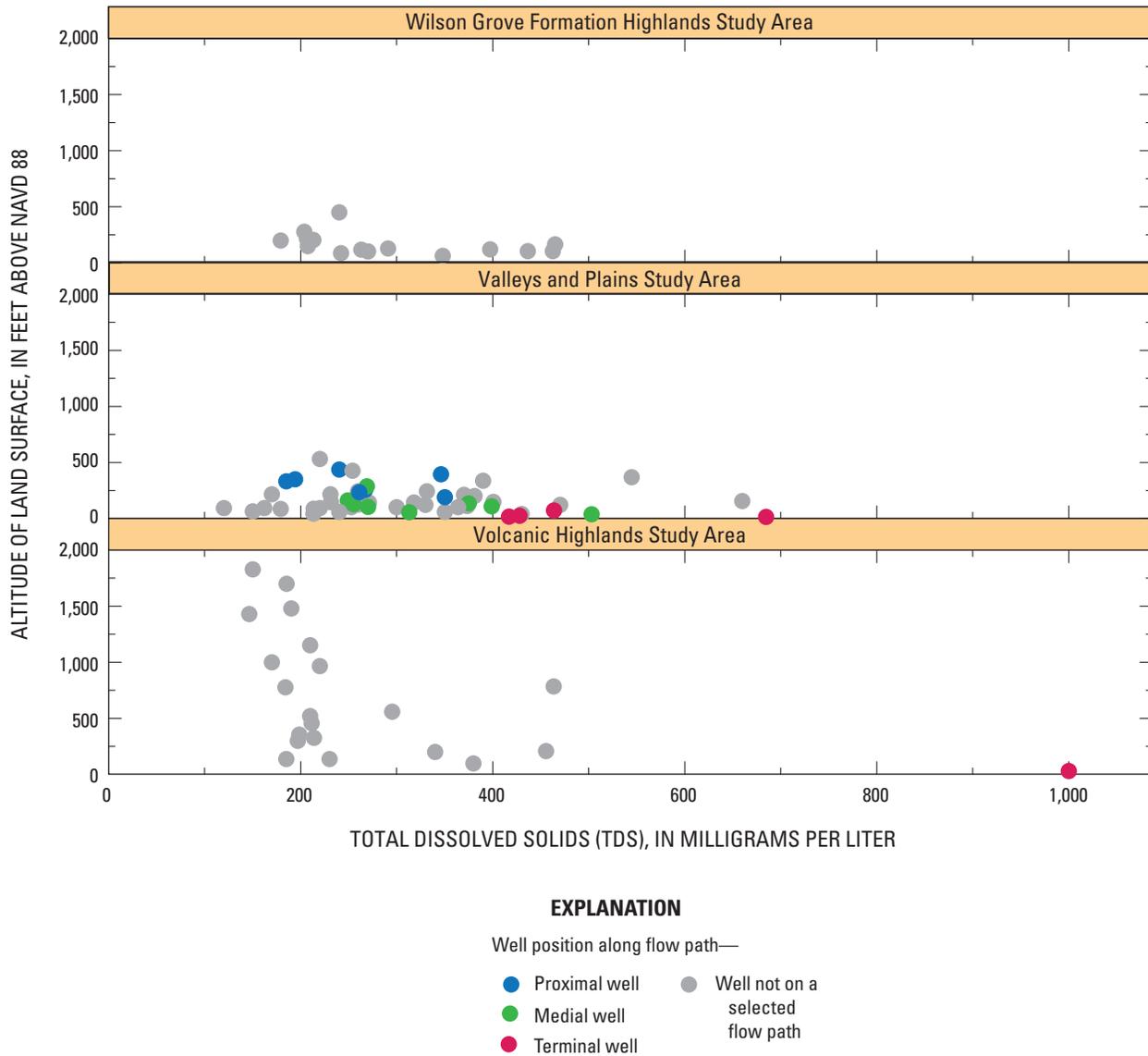
Figure 18.   Well altitude versus total dissolved solid concentrations in grid and understanding wells in the Wilson Grove Formation Highlands, Volcanic Highlands, and Valleys and Plains study areas of the North San Francisco Bay study unit, California. Positions along the flowpath (proximal, medial, or terminal) are indicated for some wells in the Valleys and Plains study area.

Trihalomethanes

Water used for drinking water and other household uses in both domestic and municipal systems commonly is disinfected with hypochlorite solutions (bleach). As a side effect to disinfecting the water, the hypochlorite reacts with organic matter to produce THMs and other chlorinated and/or brominated disinfection byproducts. The THM chloroform had a low proportion of 100 percent of the primary aquifers. Chloroform was detected in 15.7 percent of the 83 grid wells

(figs. 20, 21). Chloroform also was the most frequently detected VOC in groundwater according to the USGS National Water Quality Assessment (NAWQA) program (Zogorski and others, 2006). Potential urban sources of THMs include recharge from landscape irrigation with disinfected water, leakage from distribution or sewer systems, and industrial and commercial sources (Ivahnenko and Barbash, 2004).

Understanding Assessment for Chloroform

Chloroform was more prevalent in the VP study area (detection frequency 18 percent) than the VOL and WG study areas (fig. 20) (detection frequency 11percent, and 14 percent, respectively) (Kulongoski and others, 2006). Chloroform was significantly correlated (negatively) with land classified as natural compared with mixed land use and land classified as natural compared with urban land use (table 8). Chloroform was detected in two wells in land classified as natural, four wells each in land classified as urban and land classified as

agricultural, and three wells in land classified as mixed (fig. 21 —not all wells had well construction information). Nationally, THM concentrations have been strongly correlated with percent urban land use (Zogorski and others, 2006).

Although chloroform concentrations were not directly correlated with depth (table 10), eight of the thirteen wells in which chloroform was detected and for which construction information was available had depths to the top of the perforations of <102 ft (31 m) (fig. 22).
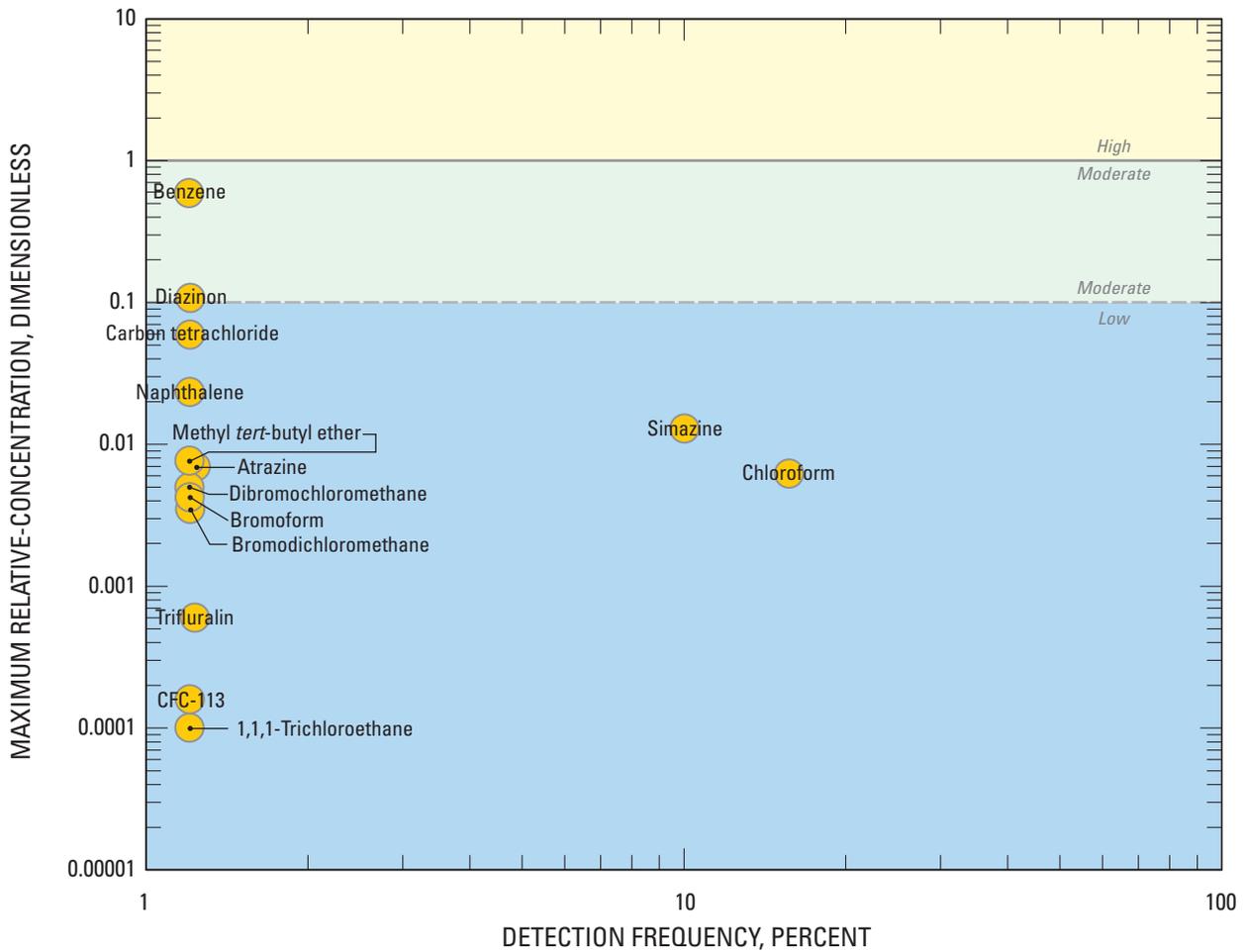
EXPLANATION

Simazine Name and center of symbol is the maximum relative-concentration for that constituent (more than 25 grid wells sampled)

Figure 19.   Detection frequency and maximum relative-concentration of organic and special interest constituents detected in grid wells in the North San Francisco Bay study unit, California. CFC-113, trichlorotrifluorethane.

Chloroform concentrations were significantly greater in groundwater classified as mixed age than in groundwater classified as pre-modern age (table 8); however, there was no significant difference between groundwater classified as modern age compared with mixed age and modern age as compared with pre-modern age. Seven of the 13 chloroform detections occurred in groundwater with mixed ages, 3 in groundwater classified as modern age, and 3 in groundwater classified as pre-modern age. Because water supplies have been disinfected with chlorine over the past 100 years, chloroform may be in relatively deep wells that do not appear to have modern (from the last 50 years) recharge water.

