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 San Diego study unit, and elsewhere in California (Landon and others, 2010), the naturally occurring inorganic constituents tend to be more prevalent in groundwater. Although 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 criteria for distinguishing constituents occurring at moderate rather than low concentrations.

Datasets for Status Assessment

USGS-Grid and -Understanding 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 Wright and others (2005). Briefly, each study area was divided into equal-area grid cells that ranged in size and number from 10 4-mi^2 cells in the Warner Valley study area to 20 approximately 15-mi^2 cells in the Temecula Valley and Alluvial Basins study areas (fig. 6A–C). Because the Hard Rock study area was so large (850 mi^2), grids were configured to provide a sampling density of approximately one well per 85 mi^2 which equaled ten grid cells. The objective of the sampling design in the Hard Rock study area was to provide an initial reconnaissance of groundwater quality outside of CDWR-defined groundwater basins. Consequently the analyses from groundwater wells sampled in the Hard Rock study area were not included when calculating aquifer-scale proportions for constituents at the study unit level.

Within each grid cell, one well was randomly selected to represent the cell (Scott, 1990). It should be noted that some cells were divided into several sections because of geographic features (fig. 6A–C). Wells were selected from the population of wells in state-wide databases maintained by the CDPH and the USGS. USGS-grid wells in the San Diego study unit were numbered in the order of sample collection with the prefix varying by study area: the Temecula Valley study area (SDTEM), the Warner Valley study area (SDWARN), the Alluvial Basins study area (SDALLV), and the Hard Rock study area (SDHDRK). Grid well numbers in the San Diego study unit are not always sequential because some grid wells

have been re-designated as understanding wells subsequent to the publication of the San Diego study unit USGS Data Series report (table A1). Wells were redesignated in order to obtain a spatially distributed grid sampling-network that would meet the requirements of the *status assessment*.

The San Diego study unit contained a total of 60 grid cells, and the USGS sampled wells in 47 of those cells (USGS-grid wells) (fig. 6A–C). All 47 USGS-grid wells sampled in the San Diego study unit were PSWs that are listed in the CDPH water-quality database. Some grid cells could not be sampled because wells were not available, the wells were inoperable or the owner declined to participate in the program. However, if there was a well adjacent (≤ 1 km) to an empty grid cell, then the adjacent well was sampled and the water quality was used to represent the previously empty grid cell. Of the 20 grid cells in the Temecula Valley and Alluvial Basins study areas, 12 and 16 grid cells, respectively, were sampled or water-quality data was available from CDPH. In the Warner Valley, 9 of 10 grid cells were sampled and in the Hard Rock study area all 10 grid cells were sampled.

Eleven understanding wells were sampled for the purpose of understanding water quality changes along flow paths or in areas where historically little water-quality data were available. USGS-understanding (nonrandomized) wells were designated with the suffix FP for flow path wells and U for other understanding wells in addition to the regular GAMA ID. The understanding wells were not included in the grid-based characterization of water quality, but were used in the spatially weighted approach and were used to examine the effects of explanatory factors, such as land use, on water quality. An in-depth analysis of how water quality changes along flow paths in the San Diego study is not presented in this report.