Chloroform concentrations were significantly correlated (positively) with wells having oxic compared with anoxic/suboxic groundwater conditions, and between wells having mixed compared with anoxic/suboxic conditions (table 8), suggesting that chloroform concentrations are greater in oxic than anoxic waters, which may result from anoxic groundwaters commonly being older than oxic groundwaters. Chloroform was significantly correlated (negatively) with the explanatory variables pH and groundwater temperature (table 10). Cooler groundwater temperatures may result from more recent groundwater recharge, while warmer temperatures and, often, higher pH result from longer residence times or interactions with the deeper hydrothermal system. These correlations suggest that cooler, younger, oxic groundwater is more likely to contain chloroform, because it was more recently recharged at land surface where exposure to anthropogenic compounds could occur.
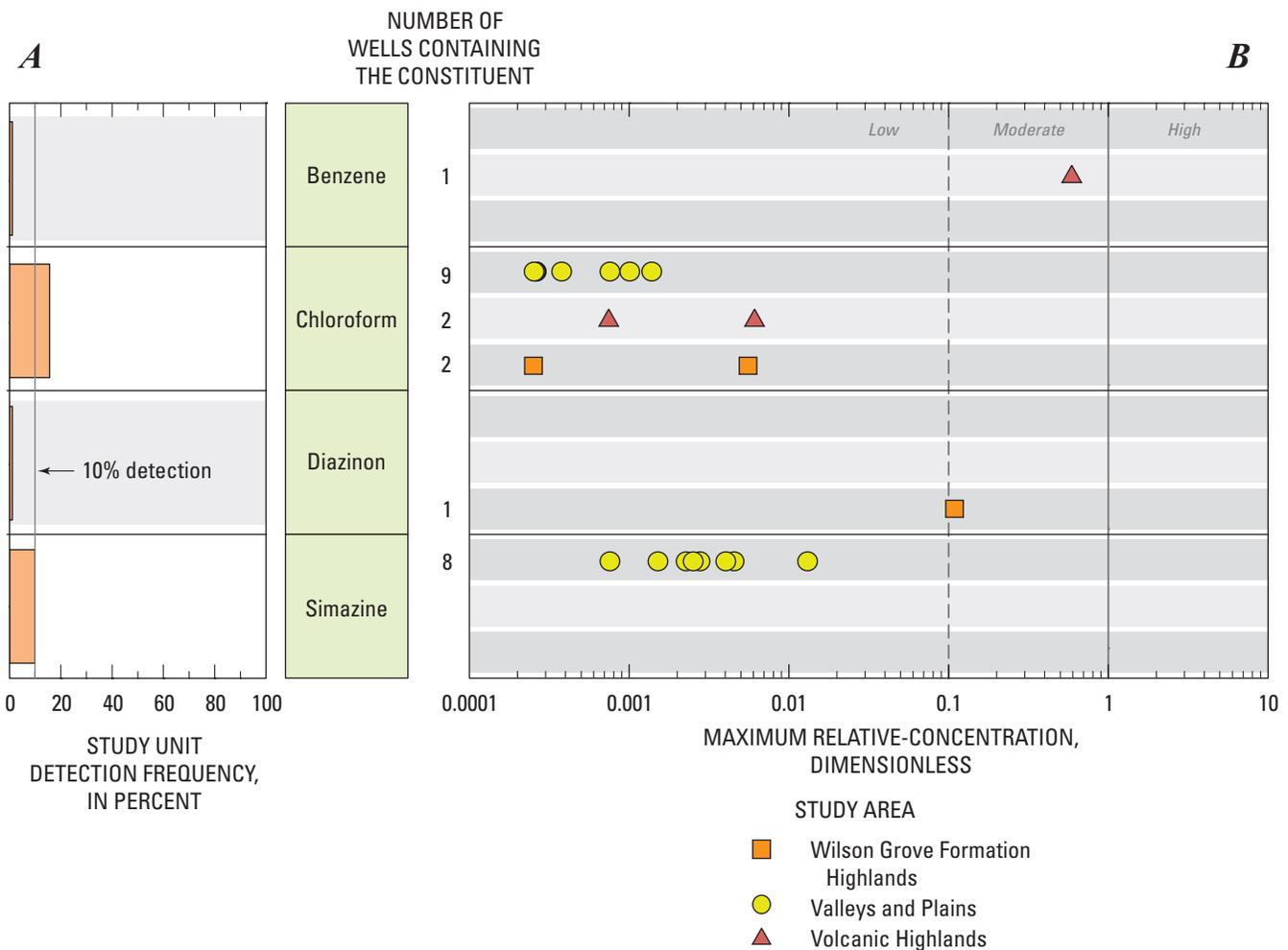
Figure 20.   *A.* Detection frequency and *B.* maximum relative-concentrations of selected organic and special-interest constituents in grid wells in the North San Francisco Bay study unit, California, August to December 2004.
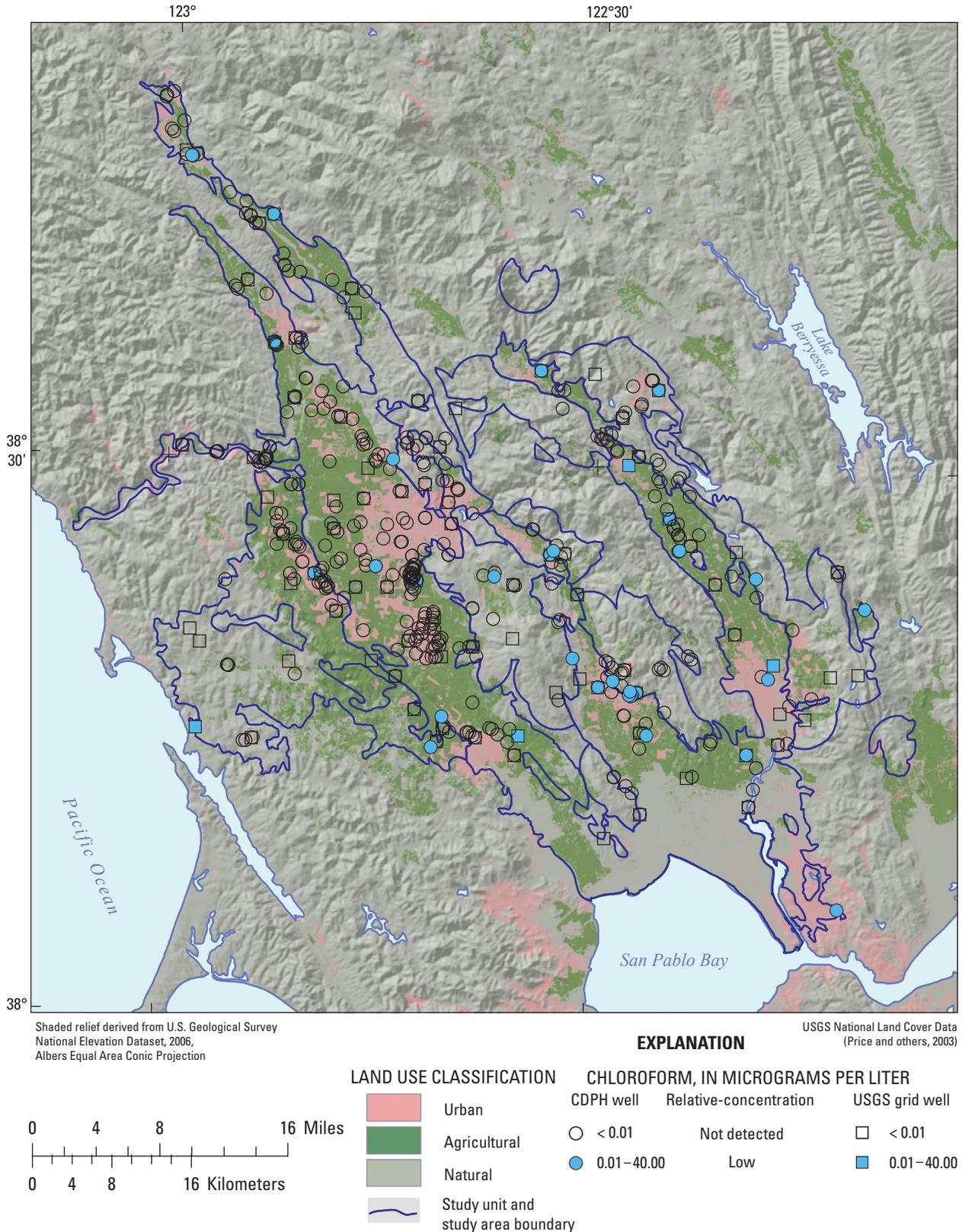
Figure 21.   Land-use classifications and the relative-concentrations of the trihalomethane chloroform in U.S. Geological Survey (USGS) grid wells and California Department of Public Health (CDPH) wells (data from the period August 30, 2001 to September 1, 2004), North San Francisco Bay study unit, California. CDPH, California Department of Public Health; <, less than.
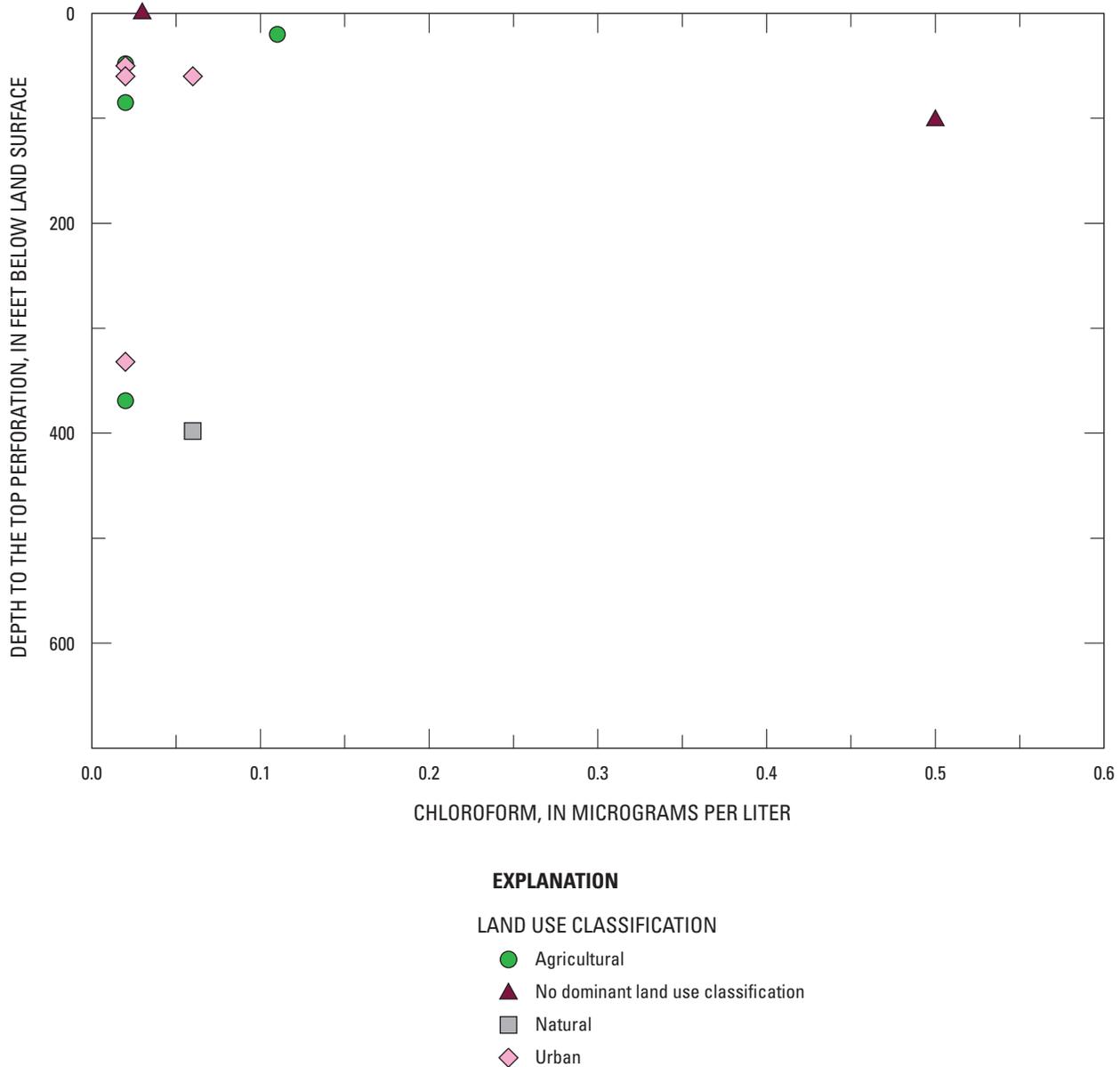
Figure 22. Concentration of chloroform as a function of depth to the top perforation and land-use classifications, North San Francisco Bay study unit, California.

In summary, most wells containing chloroform had urban or agricultural land-use classifications, had top perforations <102 ft. (31 m), and had oxic groundwater conditions.

Solvents

Solvents are used for various industrial, commercial, and domestic purposes. Two solvents, PCE and TCE, had spatially-weighted high aquifer proportions of 1.3 percent and 0.1 percent, respectively (table 4). PCE is primarily used for dry-cleaning of fabrics and degreasing metal parts, and is an ingredient in a wide range of products including paint removers, polishes, printing inks, lubricants, and adhesives. TCE has similar uses as PCE, and also may be formed by

degradation of PCE in groundwater (Vogel and McCarty, 1985). The solvent 1,2-dichloroethane was detected at high relative-concentration in one well during August 30, 2001 to September 1, 2004; however, the high relative-concentration was not the most recent value from the CDPH data used to represent that well (table 4). Solvents as a class had a high aquifer-scale proportion of 1.4 percent, and a moderate aquifer-scale proportion of 2.5 percent (table 9). None of the individual solvent compounds were detected in more than 10 percent of the wells tested.

Historically high values for the solvents dichloromethane and 1,1-dichloroethane were recorded in the CDPH database for the period before August 30, 2001, but not during the current period of study (table 6).

Understanding Assessment for Solvents

Although solvents were not measured at high relative-concentrations in more than 2 percent of the primary aquifers, they are constituents that are important to water quality. The three solvents selected for the summation were PCE, TCE, and 1,2-dichloroethane, on the basis of high relative-concentrations (table 4). Solvent concentrations were significantly greater in wells classified as modern age than in wells classified as pre-modern age (table 8). However, solvents were detected in groundwaters classified as mixed age and pre-modern age, possibly because some solvents were used before 1950 and could be present in pre-modern water. Figure 23 shows the distribution of solvents in the NSF study unit, which mostly are located around the urban areas.

Other VOCs

In the category "other VOCs," there were no grid-based high relative-concentrations and only one grid-based moderate relative-concentration (benzene, 1.2 percent; table 4). 1,1-Dichloroethene had a spatially-weighted high relative-concentration in 0.1 percent of the primary aquifers.

The constituents bis(2-ethylhexyl)phthalate (DEHP), 1,2-dibromo-3-chloropropane (DBCP), 1,2-dibromoethane (EDB), and toluene had high relative-concentrations recorded in the CDPH database for the period from August 30, 2001, to September 1, 2004, but the high relative-concentrations were not the most recent values selected for calculating aquifer proportion (table 4).

Herbicides

Low relative-concentrations of the herbicide simazine were detected in samples from the NSF study unit (figs. 19, 20). Simazine was detected in 10 percent of the grid wells, all of which were in the VP study area; the maximum concentration was 0.013 µg/L. Historically, simazine is most commonly used on vineyards and orchards in the study unit, but also is used on rights-of-way for weed control (Domagalski and Dubrovsky, 1991). Simazine was the most frequently detected triazine herbicide in groundwater in California (Troiano and others, 2001). Simazine was among the most commonly detected herbicides in groundwater in major aquifers across the United States (Gilliom and others, 2006).

Understanding Assessment for Simazine

Simazine was detected only in grid wells with ages classified as modern (6 wells) and mixed (2 wells). Simazine was significantly correlated (positive) with modern compared with mixed, mixed compared with pre-modern, and modern compared with pre-modern groundwater ages (table 8).

Simazine was detected only in wells with depths to the top perforations <100 ft (30 m) and was significantly correlated (negatively) with the depth to the top perforation, well depth, pH, and groundwater temperature (table 10). Simazine concentration was not significantly correlated with land-use classification or percent land use (fig. 24; tables 8, 10); however, 4 of the 8 grid wells containing simazine were in agricultural land-use areas, 2 were from mixed land-use areas, and 1 each was in urban and natural land-use areas. Simazine has been used in agricultural applications on citrus and vineyards, and urban settings for weed control (Gilliom and others, 2006).

The wells in which simazine was detected may be characterized as shallow (<100 ft [30 m]), containing recently recharged groundwater (modern), and predominantly in agricultural land-use areas.

Insecticides

The insecticide diazinon was detected at one grid well in the WG study area at a moderate relative-concentration (figs. 19, 20).

Special-Interest Constituents

Constituents of special interest analyzed for in the NSF study unit were NDMA, 1,2,3-TCP, and perchlorate. These constituents were selected because they recently have been found in, or are considered to have the potential to reach, drinking-water supplies (California Department of Public Health, 2008a,b,c). NDMA, 1,2,3-TCP, and perchlorate were not detected in the 83 grid wells sampled (Kulongoski and others, 2006). A high concentration of perchlorate in one well was recorded in the CDPH database before August 30, 2001 (table 6), but not during the period August 30, 2001–September 1, 2004.
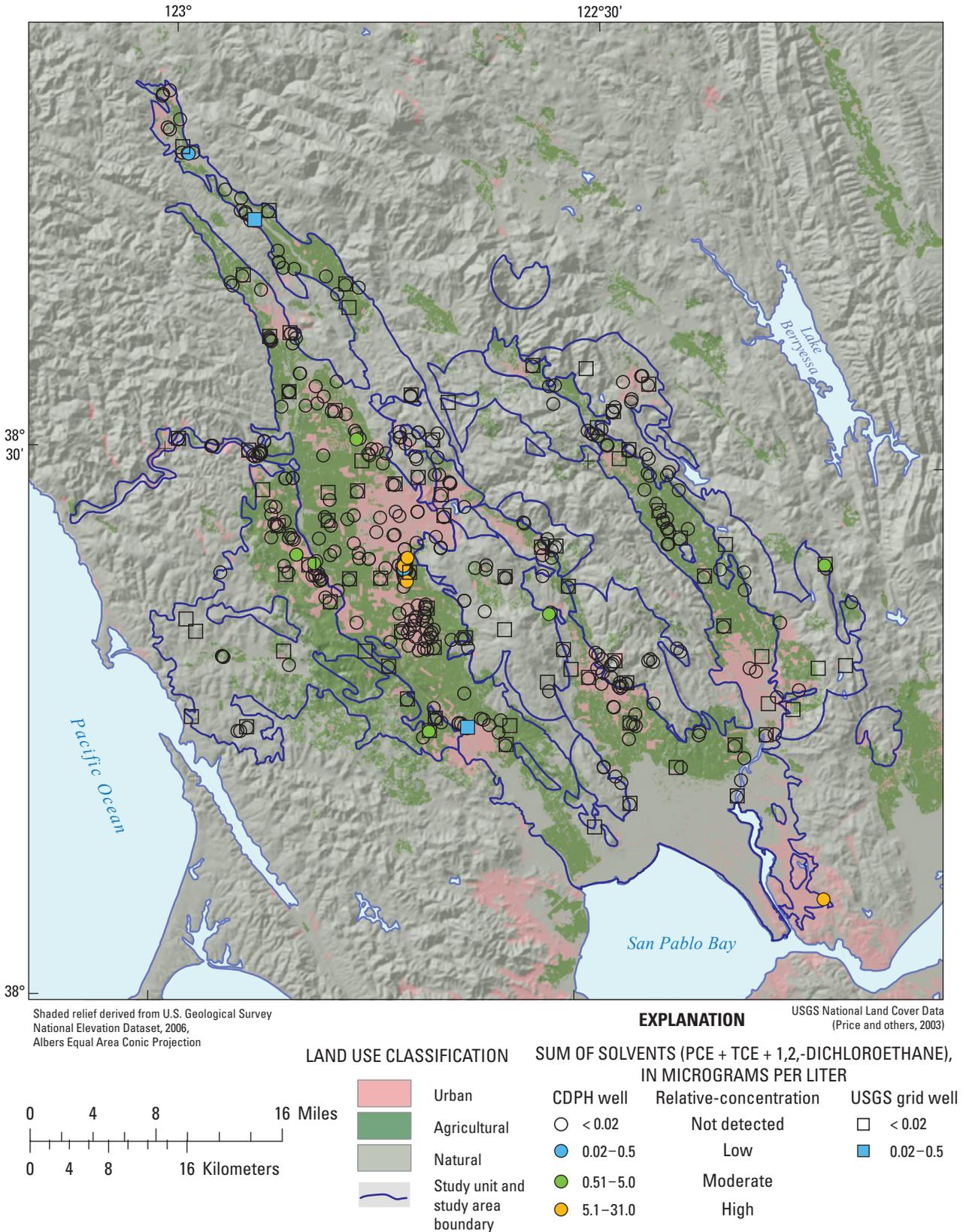
Figure 23. Land-use classification and the relative-concentrations of the sum of the solvents tetrachloroethene (PCE), trichloroethene (TCE), and 1,2-dichloroethane in U.S. Geological Survey (USGS) grid wells and California Department of Public Health (CDPH) wells (data from the period August 30, 2001 to September 1, 2004), North San Francisco Bay study unit, California. <, less than.

Shaded relief derived from U.S. Geological Survey
National Elevation Dataset, 2006,
Albers Equal Area Conic Projection

USGS National Land Cover Data
(Price and others, 2003)

EXPLANATION

LAND USE CLASSIFICATION   SIMAZINE, IN MICROGRAMS PER LITER

Urban

Agricultural

Natural

Study unit and
study area boundary

CDPH well   Relative-concentration   USGS grid well

○ < 0.005   Not detected   □ < 0.005

Low   ■ 0.006−0.052

0   4   8   16 Miles

0   4   8   16 Kilometers

Figure 24.   Land-use classifications and the relative-concentrations of the herbicide simazine in U.S. Geological Survey (USGS) grid wells and California Department of Public Health (CDPH) wells (data from the period August 30, 2001 to September 1, 2004), North San Francisco Bay study unit, California.

Summary

Groundwater quality in the approximately 1,000 mi^2 (2,590 km^2) North San Francisco Bay study unit was investigated as part of the Priority Basin Project of the Groundwater Ambient Monitoring and Assessment (GAMA) Program. The GAMA North San Francisco Bay provides a spatially unbiased characterization of untreated groundwater quality in the primary aquifers at the basin-scale. The assessment is based on water-quality and ancillary data collected by the U.S. Geological Survey (USGS) from 89 wells in 2004, and water-quality data from the California Department of Public Health (CDPH) database.

The first component of this study, the status of the current-quality of the groundwater resource, was assessed on the basis of data from samples analyzed for volatile organic compounds (VOC), pesticides, and naturally occurring inorganic constituents, such as major ions and trace elements. The status assessment characterizes the quality of groundwater resources within the primary aquifers of the North San Francisco Bay study unit, not the treated drinking water delivered to consumers by water purveyors.

Relative-concentrations (sample concentration divided by the benchmark concentration) were used for evaluating groundwater quality for those constituents that have Federal and (or) California benchmarks. Aquifer-scale proportion was used as a metric for evaluating regional-scale groundwater quality. High aquifer-scale proportion is defined as the percentage of the primary aquifers with relative-concentration greater than 1.0; proportion is based on an areal rather than a volumetric basis. Moderate and low aquifer-scale proportions were defined as the percentage of the aquifer with moderate and low relative-concentrations, respectively. Two statistical approaches, grid-based and spatially-weighted, were used to evaluate aquifer-scale proportion for individual constituents and classes of constituents. Grid-based and spatially weighted estimates were comparable in the NSF study unit (90-percent confidence intervals). However, the spatially-weighted approach was superior to the grid-based proportion when a constituent was high in a small fraction of the aquifer.

For inorganic constituents with human-health benchmarks, relative-concentrations were high in 14.0 percent of the primary aquifers, moderate in 35.8 percent, and low in 50.2 percent. The high aquifer-scale proportion of inorganic constituents primarily reflected high aquifer-scale proportions of arsenic (10.0 percent), boron (4.1 percent), and lead (1.6 percent). In contrast, relative-concentrations of organic constituents (one or more) were high in 1.4 percent, moderate in 4.9 percent, and low in 93.7 percent (not detected in 64.8 percent) of the primary aquifers. The high aquifer-scale proportion of organic constituents primarily reflected high aquifer-scale proportions of PCE (1.3 percent), TCE (0.1 percent), and 1,1-dichloroethene (0.1 percent). The inorganic constituents with secondary maximum contaminant levels, manganese and iron, had relative-concentrations that were high in 40.8 percent and 24.4 percent of the primary aquifers, respectively. Of the 255 organic and special-interest constituents analyzed for, 26 constituents were detected. Two organic constituents were frequently detected (in 10 percent or more of samples): the trihalomethane chloroform and the herbicide simazine, but both were detected at low relative-concentrations.

The second component of this work, the understanding assessment, identified the natural and human factors that affect groundwater quality by evaluating land use, physical characteristics of the wells, geochemical conditions of the aquifer, and water temperature. Results from these analyses attempt to explain the occurrence and distribution of constituents in the study unit. The understanding assessment indicated that a majority of the wells that contained nitrate had an urban or agricultural land use classification, had water of modern or mixed age classification, and had depths to their top perforations of less than 100 ft (30 m). Geochemical data are consistent with partial denitrification of nitrate in some reducing groundwaters in the terminal and deeper parts of the flow system.

High and moderate relative-concentrations of arsenic may be attributed to reductive dissolution of manganese or iron oxides or to desorption by high pH waters. Arsenic concentrations increased with increasing depth and groundwater age in all three study areas, or from mixing with hydrothermal waters. High to moderate relative-concentrations of boron were primarily associated with hydrothermal activity or high salinity waters in the Napa-Sonoma lowlands.

Simazine was detected more often in groundwater classified as having modern- and mixed-age than in pre-modern-age groundwater, while chloroform was detected most often in groundwater classified as mixed age. Simazine and chloroform also were observed in wells that had surrounding land-use classified as agricultural or land classified as urban, and which had top-perforation depths less than 102 ft (30 m). Together, the occurrence of chloroform and simazine in shallow wells with groundwater of modern or mixed age and that are located in urban or agricultural areas suggests that these constituents result from anthropogenic activities in the last 50 years.

Tritium, helium isotopes, and carbon-14 data were used to classify the predominant age of groundwater samples into three categories: modern (water that has entered the aquifer in the last 50 years), pre-modern (water that entered the aquifer more than 50 years, up to tens of thousands of years ago), and mixed (mixtures of waters with modern and pre-modern ages). Arsenic, iron, and TDS concentrations were significantly greater in groundwater having pre-modern age classification than in modern-age groundwaters, suggesting that these constituents accumulate with groundwater residence time.

Acknowledgments

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Appendix A.   Stratigraphy

Mesozoic to Early Tertiary rocks of the Franciscan Complex, Great Valley Sequence, and Coast Range Ophiolite make up the basement rocks beneath the entire study unit. Tertiary sedimentary and volcanic rocks overlie the basement and are exposed in upland areas. The volcanic rocks are part of the belt of volcanic fields that extend from 60 mi (100 km) south of San Francisco Bay to Clear Lake and are progressively younger toward the northwest (Fox and others, 1973). Quaternary sedimentary deposits underlie the valley floors and form fans along the valley margins.

Basement Rocks

The Franciscan Complex, as the name implies, includes rocks of several different lithologies, commonly: sandstone, graywacke, shale, conglomerate, chert, greenstone, and serpentinite. In places, the rocks are pervasively sheared and form mélange zones. The total thickness is unknown but is a few tens of thousands of feet (Bailey and others, 1964). These rocks have become highly indurated, having formed tens of millions of years ago and having been deeply buried and subjected to elevated temperatures. Porosity and permeability are low in Franciscan rocks because most of the original pore spaces are filled by minerals that cement the individual grains together.

Exposures of the ophiolite in the Coast Ranges have been mapped as small outcrops within larger masses of the Franciscan Complex in the Mayacmas Mountains and the southern part of the Sonoma Mountains (Fox and others, 1973; Wagner and others, 2003, 2004). The ophiolite consists of serpentinized peridotite, gabbro, and basalt that has been faulted and tectonically interleaved with the Franciscan Complex (McLaughlin and others, 2005).

Great Valley Sequence rocks are exposed on the east side of Mayacmas Mountains and have been identified in deep petroleum exploration wells at the southern end of the Sonoma Valley and beneath San Pablo Bay (Wright and Smith, 1992). The presence of Great Valley Sequence rocks beneath Sonoma Valley is supported, at least in places, by the consistently low ratios of dissolved boron to chloride in water samples from thermal wells along the east side of the valley (Donnelly-Nolan and others, 1993). Most Great Valley Sequence rocks are sandstone, shale, and minor conglomerate units. These rocks are typically well cemented and indurated. Wells drilled in these rocks generally yield little or no water (Kunkel and Upson, 1960; Page, 1986).

Most of the modern permeability in the basement rocks is due to fractures that developed in response to deformation related to the style of emplacement of the various rock packages as they were transported from the sea floor to the continent and by later folding and faulting. Because of their low permeability and specific storage capacity, the basement rocks are commonly considered to be nonwater-bearing and to form the boundaries of groundwater basins throughout the Coast Ranges (Cardwell, 1958 and California Department of Water Resources, 1958). However, the basement rocks are not truly nonwater-bearing, and in places, especially where indurated rock units are highly fractured, these units may provide limited amounts of water to wells and springs.

Younger volcanic and sedimentary rocks as well as unconsolidated sediments were deposited unconformably upon the basement rocks. The volcanic and sedimentary rocks are interbedded and, in places, are interfingered. The volcanic rocks include the Late Miocene to Early Pliocene Donnell Ranch Volcanics and Tolay Volcanics, and the younger Sonoma Volcanics. The sedimentary rocks include the Petaluma Formation, Wilson Grove Formation, Huichica Formation, Glen Ellen Formation, and several informally named mappable geologic units. Sedimentary rocks older than the Sonoma Volcanics outcrop in small patches in the southern parts of the Napa and Sonoma Valleys and are likely in the subsurface, but because their subsurface extent is poorly known and few water wells are drilled into them in this region, the sedimentary rocks are not discussed further.

Tolay and Donnel Ranch Volcanics

The Tolay Volcanics stratigraphic unit was named by Morse and Bailey (1935) and includes a thick series of mafic lavas, breccia, tuff, and agglomerate, identified in the core from a petroleum test well drilled in the Petaluma oil district. At that location, 4,165 ft (1,270 m) were penetrated without reaching the bottom. These rocks are not exposed anywhere on the Santa Rosa Plain and are not penetrated by any water wells in the area. The uppermost part of the Tolay Volcanics is interbedded with the lowermost part of the Petaluma Formation. This stratigraphic relationship suggests the Tolay Volcanics is of Late Miocene or Early Pliocene age.

The Donnell Ranch Volcanics were informally named by Youngerman (1989) for lavas and tuffs exposed between the Rodgers Creek and Tolay faults in the southern Sonoma Mountains. The Donnell Ranch Volcanics predominantly consist of mafic lavas and breccias and rhyolitic to dacitic lavas and tuffs. The ages of the Donnell Ranch and Tolay Volcanics overlap, and some uncertainty still exists in field identification and mapping of these two volcanic formations.

Sonoma Volcanics

The Sonoma Volcanics constitute an important aquifer in parts of the Santa Rosa Plain, Sonoma Valley, and Napa Valley. This heterogeneous assemblage of lithologic types has a broad range of hydraulic properties. Specific yields range from 0 to 15 percent (California Department of Water Resources, 1982, 2003). Water production from wells drilled into thick air-fall pumice units may exceed a few hundred gpm but wells drilled into unfractured lavas or welded tuffs may produce less than 10 gpm (38 L/m).

The Sonoma Volcanics are a thick, highly variable sequence of continental volcanic and volcaniclastic rocks including basalt, andesite, and rhyolite lavas interbedded with air-fall and ash-flow tuffs, debris-flow deposits, and lacustrine deposits. The total thickness of Sonoma Volcanics is at least a few thousand feet. The Sonoma Volcanics were first described by Osmont (1905) and named for Sonoma Mountain, east of Santa Rosa. The Sonoma Volcanics underlie parts of the Santa Rosa Plain where the formation is frequently penetrated by water wells. The Sonoma Volcanics are widely exposed in upland areas east of the Rodgers Creek Fault in the Sonoma Mountains, Mayacmas Mountains, and the Howell Mountains.

Recent mapping (David L. Wagner and Robert J. McLaughlin, U.S. Geological Survey, oral commun., 2003) shows the Sonoma Volcanics can be separated into older and younger members on the basis of the structural attitude of individual units, with the older member dipping more steeply than the overlying rocks. On the basis of stratigraphic relations and several argon-40/argon-39 dates, the Sonoma Volcanics were extruded and deposited over an interval from approximately 8 to 2.5 million years (Ma) (McLaughlin and others, 2005). This formation is overlain by and interfingers with continental sedimentary rocks, including the Petaluma Formation along the eastern part of Santa Rosa Valley and the Glen Ellen Formation in Sonoma Valley.

Petaluma Formation

The Petaluma Formation is dominated by fine-grained materials, either in thick beds or as interstitial material in poorly sorted silty and clayey sands or gravels. The Petaluma Formation is an important aquifer only in the northern part of Petaluma Valley. Across the study area, specific yields range from 3 to 7 percent and well yields are generally only a few gallons per minute (Cardwell, 1958; California Department of Water Resources, 2003).

The Petaluma Formation is exposed in outcrops around the margins of Santa Rosa Valley and, on the basis of geologic logs from wells, is present under a large part of the valley. The Petaluma Formation is composed of sandstone, shale, siltstone, and clay, and minor beds of nodular limestone and conglomerate. Much of the formation was deposited under brackish-water conditions but includes a continental and a marine facies (Powell and others, 2004). The continental facies extends westward from the Sonoma and Mayacmas Mountains; the transition to marine facies occurs beneath the Santa Rosa Plain. Outcrops and cuttings from deep petroleum exploration wells indicate that the total thickness of the formation probably is at least 3,000 ft (914 m) (Powell and others, 2004). The formation is well exposed along a 1- to 2-mi (1- to 3-km) wide area along the western base of the Sonoma Mountains that extends north from near Penngrove to the mouth of Tolay Creek. Age-dates on interbedded tuff units indicate the Petaluma Formation was deposited during the early Pliocene (McLaughlin and others, 2005).