Wells were sampled using a tiered analytical approach. All wells were sampled for a standard set of constituents, including VOCs, pesticides and pesticide degradates, stable isotopes of water, dissolved noble gases, and tritium (table 1). The standard set of constituents was termed the "fast" schedule. Wells on the "intermediate" schedule were sampled for all the constituents on the fast schedule, plus NDMA, perchlorate, potential waste-water indicators, and chromium species. Wells sampled on the "slow" schedule were sampled for all the constituents on the intermediate schedule, plus nutrients and dissolved organic carbon, major and minor ions, trace elements, arsenic and iron species, carbon isotopes, radon-222, radium isotopes, gross alpha and beta radiation, 1,4-dioxane and microbial constituents. Approximately 60 percent of the wells were sampled on a fast or intermediate schedule, and 40 percent were sampled on a slow schedule. Wells in areas of interest, such as along flow paths, or in places where water quality data were scarce, were given priority for slow schedule sampling.
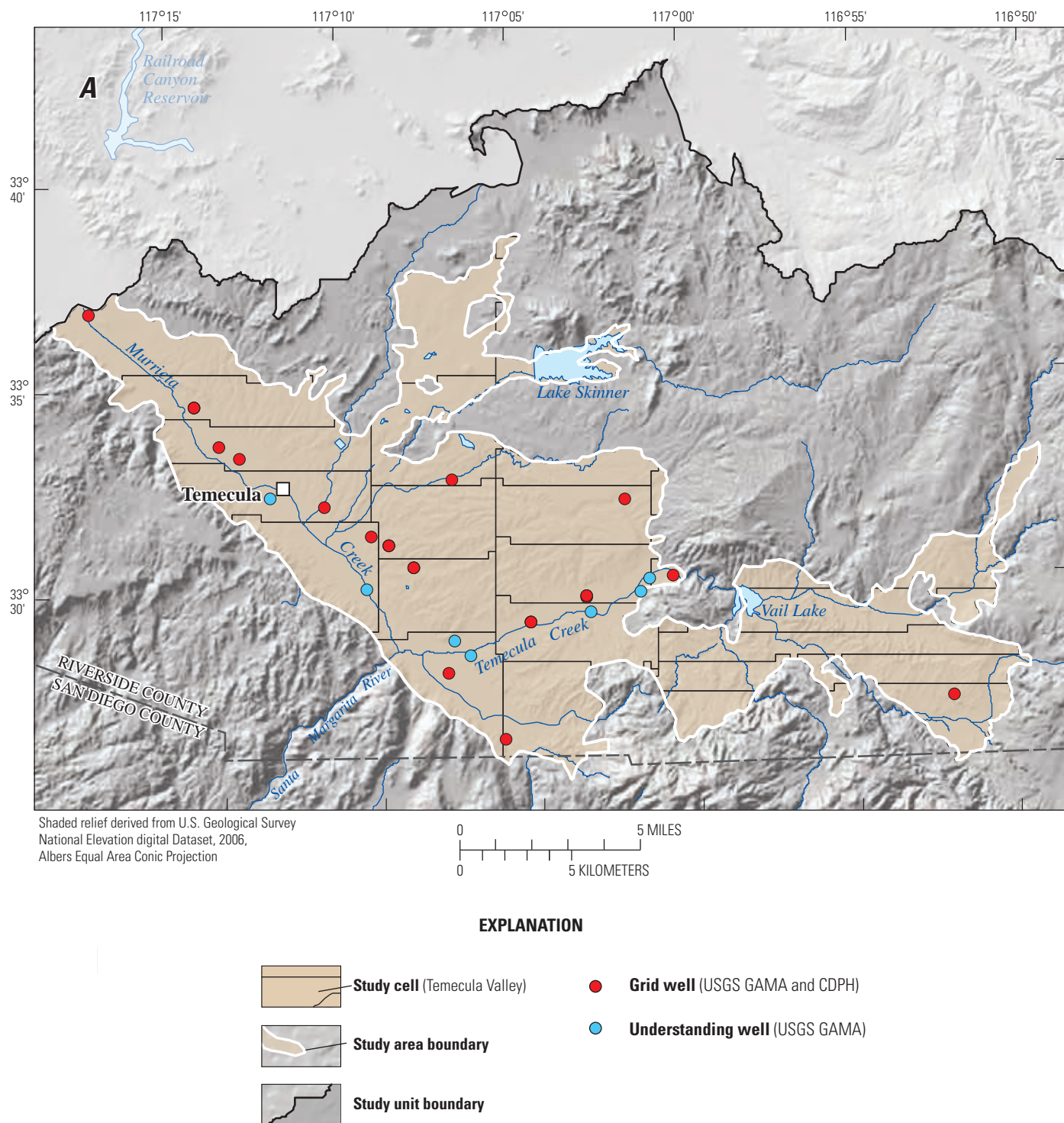
Figure 6A–C.   Locations of grid cells, California Department of Public Health (CDPH) wells, and the USGS-grid and -understanding wells sampled during May to July, 2004 for the San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit: (A) Temecula Valley, (B) Warner Valley, and (C) Alluvial Basins, and Hard Rock study areas.
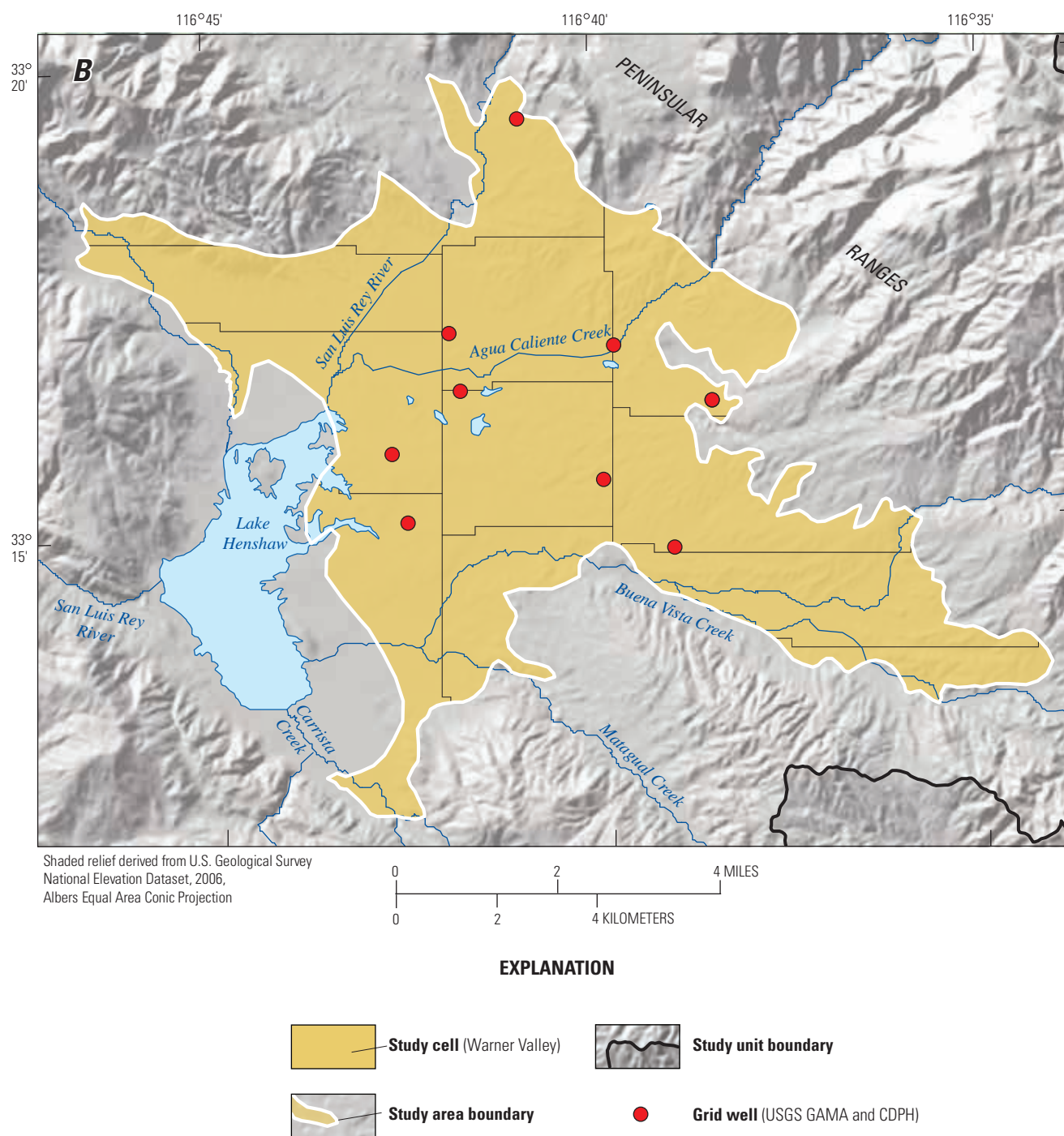
Figure 6*A*–*C*.—Continued