Wilson Grove Formation Highlands

The Wilson Grove Formation is composed of fine- to medium-grained, moderate- to well-sorted, tan to gray, uncemented to weakly cemented marine sandstone. Dickerson (1922) correlated these strata with the Merced Formation at its type locality on the San Francisco Peninsula. Fox (1983) renamed the strata Wilson Grove Formation. The formation contains marine fossils, clasts of volcanic rocks, thin beds of tuff, pebble and gravel stringers, and clay lenses. The Wilson Grove Formation interfingers with the Petaluma Formation beneath the Santa Rosa Plain. The two formations show a transition from estuarine to bathyal marine depositional environments. In most places west of the Santa Rosa Plain the Wilson Grove Formation unconformably overlies the Franciscan Complex on a highly irregular contact. The maximum thickness of the Wilson Grove is about 2,700 ft (823 m) (Powell and others, 2004). The strata of the Wilson Grove Formation have generally been assigned an age of Pliocene to Pleistocene on the basis of molluscan fossils. A Pliocene age for at least part of the formation was validated using the ^{40}Ar/^{39}Ar isotopic technique run on samples of intercalated Roblar tuff, which gave an age of 6.26 Ma (McLaughlin and others, 2005).

Huichica Formation

The Huichica Formation was first named by Weaver (1949) for massive silt beds that crop out in the southeastern part of Sonoma Valley and later were recognized in a small part of eastern Napa Valley (Kunkel and Upson, 1960). The Huichica Formation is overlain by older and younger alluvium and unconformably overlies the Sonoma Volcanics. The base of the Huichica contains pebble and gravel sized volcanic clasts derived from the Sonoma Volcanics, indicating coeval deposition for parts of the two formations. Most of the Huichica Formation consists of deformed continental yellow silt and clay deposits with lenses of silty gravel and sand. In Sonoma Valley, the maximum thickness of the Huichica Formation attains is 900 ft (274 m) (Kunkel and Upson, 1960). The high proportion of fine-grained materials making up the Huichica results in very low permeability and very low well yields. Few wells produce enough water even for single domestic users (California Department of Water Resources, 2004).

Glen Ellen Formation

The Glen Ellen Formation was first described by Weaver (1949) for continental deposits that crop out near Glen Ellen in Sonoma Valley. The name has since been applied to rocks of a similar appearance in Petaluma Valley, the Santa Rosa Plain, and Alexander Valley. The formation consists of clay-rich stratified deposits of poorly sorted sand, silt, and gravel. Beds grade laterally and vertically between coarse- and fine-grained, commonly over distances of a few tens to a few hundreds of feet. Bedding is thick to massive and often has lenticular form. Most of the clasts and probably much of the matrix were derived from the Sonoma Volcanics. The sedimentary rocks making up this formation were probably originally deposited as alluvial fans and piedmont. Some of the material beneath and adjacent to Santa Rosa Valley was probably deposited in lagoons or shallow bays and may grade into a marine facies.

The Glen Ellen Formation is of late Pliocene age as indicated by stratigraphic relations and $^{40}Ar/^{39}Ar$ radiometric age dates of intercalated Putah Tuff (McLaughlin and others, 2005). Beneath Santa Rosa Valley, the Glen Ellen Formation rests directly upon the basement rocks of the Franciscan Complex in places but more generally overlies the Sonoma Volcanics, or the Wilson Grove or Petaluma Formations. The Glen Ellen Formation interfingers with the Wilson Grove and Sonoma Volcanics beneath parts of the Santa Rosa Plain. In Sonoma Valley, the Glen Ellen overlies Franciscan basement or the Sonoma Volcanics. Along the valley margins in Sonoma Valley and the Santa Rosa Plain, the Glen Ellen is overlain by alluvial units of Quaternary age. The thickness of the Glen Ellen Formation varies greatly but generally is a few hundred feet thick or less. However, the maximum thickness of the formation may be about 3,000 ft (914 m) in Santa Rosa Valley (Cardwell, 1958).

In Sonoma Valley, Santa Rosa Plain, and Alexander Valley, the Glen Ellen Formation is an important aquifer and provides water for domestic and agricultural uses. The large fraction of fine-grained material in the formation causes the permeability and well yields to be low. Average specific yields for the Glen Ellen range from 3 to 7 percent (California Department of Water Resources, 2003). Well yields depend on the total thickness of coarse-grained materials and vary from a few to a few hundred gpm The amount of groundwater existing under unconfined and semiconfined conditions depends on the thickness and continuity of overlying fine-grained materials.

Appendix B.   Use of Data from the California Department of Public Health (CDPH) Database

For the NSF study unit, the historical CDPH database contains over 309,000 records distributed across more than 790 wells, requiring targeted retrievals to manageably use the data to assess water-quality. The paragraphs below summarize the selection process for wells and data from the CDPH database for use in the grid-based assessment of status.

The strategy used to select CDPH inorganic data for a single well in each cell where the USGS did not obtain a sample for analysis for inorganic constituents involved prioritizing data from different sources. The first choice was to select CDPH data for the grid well sampled by the USGS for other constituents, provided the CDPH data met quality-control criteria. Cation/anion balance was used as the quality-control assessment metric. Because water is electrically neutral and must have a balance between positive (cations) and negative (anions) electrically charged dissolved species, the cation/anion balance is commonly used as a quality-assurance criterion for water sample analysis (Hem, 1970). An imbalance greater than or equal to ($\geq$) 10 percent may indicate uncertainty in the quality of the data. The most recent CDPH data from the well were evaluated to determine whether the cation/anion imbalance was <10 percent; if so, the CDPH inorganic data for the well were selected for use as grid-well data (USGS grid well with CDPH inorganic data). It was assumed that if analyses met the high-quality-control criterion—cation/anion balance—for major and minor elements, then analyses at these wells for trace elements, nutrients, and radiochemical constituents would also be of high quality. This approach resulted in the selection of inorganic data from the CDPH database for 24 USGS grid wells. To identify the USGS wells that incorporated CHDPH inorganic data, a well ID was created that added –DG– to the GAMA ID for these wells (for example, VP-01 with CDPH data was assigned the well identification: VP-DG-01; table B1).

If the first step did not yield CDPH inorganic data for the USGS grid well, the second step was to search the CDPH database to identify the highest ranked well with a cation/anion imbalance <10 percent in each grid cell. This step resulted in selecting CDPH inorganic data for non-USGS-sampled wells for six grid cells. These six CDPH grid wells were not co-located with their cell's respective USGS grid well. To identify these new CDPH wells, a well ID was created that added "–DPH–" after the study unit prefix and then a sequential number starting after the last GAMA ID for the study area (for example, CDPH grid well VP-DPH-55, table B1). If no wells in a grid cell met the cation/anion balance criteria or there was insufficient data to evaluate charge balance, the third choice for the CDPH grid well was to select the highest randomly ranked CDPH well that had any of the needed inorganic data. This resulted in selecting CDPH inorganic data for 17 USGS grid wells and 9 additional wells for a total of 28 wells. If the well was a USGS grid well, a well ID was created that added "–DG–" to the GAMA ID (for example, VP-DG-01), or if the well was a new CHDP-grid well, "–DPH–" was added after the study unit prefix and then a sequential number starting after the last GAMA ID for the study area (for example, CDPH grid well VP-DPH-51).In some cases, to achieve one value for each constituent per cell, it was necessary to select an additional well in a cell for data, hence some cells have multiple CDPH wells.

The result of these steps was one grid well per cell having data from the USGS database, the CDPH database, or both database. Inorganic data from the CDPH database were used for 63 grid wells. Data was available for 63 grid wells for nitrate plus nitrite and for 0 to 54 wells for most other inorganic constituents (table 2). In combination with USGS grid well inorganic data (19 to 29 wells), inorganic data was available for 89 of the 100 grid cells. Estimates of aquifer-scale proportion for constituents based on a smaller number of wells are subject to a larger error associated with the 90-percent confidence intervals (on the basis of Jeffrey's interval for the binomial distribution).

Differences in constituent LRLs or MDLs associated with USGS and CDPH data did not affect analysis of high or moderate relative-concentrations because concentrations greater than one-half of water-quality benchmarks were substantially higher than the reporting levels. Several types of comparisons between USGS-collected and CDPH data are described in Appendix F.

Table B1.   Grid cell number, U.S. Geological Survey (USGS) well identification number, land use categories, land use classification, well construction information, and the normalized position along a flowpath for wells sampled August to December 2004 for the North San Francisco Bay study unit, California.

[CDPH, California Department of Public Health; DOM, domestic well; FP, flow-path (understanding) well; ft, foot; IND, industrial well; IRR, irrigation well; m, meter; LSD, land surface datum; na, no data available; nd, no data collected; no CDPH data, no CDPH water-quality data available; no USGS well, USGS GAMA-grid well was not sampled in that cell; PSW, public supply well; USGS data, USGS-GAMA data available for the grid well; VP, Valleys and Plains study area well; VOL, Volcanic Highlands study area well; WG, Wilson Grove Formation Highlands study area well. A USGS GAMA well identification number indicates the use of data from a USGS-grid well; a CDPH GAMA well identification number with "DG" indicates the use of CDPH inorganic constituent data at a USGS-grid well, and a CDPH GAMA well identification number with "DPH" indicates a CDPH-grid well with no USGS data]

			Land use catagories				Construction information				
Grid cell number	USGS-GAMA well identification number indicating data source	Well type	Agricul-tural land use	Natural land use	Urban land use	Land use classifi-cation	Well depth	Top of perfora-tions	Bottom of perfora-tions	Length from top of uppermost perforated interval to bottom of well	Normalized position along flowpath
			within 500 meters of the well, in percent				in feet below LSD				dimension-less
Volcanic Highlands study area grid wells											
1	VOL-06	VOL-DG-06	PSW	0	97	3	Natural	280	200	280	80	na
2	VOL-08	VOL-DG-08	PSW	0	100	0	Natural	na	na	na	na	na
3	VOL-10	No CDPH data	PSW	0	100	0	Natural	136	76	136	60	na
3		VOL-DPH-22	PSW	0	100	0	Natural	na	na	na	na	na
4	VOL-05	VOL-DG-05	PSW	0	100	0	Natural	510	330	510	180	na
5	VOL-01	USGS data	PSW	0	45	55	Urban	323	na	na	na	na
6	VOL-02	No CDPH data	PSW	0	96	4	Natural	380	na	na	na	na
6		VOL-DPH-23	PSW	0	100	0	Natural	na	na	na	na	na
7	VOL-09	VOL-DG-09	PSW	0	100	0	Natural	na	na	na	na	na
8	VOL-07	VOL-DG-07	PSW	6	94	0	Natural	395	215	395	180	na
9	VOL-20	USGS data	PSW	0	88	12	Natural	250	170	250	80	na
10	VOL-03	VOL-DG-03	PSW	44	27	28	Mixed	500	102	na	na	na
10		VOL-DPH-27	PSW	na	na	na	na	na	na	na	na	na
11	VOL-14	USGS data	PSW	45	44	12	Mixed	417	57	417	360	na
12	VOL-18	VOL-DG-18	PSW	50	42	8	Agricultural	670	135	660	525	na
13	VOL-19	USGS data	PSW	4	90	6	Natural	705	285	705	420	na
14	VOL-17	No CDPH data	PSW	0	100	0	Natural	265	na	na	na	na
14		VOL-DPH-24	PSW	50	49	1	Agricultural	646	na	390	na	na
15	No USGS well	No CDPH data		nd	nd	nd	nd	nd	nd	nd	nd	nd
16	VOL-11	VOL-DG-11	PSW	0	83	17	Natural	555	398	555	157	na
17	VOL-16	No CDPH data	PSW	33	66	0	Natural	423	75	419	344	na
17		VOL-DPH-25	PSW	58	42	0	Agricultural	na	na	na	na	na
18	VOL-15	VOL-DG-15	PSW	0	93	7	Natural	115	65	113	48	na
19	VOL-12	No CDPH data	DOM	37	63	0	Natural	368	148	368	220	na
19		VOL-DPH-26	PSW	81	17	2	Agricultural	na	na	na	na	na
20	VOL-13	VOL-DG-13	PSW	0	97	3	Natural	510	30	510	480	na
Valleys and Plains study area grid wells											
1	VP-21	VP-DG-21	PSW	8	56	36	Natural	314	80	310	230	na
2	VP-04	VP-DG-04	PSW	95	4	1	Agricultural	397	na	na	na	na
3	VP-07	VP-DG-07	PSW	40	5	55	Urban	685	295	670	375	na
4	VP-03	VP-DG-03	PSW	36	2	62	Urban	120	55	85	30	na
4		VP-DPH-58	PSW	na	na	na	na	na	na	na	na	0.92
5	VP-12	No CDPH data	PSW	83	16	1	Agricultural	808	650	800	150	na
6	VP-14	VP-DG-14	PSW	74	0	25	Agricultural	550	507	547	40	na
6		VP-DPH-59	PSW	na	na	na	na	na	na	na	na	na

Table B1.   Grid cell number, U.S. Geological Survey (USGS) well identification number, land use categories, land use classification, well construction information, and the normalized position along a flowpath for wells sampled August to December 2004 for the GAMA Priority Basins Project North San Francisco Bay study unit, California.—Continued

[CDPH, California Department of Public Health; DOM, domestic well; FP, flow-path (understanding) well; ft, foot; IND, industrial well; IRR, irrigation well; m, meter; LSD, land surface datum; na, no data available; nd, no data collected; no CDPH data, no CDPH water-quality data available; no USGS well, USGS GAMA-grid well was not sampled in that cell; PSW, public supply well; USGS data, USGS-GAMA data available for the grid well; VP, Valleys and Plains study area well; VOL, Volcanic Highlands study area well; WG, Wilson Grove Formation Highlands study area well. A USGS GAMA well identification number indicates the use of data from a USGS-grid well; a CDPH GAMA well identification number with "DG" indicates the use of CDPH inorganic constituent data at a USGS-grid well, and a CDPH GAMA well identification number with "DPH" indicates a CDPH-grid well with no USGS data]

Grid cell number	USGS-GAMA well identification number indicating data source		Well type	Land use catagories			Land use classifi-cation	Construction information				Normalized position along flowpath
				Agricul-tural land use	Natural land use	Urban land use		Well depth	Top of perfora-tions	Bottom of perfora-tions	Length from top of uppermost perforated interval to bottom of well	
				within 500 meters of the well, in percent				in feet below LSD				dimension-less
7	VP-11	VP-DG-11	PSW	13	43	45	Mixed	80	60	70	10	0.66
8	VP-10	USGS data	PSW	0	68	32	Natural	99	75	95	20	0.76
9	VP-08	VP-DG-08	PSW	55	45	0	Agricultural	102	70	88	18	0.55
10	VP-15	VP-DG-15	PSW	46	2	52	Urban	60	40	60	20	na
11	VP-02	No CDPH data	PSW	58	9	33	Agricultural	350	65	341	276	na
12	VP-05	VP-DG-05	PSW	47	4	49	Mixed	502	130	450	320	na
13	VP-06	VP-DG-06	PSW	75	2	23	Agricultural	700	170	680	510	na
14	VP-22	VP-DG-22	PSW	76	3	21	Agricultural	502	60	502	442	na
15	No USGS well	VP-DPH-51	PSW	47	53	0	Natural	na	na	na	na	na
17	VP-35	USGS data	PSW	95	5	0	Agricultural	300	85	300	215	na
18	VP-01	VP-DG-01	PSW	77	16	7	Agricultural	864	441	862	421	na
19	VP-23	VP-DG-23	PSW	61	2	37	Agricultural	530	369	530	161	na
20	VP-20	No CDPH data	IRR	89	0	11	Agricultural	110	70	110	40	na
20		VP-DPH-56	PSW	43	4	53	Urban	na	na	na	na	na
21	VP-18	VP-DG-18	PSW	67	14	19	Agricultural	63	48	70	22	0.49
21		VP-DPH-60	PSW	na	na	na	na	na	na	na	na	na
22	VP-42	VP-DG-42	PSW	83	11	6	Agricultural	209	55	209	154	0.10
23	VP-30	USGS data	PSW	52	43	4	Agricultural	na	na	na	na	0.08
24	VP-29	USGS data	PSW	67	12	21	Agricultural	120	62	120	58	0.18
25	VP-19	USGS data	PSW	0	36	64	Urban	100	20	60	40	0.49
26	VP-09	VP-DG-09	PSW	17	14	68	Urban	400	260	400	140	na
27	VP-24	VP-DG-24	PSW	0	22	78	Urban	85	65	85	20	na
28	VP-16	VP-DG-16	PSW	0	12	88	Urban	206	50	100	50	na
29	No USGS well	No CDPH data		nd	nd	nd	nd	nd	nd	nd	nd	nd
30	VP-28	No CDPH data	PSW	0	100	0	Natural	216	116	216	100	na
31	No USGS well	VP-DPH-53	PSW	0	96	4	Natural	na	na	na	na	0.96
32	No USGS well	VP-DPH-54	PSW	0	98	2	Natural	na	na	na	na	0.8
33	VP-43	No CDPH data	DOM	0	94	6	Natural	790	690	790	100	0.41
33		VP-DPH-57	PSW	na	na	na	na	na	na	na	na	na
34	VP-25	VP-DG-25	PSW	13	0	87	Urban	265	160	265	105	na
35	VP-13	VP-DG-13	PSW	0	100	0	Natural	na	na	na	na	na
36	VP-17	No CDPH data	PSW	84	16	0	Agricultural	na	na	na	na	0.32
37	VP-26	USGS data	PSW	97	3	0	Agricultural	600	125	600	475	0.29
38	VP-31	VP-DG-31	PSW	74	26	0	Agricultural	315	20	315	295	0.19
39	VP-27	VP-DG-27	PSW	28	19	53	Urban	372	50	372	322	0.06
40	VP-34	USGS data	PSW	80	10	10	Agricultural	258	41	258	217	0.17

Table B1. Grid cell number, U.S. Geological Survey (USGS) well identification number, land use categories, land use classification, well construction information, and the normalized position along a flowpath for wells sampled August to December 2004 for the GAMA Priority Basins Project North San Francisco Bay study unit, California.—Continued

[CDPH, California Department of Public Health; DOM, domestic well; FP, flow-path (understanding) well; ft, foot; IND, industrial well; IRR, irrigation well; m, meter; LSD, land surface datum; na, no data available; nd, no data collected; no CDPH data, no CDPH water-quality data available; no USGS well, USGS GAMA-grid well was not sampled in that cell; PSW, public supply well; USGS data, USGS-GAMA data available for the grid well; VP, Valleys and Plains study area well; VOL, Volcanic Highlands study area well; WG, Wilson Grove Formation Highlands study area well. A USGS GAMA well identification number indicates the use of data from a USGS-grid well; a CDPH GAMA well identification number with "DG" indicates the use of CDPH inorganic constituent data at a USGS-grid well, and a CDPH GAMA well identification number with "DPH" indicates a CDPH-grid well with no USGS data]

Grid cell number	USGS-GAMA well identification number indicating data source		Well type	Land use catagories			Land use classifi-cation	Construction information				Normalized position along flowpath
				Agricul-tural land use	Natural land use	Urban land use		Well depth	Top of perfora-tions	Bottom of perfora-tions	Length from top of uppermost perforated interval to bottom of well	
				within 500 meters of the well, in percent				in feet below LSD				dimension-less
41	VP-37	USGS data	PSW	5	1	94	Urban	360	60	350	290	0.46
42	VP-38	USGS data	PSW	76	11	13	Agricultural	770	210	770	560	0.60
43	VP-44	USGS data	PSW	80	15	5	Agricultural	318	140	302	na	0.77
44	No USGS well	No CDPH data		nd	nd	nd	nd	nd	nd	nd	nd	nd
45	No USGS well	No CDPH data		nd	nd	nd	nd	nd	nd	nd	nd	nd
46	No USGS well	VP-DPH-55	PSW	2	98	0	Natural	na	na	na	na	na
47	No USGS well	No CDPH data		nd	nd	nd	nd	nd	nd	nd	nd	nd
48	No USGS well	No CDPH data		nd	nd	nd	nd	nd	nd	nd	nd	nd
49	VP-36	USGS data	PSW	1	87	12	Natural	306	145	300	155	1.00
50	VP-40	USGS data	PSW	19	45	37	Mixed	na	na	na	na	0.87
51	VP-48	USGS data	PSW	77	3	20	Agricultural	200	60	200	140	0.89
52	VP-47	USGS data	PSW	49	42	8	Mixed	79	na	na	79	0.09
53	VP-39	USGS data	PSW	35	65	0	Natural	460	56	460	404	0.26
54	VP-50	USGS data	PSW	35	17	48	Mixed	199	na	na	na	0.32
55	VP-46	USGS data	PSW	93	4	3	Agricultural	180	40	180	140	0.44
56	VP-32	USGS data	PSW	64	36	0	Agricultural	400	na	na	na	0.49
57	VP-33	USGS data	PSW	68	18	14	Agricultural	na	na	na	na	0.59
58	VP-45	USGS data	PSW	79	5	15	Agricultural	na	na	na	na	0.69
59	VP-41	USGS data	PSW	20	29	51	Urban	235	60	235	175	0.75
60	VP-49	USGS data	PSW	0	79	21	Natural	220	140	220	80	0.83
Wilson Grove Formation Highlands study area grid wells												
1	WG-06	WG-DG-06	PSW	2	97	1	Natural	161	na	na	na	na
2	No USGS well	No CDPH data		nd	nd	nd	nd	nd	nd	nd	nd	nd
3	No USGS well	WG-DPH-15	PSW	43	55	2	Natural	na	na	na	na	na
3		WG-DPH-22	PSW	na	na	na	na	na	na	na	na	na
4	WG-13	WG-DG-13	PSW	0	100	0	Natural	275	na	na	na	na
5	WG-05	No CDPH data	PSW	0	98	2	Natural	215	135	215	na	na
5		WG-DPH-21	PSW	0	100	0	Natural	na	na	na	na	na
6	WG-09	No CDPH data	PSW	31	7	61	Urban	na	na	na	na	na
7	No USGS well	WG-DPH-16	PSW	58	9	33	Agricultural	na	na	na	na	na
8	No USGS well	WG-DPH-17	PSW	0	95	5	Natural	na	na	na	na	na
9	No USGS well	WG-DPH-18	PSW	45	54	1	Natural	na	na	na	na	na
10	WG-10	USGS data	PSW	0	98	2	Natural	190	70	190	120	na
11	No USGS well	No CDPH data		nd	nd	nd	nd	nd	nd	nd	nd	nd
12	WG-14	WG-DG-14	PSW	24	59	17	Natural	295	155	295	140	na

Table B1.   Grid cell number, U.S. Geological Survey (USGS) well identification number, land use categories, land use classification, well construction information, and the normalized position along a flowpath for wells sampled August to December 2004 for the GAMA Priority Basins Project North San Francisco Bay study unit, California.—Continued

[CDPH, California Department of Public Health; DOM, domestic well; FP, flow-path (understanding) well; ft, foot; IND, industrial well; IRR, irrigation well; m, meter; LSD, land surface datum; na, no data available; nd, no data collected; no CDPH data, no CDPH water-quality data available; no USGS well, USGS GAMA-grid well was not sampled in that cell; PSW, public supply well; USGS data, USGS-GAMA data available for the grid well; VP, Valleys and Plains study area well; VOL, Volcanic Highlands study area well; WG, Wilson Grove Formation Highlands study area well. A USGS GAMA well identification number indicates the use of data from a USGS-grid well; a CDPH GAMA well identification number with "DG" indicates the use of CDPH inorganic constituent data at a USGS-grid well, and a CDPH GAMA well identification number with "DPH" indicates a CDPH-grid well with no USGS data]

Grid cell number	USGS-GAMA well identification number indicating data source	Well type	Land use catagories			Land use classifi-cation	Construction information				Normalized position along flowpath
			Agricul-tural land use	Natural land use	Urban land use		Well depth	Top of perfora-tions	Bottom of perfora-tions	Length from top of uppermost perforated interval to bottom of well	
			within 500 meters of the well, in percent				in feet below LSD				dimension-less
13	WG-03	No CDPH data	PSW	56	14	30	Agricultural	552	270	552	282	na
14	WG-08	USGS data	PSW	0	1	99	Urban	600	332	600	268	na
15	WG-01	WG-DG-01	PSW	49	1	50	Urban	350	90	350	260	na
15		WG-DPH-23	PSW	na	na	na	na	na	na	na	na	na
15		WG-DPH-25	PSW	87	10	3	Agricultural	na	na	na	na	na
16	WG-04	No CDPH data	PSW	28	5	67	Urban	452	432	452	20	na
16		WG-DPH-24	PSW	na	na	na	na	na	na	na	na	na
17	WG-12	WG-DG-12	PSW	83	5	12	Agricultural	261	100	128	28	na
18	WG-02	WG-DG-02	PSW	88	8	4	Agricultural	240	na	na	na	na
19	WG-11	WG-DG-11	PSW	73	3	24	Agricultural	na	na	na	na	na
20	WG-07	WG-DG-07	PSW	95	1	4	Agricultural	550	140	540	400	na
USGS-Understanding wells											
9	VOL-04	USGS data	PSW	0	100	0	Natural	542	na	na	na	na
5	VPFP-01	USGS data	PSW	88	2	10	Agricultural	1,040	410	1,020	610	na
11	VPFP-02	USGS data	PSW	3	0	96	Urban	231	61	231	170	na
53	VPFP-03	USGS data	IRR	12	55	33	Natural	25	13	25	12	0.05
7	VPFP-04	USGS data	PSW	0	71	29	Natural	99	75	95	20	0.86
14	WGFP-01	USGS data	PSW	17	7	76	Urban	528	138	528	390	na
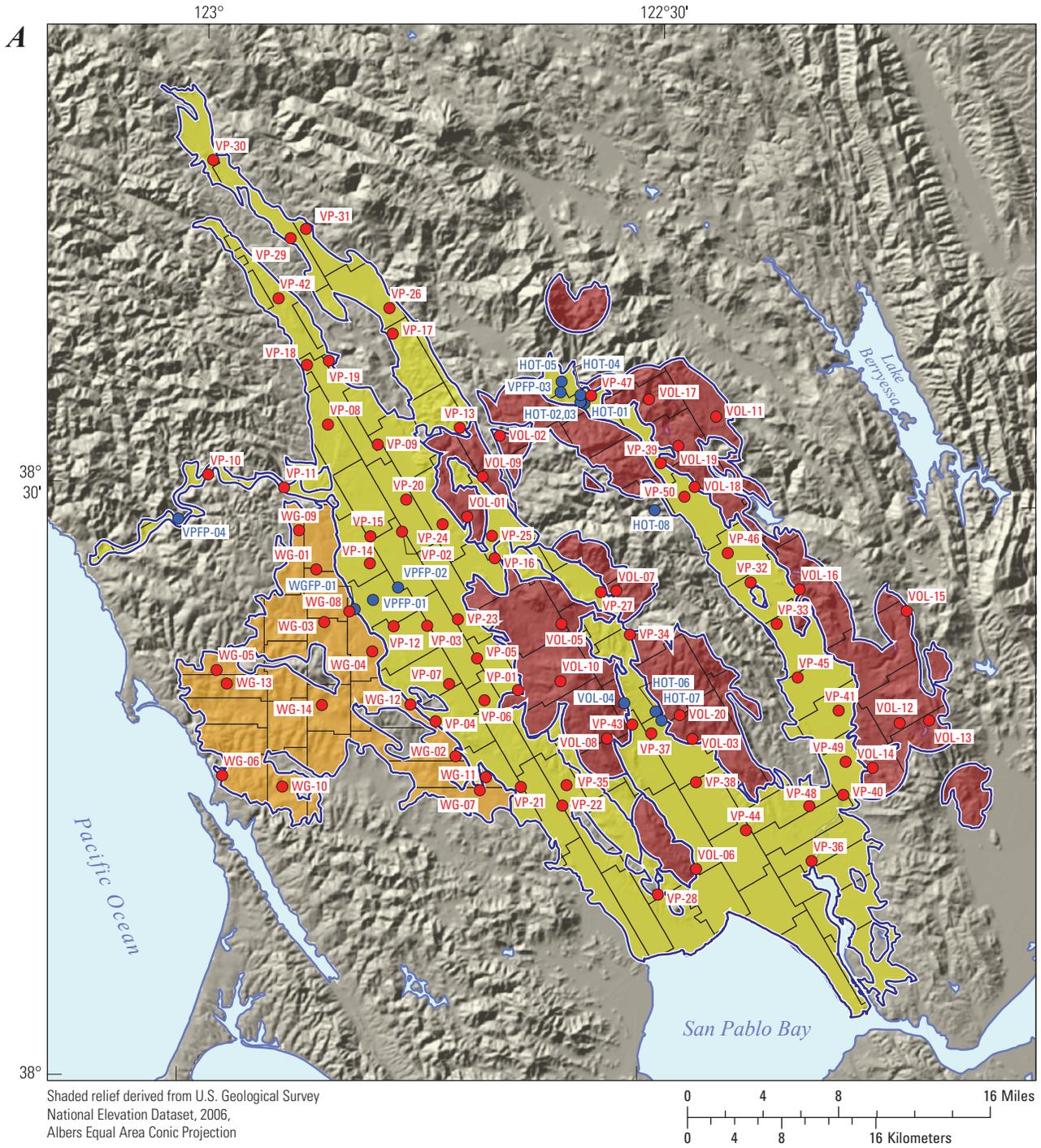
Figure B1.   Identifiers and locations of *A*. U.S. Geological Survey (USGS) grid and understanding wells sampled during August to December, 2004, and *B*. grid wells for which data for inorganic constituents from the California Department of Public Health (CDPH) were used, North San Francisco Bay study unit, California.

B
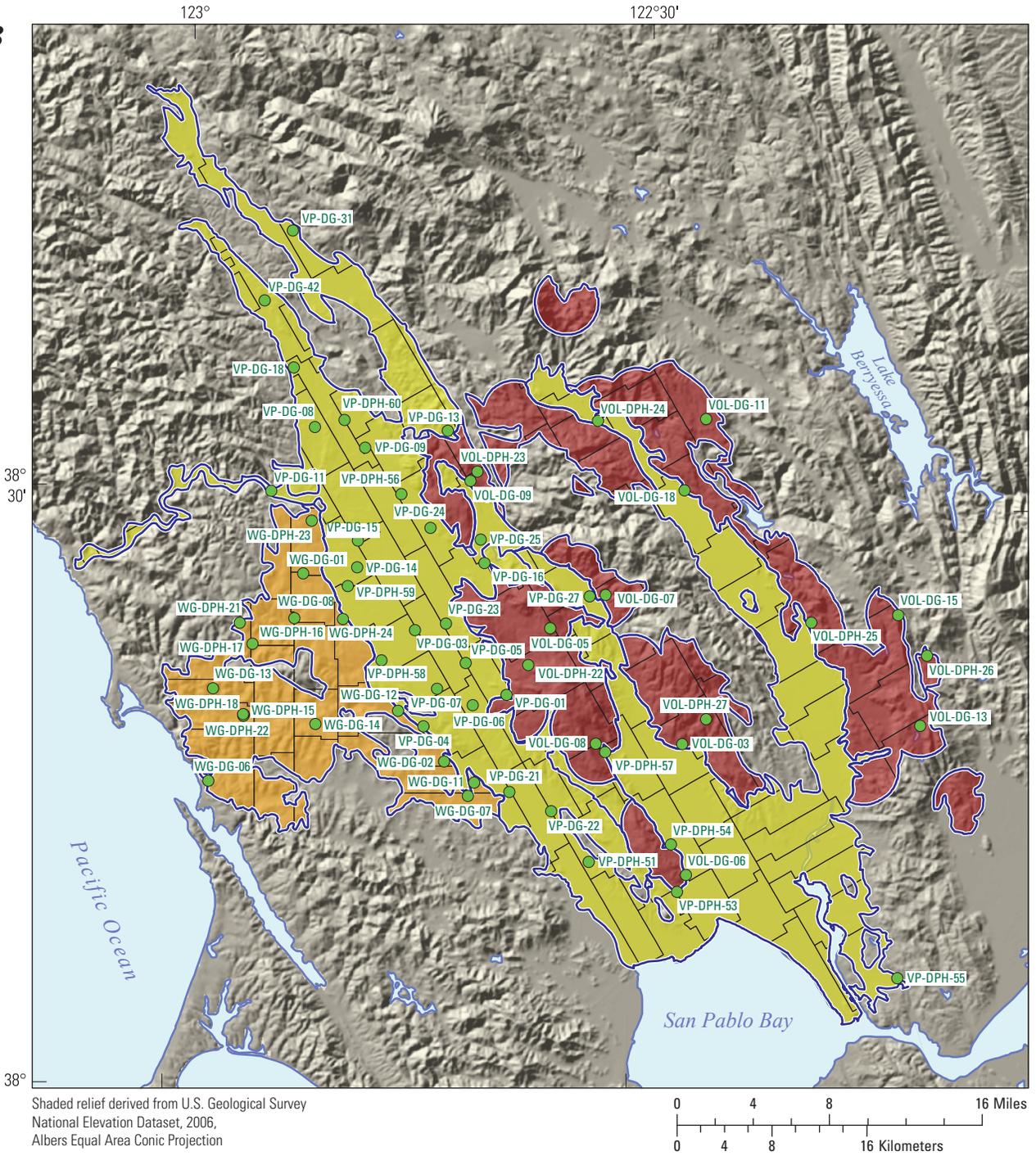
Shaded relief derived from U.S. Geological Survey
National Elevation Dataset, 2006,
Albers Equal Area Conic Projection

EXPLANATION

STUDY AREA

Wilson Grove Formation Highlands

Valleys and Plains

Volcanic Highlands

Study unit and study area boundary

Grid cell

CDPH well

Figure B1.   Continued.

Appendix C.   Calculating Total Dissolved Solids

Specific conductance, an electrical measure of TDS, was measured for the 83 grid and 6 understanding wells sampled by the USGS, whereas TDS was only measured for 41 of these wells. For wells that had no measured TDS, TDS values were calculated from specific conductance (SC) values using a linear regression equation (TDS = 0.56*SC + 58). The TDS values estimated using the regression equation closely matched measured TDS values ($r^2 = 0.96$). TDS values from the CDPH were combined with USGS measured and calculated TDS values.

Appendix D.   Estimation of Aquifer-Scale Proportions

Two statistical approaches, grid-based and spatially-weighted, were selected to evaluate the proportions of the primary aquifers in the NSF study unit that had high, moderate or low relative-concentrations (compared to benchmarks) of constituents. The grid-based and spatially-weighted estimations of aquifer-scale proportions, based on a spatially-distributed grid cell network across the study unit, are intended to characterize the water quality of the primary aquifers, at depths from which drinking water is usually drawn. These approaches assign weights to wells based upon a single well per cell (grid-based) or the number of wells per cells (spatially-weighted). Raw detection frequencies, derived from the percentage of the total number of wells with high or moderate relative-concentrations, were also calculated for individual constituents, but were not used for estimating aquifer-scale proportion because this method creates spatial bias towards regions with large numbers of wells.

Grid-based: One well in each grid cell, a "grid well," was randomly selected to represent the primary aquifers. Most grid wells were USGS grid wells that were sampled for the NSF study. Additional data for CDPH grid wells were selected to provide data for grid cells that did not have USGS grid well data. The relative-concentration for each constituent (concentration relative to its benchmark) was then evaluated for each grid well. The proportion of the primary aquifers that had high relative-concentrations was calculated by dividing the number of cells with concentrations > the benchmark (relative-concentration >1) by the total number of grid-wells in the NSF study unit. Proportions containing moderate and low relative-concentrations were calculated similarly. Confidence intervals for grid-based aquifer proportions were computed using the Jeffrey's interval for the binomial distribution

(Brown and others, 2001). The grid-based estimate is spatially unbiased. However, the grid-based approach may not detect constituents that exist at high concentrations in small proportions of the primary aquifers.

Spatially-weighted: The spatially-weighted approach relied upon USGS grid well data, CDPH data from August 30, 2001 to September 1, 2004 (most recent analyses per well for all wells within each grid cell), and selected USGS-understanding public-supply well data. However, instead of data from only one well per grid cell, the spatially-weighted approach calculates the high, moderate and low relative-concentrations for all the wells in each cell. The high, moderate and low aquifer-scale proportions are calculated from the percentage of cells with high, moderate, or low relative-concentrations (Isaaks and Srivastava, 1989). The resulting proportions are spatially unbiased. Confidence intervals for spatially-weighted estimates of aquifer-scale proportion are not described in this report.

The raw detection frequency approach is merely the percentage (frequency) of wells within the study unit that had high relative-concentrations. It was calculated by considering all of the available data in the period from August 30, 2001 to September 1, 2004 for the USGS grid well data, the CDPH well data (the most recent analysis per well for all wells), and USGS-understanding wells. However, this approach is not spatially unbiased because the CDPH and USGS-understanding wells are not uniformly distributed. Consequently, high values (or low values) for wells clustered in a particular area represent a small part of the primary aquifers, and could be given a disproportionately high (or low) weight compared to that given by spatially unbiased approaches. Raw detection frequencies of high relative-concentrations are provided to identify constituents for discussion in this report, but were not used to assess aquifer-scale proportions.

Appendix E.   Ancillary Data

Land-use classifications and percentages of each, well construction information, normalized position along flowpath, geochemical conditions, and groundwater age data and classifications are listed in tables B1, E1, and E2.

Land-Use Classification

Land use was classified using an enhanced version of the satellite derived (98 ft (30 m) pixel resolution) USGS National Land Cover Dataset (Voglemann and others, 2001; Price and others, 2003). 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. One pixel in the dataset imagery represents a land area of 9,688 ft^2 (900 m^2), calculated from the pixel radius of 98 ft (30 m). The imagery was classified into 25 land-cover categories (Nakagaki and Wolock, 2005). These 25 land-cover categories were aggregated into 4 principal land-use classes: urban, agricultural, natural, and mixed. Each pixel was assigned a land use class if >50 percent of the land cover in that area could be associated with a single land use. If no land cover was >50 percent of the pixel area, the classification of mixed was assigned.

Land-use classes for the study unit, for study areas, and for circles with a radius of 1,640 ft (500 m), around each well were assigned using the USGS National Land Cover Dataset (Johnson and Belitz, 2009). Land-use classifications for the study unit and the study areas (fig. 4) were calculated from the land cover of each pixel in the study unit and the study areas. Land use assigned to the area surrounding an individual well (table B1) was calculated from land use within the area of a circle around each well (radius of 1,640 ft (500 m) and land area of 8,449,627 ft^2 (785,398 m^2). For some analyses of constituent distributions (fig. 16*B*), the land-use classes urban and agricultural were combined into a single class urban/ agriculture to represent land used for anthropogenic purposes.

Well-Construction Information

Most well-construction data were from driller's logs and are given in table B1. Other sources were ancillary records of well owners and the USGS National Water Information System database. Well identification verification procedures are described by Kulongoski and others (2006).

Normalized Position of Wells along Flow Paths

The normalized position of wells within the alluvial valleys in relation to the groundwater flow system was an additional factor examined for the understanding of water quality in the NSF study unit (table B1). Three flowpaths were considered in this study: the Napa Valley flowpath, the Sonoma Valley flowpath, and the Russian River flowpath. Groundwater in the alluvium moves under a natural hydraulic gradient that conforms in a general way to the surface topography (Faye, 1973). In the Napa and Sonoma Valleys, groundwater flows generally from the northern part of the valley southward towards the San Pablo Bay (fig. 8). In the Alexander Valley and the Healdsburg area of the Santa Rosa Valley, groundwater flows generally from north to south towards the Lower Russian River Valley and then flows west (figs. 2, 8). Normalized position along the flowpath was determined by calculating the valley length (from the northernmost point in the valley to the discharge location). Then a perpendicular line was drawn from each well to the valley upgradient-downgradient axis (typically the location of the river), demarking the normalized position, or distance along the flowpath. Positions were normalized by dividing the projected location's distance along the flow path by the total length of the system, resulting in a value from 0 to 1; normalized positions are given in table B1. Lower values of normalized position indicate locations in the upgradient or proximal portion of the flow system and higher values of position indicate locations in the downgradient or distal portion of the flow system. Plotting data with respect to normalized position along the flowpath also allows aerially distributed data to be aggregated into a single diagrammatic cross-section.

Classification of Geochemical Condition

Geochemical conditions investigated as potential explanatory variables in this report include oxidation-reduction characteristics, dissolved oxygen, and ratios of iron, arsenic and chromium species (table E1). Oxidation-reduction (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 (TEAP); one TEAP typically dominates at a particular time and aquifer location (Chapelle and others, 1995; Chapelle, 2001). The predominant TEAPs are oxygen-reduction (causing oxic conditions), nitrate-reduction, manganese-reduction, iron-reduction, sulfate-reduction, and methanogenesis. The presence of redox-sensitive chemical species suggesting more than one TEAP may indicate mixed waters from different redox zones upgradient of the well, a well screened across more than one redox zone, or spatial heterogeneity in microbial activity in the aquifer. Different redox elements (for example; iron, manganese, and sulfur) tend not to reach overall equilibrium in most natural water systems (Lindberg and Runnels, 1984); therefore, a single redox measurement usually cannot represent the system, further complicating the assessment of redox conditions.

Table E1. Oxidation-reduction constituents, redox classification, and iron, arsenic, and chromium species ratios for samples from the North San Francisco Bay study unit, California.

[anoxic/suboxic, cm³STP/g, cubic centimeter at standard temperature and pressure per gram of water; dissolved oxygen <0.5 mg/L (milligram per liter); indeterminant, insufficient data to determine redox classification; µg/L, microgram per liter; N, nitrogen; na, no data available; oxic, dissolved oxygen ≥0.5 mg/L; redox, oxidation-reduction; O₂, oxygen; NO₃, nitrate; Mn, manganese; Fe, iron; As, arsenic; Cr, chromium. >, greater than; ≥, greater than or equal to; <, less than; —, not detected]

	Oxidation-reduction constituent									
USGS-GAMA well identification number	Dissolved oxygen	Nitrate plus nitrite, as nitrogen	Manganese	Iron	Sulfate	Methane x 10⁻⁴	Redox classification	Fe(III)/ Fe(II)	As(V)/ As(III)	Cr(VI)/ Cr(III)
	Oxidation-reduction threshold value									
	>0.5	>0.5	>50	>100	>4	>1				
	Possible redox type if concentration >redox threshold value									
	O₂	NO₃	Mn	Fe						
	Analysis reporting level and associated units									
	0.1	0.06	0.18	5.0	0.18	0.1				
	mg/L	mg/L	µg/L	µg/L	mg/L	x 10⁻⁴ cm³STP/g				
VOL-01	3.2	0.05	4.8	80	1.42	na	Oxic	0.2	>10	2.0
VOL-05	na	1.45	na	na	2.40	na	Indeterminate	na	na	>10
VOL-07	na	1.38	na	na	6.10	na	Indeterminate	na	na	9.2
VOL-09	na	na	27	na	9.10	na	Indeterminate	na	na	>10
VOL-11	na	1.06	na	na	8.70	na	Indeterminate	na	na	5.8
VOL-14	4.3	0.79	10.7	na	7.40	na	Oxic	<0.01	>10	>10
VOL-15	na	na	110	1,900	13	na	Indeterminate	na	na	10.4
VOL-18	0.2	na	na	240	3.10	na	Anoxic/suboxic	na	na	<0.01
VOL-19	1.9	0.03	127	235	5.94	na	Mixed	0.1	1.1	>10
VOL-20	2.9	0.10	0.3	4	4.56	na	Oxic	>10	>10	>10
VP-01	na	na	37	570	5.00	na	Indeterminate	na	na	>10
VP-04	na	na	150	1,600	11	na	Indeterminate	na	na	<0.01
VP-06	na	5.20	na	na	8.60	na	Indeterminate	na	na	3.5
VP-07	na	1.04	150	190	7.90	na	Mixed	na	na	—
VP-08	na	1.27	na	na	18	na	Indeterminate	na	na	2.5
VP-09	na	0.99	na	na	2.90	na	Indeterminate	na	na	>10
VP-10	0.1	0.31	203	117	11.3	na	Anoxic/suboxic	na	na	na
VP-11	na	1.20	na	190	14	na	Indeterminate	na	na	—
VP-16	na	na	75	180	0.00	na	Indeterminate	na	na	na
VP-18	na	0.72	na	na	12	na	Indeterminate	na	na	>10
VP-19	0.4	0.09	42.2	10	9.63	na	Anoxic/suboxic	0.3	—	>10
VP-21	na	3.16	na	na	23	na	Indeterminate	na	na	>10
VP-22	na	2.48	na	na	19	Methane	Indeterminate	na	na	>10
VP-23	na	4.07	na	na	43	na	Indeterminate	na	na	>10
VP-25	na	1.02	42	na	1.40	na	Indeterminate	na	na	3.6
VP-26	0.1	0.04	241	21	21.7	na	Anoxic/suboxic	1.4	>10	>10
VP-27	na	3.16	150	210	13	na	Mixed	na	na	4.2
VP-29	5.7	1.89	0.1	na	26.2	na	Oxic	—	—	>10
VP-30	0.6	0.62	36.8	13	19.1	na	Oxic	0.4	—	>10
VP-32	0.0	na	129	5	32.1	na	Anoxic/suboxic	na	na	8.3
VP-33	na	na	139	1,090	19.3	na	Indeterminate	na	na	>10
VP-34	0.2	0.06	434	999	2.58	0.41	Anoxic/suboxic	0.05	0.15	7.8

Table E1. Oxidation-reduction constituents, redox classification, and iron, arsenic, and chromium species ratios for samples from the North San Francisco Bay study unit, California.—Continued

[anoxic/suboxic, cm^{3}STP/g, cubic centimeter at standard temperature and pressure per gram of water; dissolved oxygen <0.5 mg/L (milligram per liter); indeterminant, insufficient data to determine redox classification; µg/L, microgram per liter; N, nitrogen; na, no data available; oxic, dissolved oxygen ≥0.5 mg/L; redox, oxidation-reduction; O$_2$, oxygen; NO$_3$, nitrate; Mn, manganese; Fe, iron; As, arsenic; Cr, chromium. >, greater than; ≥, greater than or equal to; <, less than; —, not detected]

	Oxidation-reduction constituent									
	Dissolved oxygen	Nitrate plus nitrite, as nitrogen	Manganese	Iron	Sulfate	Methane x 10^{-4}				
	Oxidation-reduction threshold value									
	>0.5	>0.5	>50	>100	>4	>1				
	Possible redox type if concentration >redox threshold value									
	O$_2$	NO$_3$	Mn	Fe						
USGS-GAMA well identification number	Analysis reporting level and associated units						Redox classification	Fe(III)/ Fe(II)	As(V)/ As(III)	Cr(VI)/ Cr(III)
	0.1	0.06	0.18	5.0	0.18	0.1				
	mg/L	mg/L	µg/L	µg/L	mg/L	x 10^{-4} cm^{3}STP/g				
VP-35	na	4.52	3.6	17	21.2	na	Mixed	na	na	—
VP-36	na	0.00	1,220	671	12.4	na	Mixed	na	na	1.0
VP-37	3.5	3.22	6.4	na	14.8	0.32	Oxic	>10	>10	3.9
VP-38	0.1	0.06	14.5	12	1.72	4.87	Anoxic/suboxic	0.3	4.8	3.3
VP-39	0.8	na	78.1	43	5.46	na	Oxic	na	na	<0.01
VP-40	0.1	0.06	40.1	331	3.17	8.03	Anoxic/suboxic	0.09	—	4.0
VP-41	1.2	3.61	928	na	23.6	na	Oxic	na	na	0.0
VP-42	na	1.38	130	670	2.10	na	Mixed	na	na	na
VP-43	na	na	na	65	12	na	Indeterminate	na	na	>10
VP-44	na	2.94	135	310	239	na	Mixed	na	na	<0.01
VP-45	0.3	0.06	50.1	135	19.9	na	Anoxic/suboxic	—	—	>10
VP-46	1.1	2.48	1.6	22	43.7	na	Oxic	0.3	—	16.0
VP-47	na	0.68	0.4	na	37.9	na	Indeterminate	na	na	>10
VP-48	0.0	0.00	181	714	14.9	na	Anoxic/suboxic	na	na	2.5
VP-49	0.1	0.06	435	362	7.12	na	Anoxic/suboxic	<.01	<.01	5.5
VP-50	0.7	0.05	687	57	3.84	na	Mixed	0.5	>10	>10
VPFP-01	0.1	0.06	66.4	36	4.70	na	Anoxic/suboxic	0.2	>10	0.2
VPFP-02	0.3	1.55	355	na	15.4	na	Anoxic/suboxic	>10	>10	>10
VPFP-03	7.4	na	938	4	32.7	na	Oxic	na	na	>10
WG-06	na	1.08	na	na	28	na	Indeterminate	na	na	1.5
WG-08	0.8	1.21	12.9	40	20.3	na	Oxic	—	—	2.3
WG-10	0.1	0.06	0.5	na	5.87	na	Anoxic/suboxic	>10	—	12.5
WG-11	na	1.29	na	99	20	na	Indeterminate	na	na	na
WGFP-01	0.2	0.06	16	29	15.9	na	Anoxic/suboxic	na	na	>10

Table E2. Noble gas based recharge temperature, tritium, terrigenic helium, percent modern carbon, and age classification of samples, North San Francisco Bay study unit, California.

[°C, degrees Celsius; ns, not sampled]

USGS GAMA well identification number	Noble gas based recharge temperature, in °C	Tritium, in tritium units	Terrigenic helium, percentage of total helium	Percent modern carbon	Age classification
VOL-01	15.8	<1	1.4	68.7	Pre-Modern
VOL-02	ns	<1	ns	ns	ns
VOL-03	20.0	<1	68.6	ns	Pre-Modern
VOL-04	13.0	<1	11.7	ns	Pre-Modern
VOL-05	14.6	<1	0.0	ns	Mixed
VOL-06	16.1	<1	72.9	ns	Pre-Modern
VOL-07	17.5	<1	8.4	ns	Pre-Modern
VOL-08	16.9	<1	2.1	ns	Mixed
VOL-09	13.7	<1	15.4	ns	Pre-Modern
VOL-10	11.8	2.4	0.0	ns	Modern
VOL-11	13.8	<1	0.7	ns	Mixed
VOL-12	15.2	<1	31.0	ns	Pre-Modern
VOL-13	13.6	3.1	0.0	93.1	Modern
VOL-14	15.2	1.3	0.0	ns	Modern
VOL-15	13.2	<1	9.3	ns	Pre-Modern
VOL-16	20.2	<1	86.0	ns	Pre-Modern
VOL-17	14.1	<1	12.0	ns	Pre-Modern
VOL-18	14.8	<1	70.9	ns	Pre-Modern
VOL-19	16.1	<1	4.1	52.0	Pre-Modern
VOL-20	13.5	<1	4.7	47.7	Pre-Modern
VP-01	11.4	<1	80.3	ns	Pre-Modern
VP-02	16.8	<1	1.6	ns	Mixed
VP-03	14.6	<1	28.4	ns	Pre-Modern
VP-04	14.8	<1	12.9	ns	Pre-Modern
VP-05	12.1	<1	80.1	ns	Pre-Modern
VP-06	14.4	<1	17.9	ns	Pre-Modern
VP-07	13.8	<1	34.8	ns	Pre-Modern
VP-08	15.4	2.3	4.3	ns	Modern
VP-09	13.1	<1	20.1	ns	Pre-Modern
VP-10	14.6	2.3	21.2	104.4	Mixed
VP-11	20.6	2.0	0.0	ns	Modern
VP-12	20.5	<1	0.0	ns	Mixed
VP-13	15.0	<1	3.4	ns	Pre-Modern
VP-14	10.9	<1	76.5	ns	Pre-Modern
VP-15	13.4	1.6	0.0	ns	Modern
VP-16	13.8	<1	71.6	ns	Pre-Modern
VP-17	16.1	2.1	4.6	ns	Modern
VP-18	14.6	2.0	0.0	ns	Modern
VP-19	21.4	2.1	4.3	97.4	Modern
VP-20	13.4	2.1	13.5	ns	Mixed

Table E2.   Noble gas based recharge temperature, tritium, terrigenic helium, percent modern carbon, and age classification of samples, North San Francisco Bay study unit, California.—Continued

[°C, degrees Celsius; ns, not sampled]

USGS GAMA well identification number	Noble gas based recharge temperature, in °C	Tritium, in tritium units	Terrigenic helium, percentage of total helium	Percent modern carbon	Age classification
VP-21	14.1	2.5	0.0	ns	Modern
VP-22	15.9	2.0	19.8	ns	Mixed
VP-23	12.1	<1	76.8	ns	Pre-Modern
VP-24	15.0	<1	50.4	ns	Pre-Modern
VP-25	15.3	<1	22.8	ns	Pre-Modern
VP-26	14.5	<1	65.6	13.1	Pre-Modern
VP-27	14.4	1.5	27.2	ns	Mixed
VP-28	14.9	1.7	40.2	ns	Mixed
VP-29	15.2	2.3	0.0	104.5	Modern
VP-30	14.3	2.6	41.0	70.0	Mixed
VP-31	16.8	1.4	19.5	ns	Mixed
VP-32	15.0	<1	60.0	ns	Pre-Modern
VP-33	16.3	<1	11.5	ns	Pre-Modern
VP-34	20.1	<1	93.9	19.7	Pre-Modern
VP-35	14.4	<1	1.2	ns	Modern
VP-36	11.4	<1	74.8	ns	Pre-Modern
VP-37	18.4	1.8	11.7	96.5	Mixed
VP-38	13.7	<1	95.8	0.6	Pre-Modern
VP-39	15.0	<1	48.7	ns	Pre-Modern
VP-40	14.7	<1	92.7	13.3	Pre-Modern
VP-41	16.2	2.2	65.4	ns	Mixed
VP-42	14.9	<1	0.0	ns	Mixed
VP-43	14.9	<1	19.3	ns	Pre-Modern
VP-44	ns	<1	ns	ns	ns
VP-45	12.9	<1	79.3	6.7	Pre-Modern
VP-46	17.2	2.3	65.4	ns	Mixed
VP-47	18.5	2.4	8.1	ns	Mixed
VP-48	14.9	<1	83.1	ns	Pre-Modern
VP-49	ns	<1	96.9	2.2	Pre-Modern
VP-50	13.0	<1	44.6	19.1	Pre-Modern
VPFP-01	12.7	<1	54.6	24.0	Pre-Modern
VPFP-02	14.0	<1	7.5	84.7	Pre-Modern
VPFP-03	16.3	2.4	95.9	ns	Mixed
VPFP-04	12.5	2.5	13.1	ns	Mixed
WG-01	14.4	<1	0.0	ns	Mixed
WG-02	16.2	<1	1.1	ns	Mixed
WG-03	15.0	<1	0.0	ns	Mixed
WG-04	15.5	<1	0.0	ns	Mixed
WG-05	ns	<1	ns	ns	ns
WG-06	ns	1.9	ns	ns	ns

Table E2. Noble gas based recharge temperature, tritium, terrigenic helium, percent modern carbon, and age classification of samples, North San Francisco Bay study unit, California.—Continued

[°C, degrees Celsius; ns, not sampled]

USGS GAMA well identification number	Noble gas based recharge temperature, in °C	Tritium, in tritium units	Terrigenic helium, percentage of total helium	Percent modern carbon	Age classification
WG-07	12.0	<1	64.7	ns	Pre-Modern
WG-08	15.7	<1	1.5	57.5	Pre-Modern
WG-09	15.2	<1	0.0	ns	Mixed
WG-10	ns	<1	ns	23.4	Pre-Modern
WG-11	15.6	<1	20.8	ns	Pre-Modern
WG-12	14.6	<1	14.4	ns	Pre-Modern
WG-13	ns	<1	ns	ns	ns
WG-14	15.3	<1	48.8	ns	Pre-Modern
WGFP-01	14.4	<1	3.9	45.2	Pre-Modern

Groundwater-Age Classification

Groundwater recharge temperature from noble gases, age data and classifications are listed in table E2. Groundwater dating techniques indicate the time since the groundwater was last in contact with the atmosphere. Techniques used to estimate groundwater residence times or 'age' include those based on tritium (for example: Tolstikhin and Kamenskiy, 1969; Torgersen and others, 1979),tritium combined with its decay product helium-3 (for example, Takaoka and Mizutani, 1987; Poreda and others, 1988), carbon-14 activities (for example, Vogel and Ehhalt, 1963; Plummer and others, 1993), and dissolved noble gases, particularly helium-4 accumulation (for example: Davis and DeWiest, 1966; Andrews and Lee, 1979; Kulongoski and others, 2008).

Tritium (^{3}H) 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), by above-ground nuclear explosions, and by the operation of nuclear reactors. Tritium enters the hydrological cycle following oxidation to tritiated water (HTO). Consequently, the presence of ^{3}H in groundwater may be used to identify water that has exchanged with the atmosphere in the past 50 years. By determining the ratio of ^{3}H to ^{3}He, resulting from the radioactive decay of ^{3}H, the time that the water has resided in the aquifer can be calculated more precisely than by using tritium alone (for example: Takaoka and Mizutani, 1987; Poreda and others, 1988).

Carbon-14 is a widely used chronometer based on the radiocarbon content of dissolved inorganic carbonate species in 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, dissolved in precipitation, and incorporated into the hydrologic cycle. ^{14}C activity in groundwater, expressed as percent modern carbon (pmc), reflects exposure to the atmospheric ^{14}C source and is governed by the decay constant of ^{14}C (with a half-life of 5,730 yr). ^{14}C can be used to estimate groundwater ages ranging from 1,000 to less than 30,000 years before present because of its half-life. Calculated ^{14}C ages in this study are referred to as "uncorrected" because they have not been adjusted to consider exchanges with sedimentary sources of carbon (Fontes and Garnier, 1979). The ^{14}C age (residence time) is calculated on the basis of the decrease in ^{14}C activity due to radioactive decay since groundwater recharge, relative to an assumed initial ^{14}C concentration (Clarke and Fritz, 1997). Average initial ^{14}C activity of 99 percent modern carbon (pmc) was assumed for this study, with estimated errors on calculated groundwater ages of up to ±20 percent.

Helium (He) is a naturally occurring inert gas initially included during the accretion of the planet, and later produced by the radioactive decay of lithium, thorium, and uranium in the earth. Measured He concentrations in groundwater is the sum of several He components including air-equilibrated He (He_{eq}), He from dissolved-air bubbles (He_a), terrigenic He (He_{ter}), and tritiogenic He-3 (^3He_t). Helium (^{3}He and ^{4}He) concentrations in groundwater often exceed the expected solubility equilibrium values, a function of the temperature of the water, as a result of subsurface production of both isotopes and their subsequent release into the groundwater (for example, Morrison and Pine, 1955; Andrews and Lee, 1979; Torgersen, 1980; Andrews, 1985; Torgersen and Clarke, 1985). The presence of terrigenic He in groundwater, from its production in aquifer material or deeper in the crust, is indicative of long groundwater residence times. The amount of terrigenic helium is defined as the concentration of the total measured helium minus the fraction due to air equilibration

$[He_{eq}]$ and dissolved air bubbles $[He_a]$. For the purposes of this study, percent terrigenic He is used to identify groundwater with residence times greater than 100 yr. Percent terrigenic He is defined as the concentration of terrigenic He (as defined previously) divided by the total measured He in the sample (corrected for air-bubble entrainment). Samples with greater than 5 percent terrigenic He indicate groundwater has a residence time of more than 100 yr.

Recharge temperatures for 82 samples were calculated from dissolved neon, argon, krypton, and xenon data using methods described by Aeschbach-Hertig and others (1999). The only modeled recharge temperatures accepted were those for which the probability was greater than 1 percent that the sum of the squared deviations between the modeled and the measured concentrations (weighted with the experimental 1-sigma errors) was equal to or greater than the observed value (Aeschbach-Hertig and others, 2000). The recharge temperature with the highest probability for each sample was used in this report.

$^3H/^3He$ ages were computed as described by Poreda and others (1988). The $^3He/^4He$ of samples was determined by the linear regression of the percentage of terrigenic He and δ^3He [$\delta^3He = (R_{meas}/R_{atm}-1) \times 100$] of samples containing less than 1 tritium unit. Calculations of the noble gas temperature and ^3He to ^4He ratios are useful because they constrain helium-based groundwater ages further.

In this study, the age distributions of samples are classified as pre-modern, modern, and mixed. Groundwater with tritium activity less than 1 tritium unit (TU), percent terrigenic He greater than 5 percent, and ^{14}C less than 90 pmc was designated as pre-modern, defined as having been recharged before 1950. Groundwater with tritium activities greater than 1 TU, percent terrigenic He less than 5 percent and ^{14}C greater than 90 pmc is designated as modern, defined as having been recharged after 1950. Samples with pre-modern and modern components are designated as mixed

groundwater, which includes substantial fractions of old and young waters. In reality, pre-modern groundwater could contain very small fractions of modern water and modern groundwater could contain small fractions of pre-modern water. Previous investigations have used a range of tritium values from 0.3 to 1.0 TU as thresholds for distinguishing pre-1950 from post-1950 water (Michel, 1989; Plummer and others, 1993; Michel and Schroeder, 1994; Clark and Fritz, 1997; Manning and Solomon, 2005). By using a tritium value of 1.0 TU for the threshold in this study, the age classification scheme allows a slightly larger fraction of modern water to be classified as pre-modern than if a lower threshold were used. A lower threshold for tritium would result in fewer samples classified as pre-modern than mixed when other tracers, such as carbon-14 and terrigenic helium, would suggest that they were primarily pre-modern. This higher threshold was considered more appropriate for this study since many of the wells were production wells with long screens and mixing of waters of different ages is likely to occur.

Tritium, percent modern carbon, and percent terrigenic helium, and sample age classifications are reported in Appendix E: table E2. Because of uncertainties in age distributions, in particular those caused by mixing waters of different ages in wells with long perforation intervals and high withdrawal rates, these age estimates were not specifically used for statistically quantifying the relation between age and water quality in this report. While more sophisticated lumped parameter models used for analyzing age distributions that incorporate mixing are available (for example, Cook and Böhlke, 2000), use of these alternative models to characterize age mixtures was beyond the scope of this report. Rather, classification into modern, mixed, and pre-modern categories was sufficient to provide an appropriate and useful characterization for the purposes of examining groundwater quality.

Appendix F.   Comparison of California Department of Public Health (CDPH) and USGS–GAMA Data

CDPH and GAMA data were compared to assess the validity of combining data from these different sources. Because the LRLs or MDLs for most organic constituents and trace elements were substantially lower for data collected by the USGS GAMA Priority Basin Project than data from the CDPH database (table 3), only relatively high concentrations of constituents could be compared, and as a result, there were insufficient data to rigorously evaluate. However, concentrations of inorganic constituents (calcium, magnesium, sodium, alkalinity, chloride, sulfate, TDS, nitrate plus nitrite as nitrogen), which generally are prevalent at concentrations substantially above LRLs, were compared for each well using data from both sources. Forty-one wells had major ion or nitrate data from the USGS-database and the CDPH database. Wilcoxon signed rank tests of paired analyses for these eight constituents indicated no significant differences between USGS–GAMA and CDPH data for these constituents. While differences between the paired data sets existed for a few wells, most sample pairs plotted close to a 1 to 1 line (fig. F1). These plots indicated that the GAMA and CDPH inorganic data were comparable.

Major-ion data for grid wells with sufficient data (USGS and CDPH data) were plotted on Piper diagrams (Piper, 1944) with all CDPH major ion data to determine whether the grid wells represented the range of groundwater types that have historically been observed in the study unit. Piper diagrams show the relative abundance of major cations and anions (on a charge equivalent basis) as a percentage of the total ion content of the water (fig. F2). Piper diagrams are often used to define groundwater type (Hem, 1970). All cation/anion data in the CDPH database that had a cation/anion balance <10 percent were retrieved and plotted on these Piper diagrams for comparison with grid well data.

The range of water types in grid wells and noted in historical CDPH data were similar (fig. F2). In most wells, no single cation accounted for more than 10 percent of the total cations, and bicarbonate accounted for more than 10 percent of the total anions. Waters in these wells are described as *mixed cation-bicarbonate* type waters. There were also many wells that contained *mixed cation-mixed anion* type waters, indicating that no single cation and no single anion accounted for more than 10 percent of the total. Waters in a minority of wells are classified as sodium-chloride type waters, indicating that sodium and chloride accounted for more than 10 percent of the total cations and anions, respectively.

The determination that the range of relative abundance of major cations and anions in grid wells is similar to the range of those in all CDPH wells indicates that the grid wells represent the types of water present within the NSF study unit.

A minor difference between grid data and CDPH data was evident: a minority of GAMA wells (8 wells) had higher sodium plus potassium as the dominant cations and sulfate plus chloride as the dominant anions (right side of center diagram, fig. F2). These were the hydrothermal wells and spring, which are not used for public drinking water supply (fig. F3), so it was not surprising that this type of water was not recorded in the CDPH database. Results from the analyses of these wells are provided here for reference and will be discussed in a subsequent report.
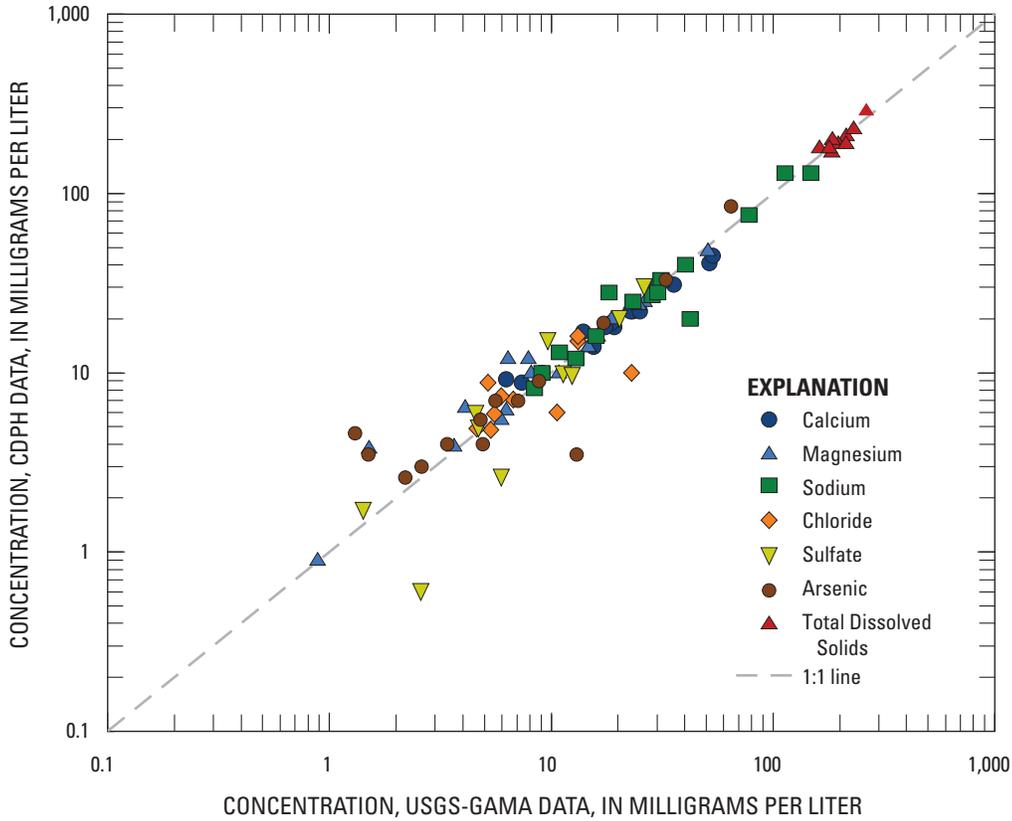
Figure F1.   Paired inorganic constituent concentrations comparing USGS–GAMA data and California Department of Health (CDPH) data from the period August 30, 2001, to September 1, 2004, North San Francisco Bay study unit, California. USGS, U.S. Geological Survey; TDS, total dissolved solids.
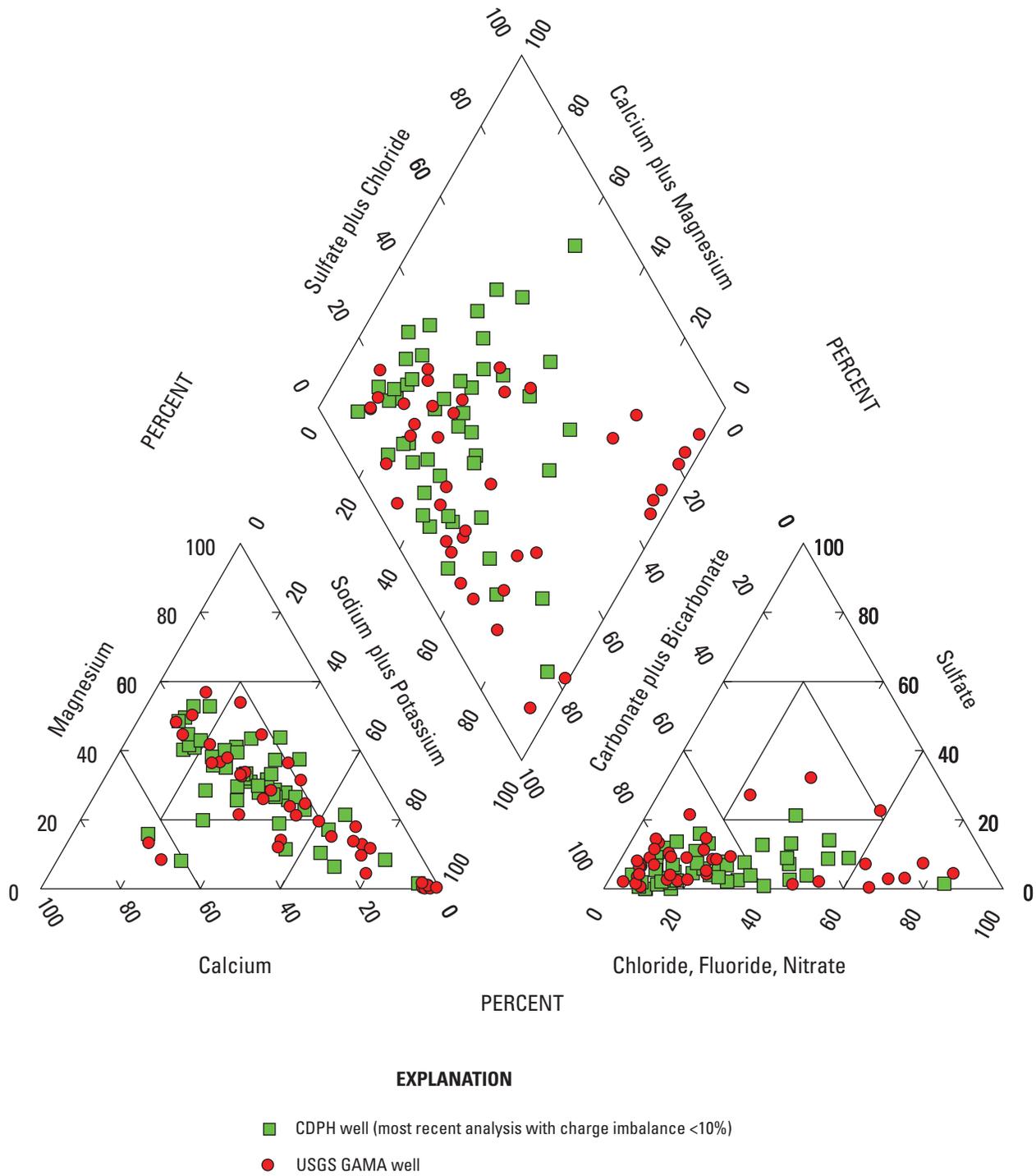
Figure F2.   Wells sampled for the North San Francisco Bay study unit, California, and wells that have constituents with a charge imbalance less than 10 percent recorded by the California Department of Public Health (CDPH) database. <, less than; %, percent.
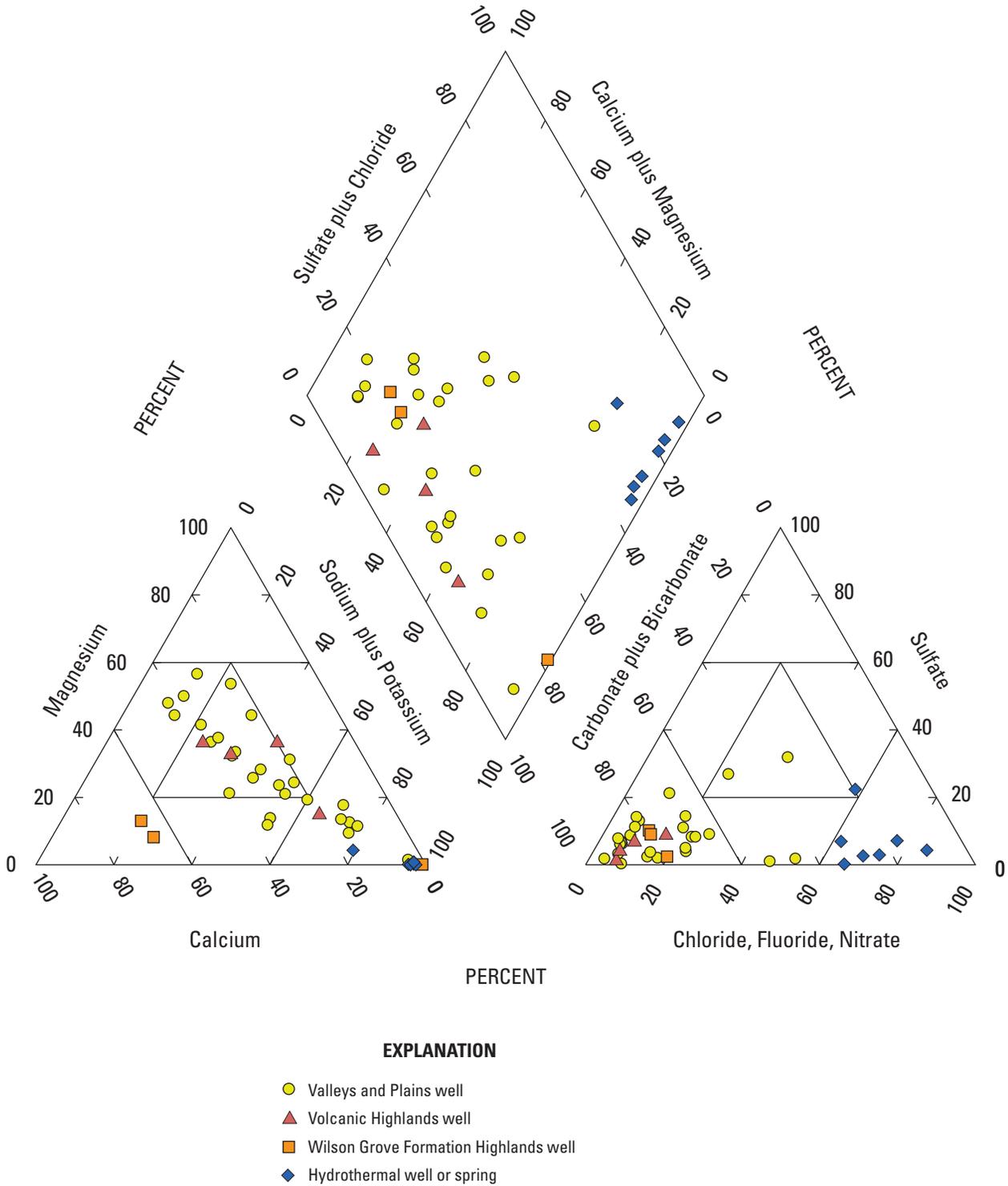
Figure F3.   Constituents with a charge imbalance of less than 10 percent, organized by study area in the North San Francisco Bay study unit, California.

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