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

EXPLANATION

Study cell (Alluvial Basins)

Study cell (Hard Rock)

Study unit boundary

● Grid well (USGS GAMA and CDPH)
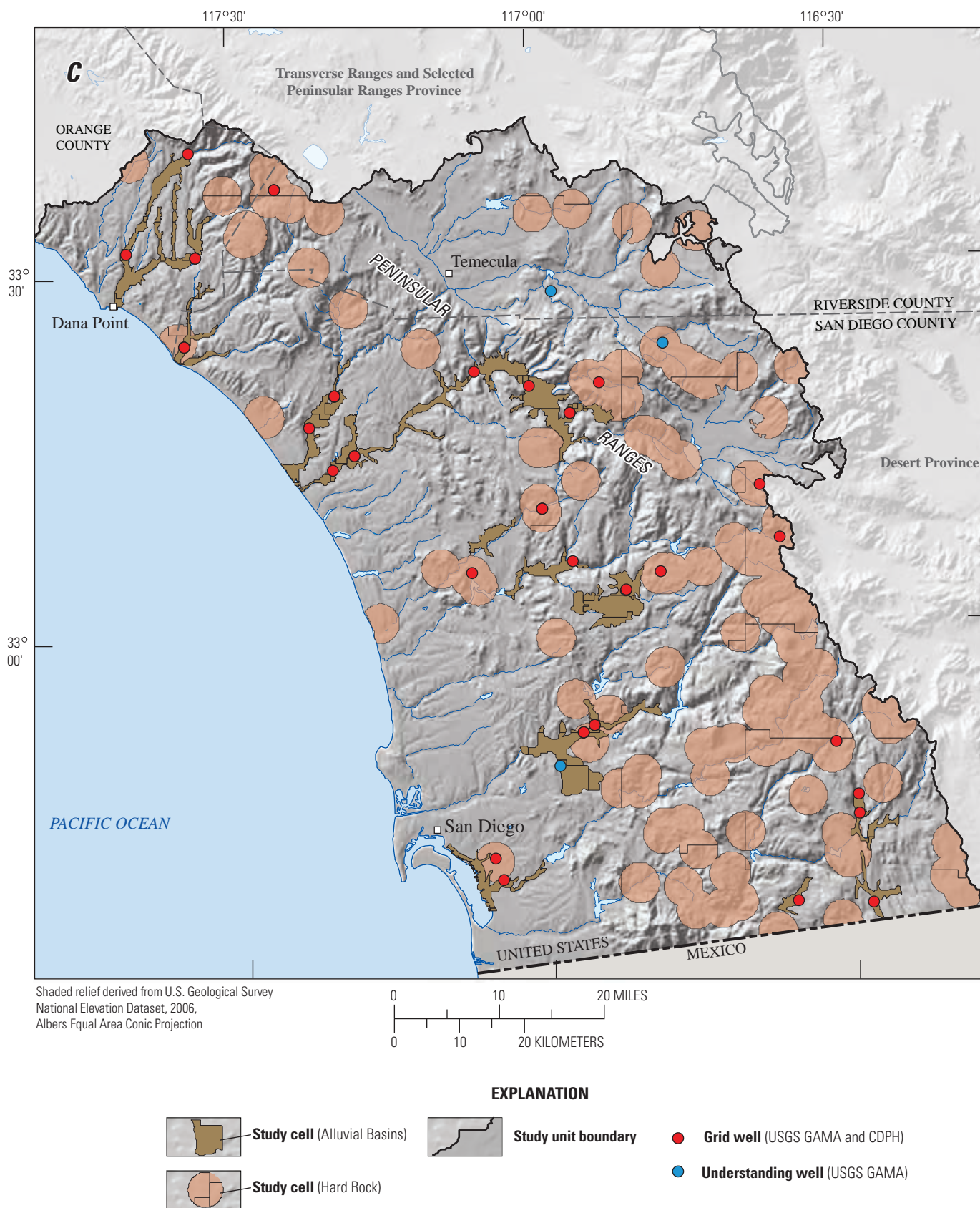
● Understanding well (USGS GAMA)

Figure 6*A*–*C*.—Continued

Table 1. Constituent class and numbers of constituents and wells sampled for each analytical group in the San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May 17–July 29, 2004.

[NDMA, *N*-Nitrosodimethylamine; USGS, U.S. Geological Survey]

	Sampling schedule		
	Fast	Intermediate	Slow
Well summary	**Number of wells**		
Total number of wells	8	26	24
Number of grid wells sampled	6	22	19
Number of understanding wells sampled	2	4	5
Analyte Groups[1]	**Number of constituents**		
Specific conductance and temperature	2	2	2
Volatile organic compounds (VOCs)	88	88	88
Pesticides and degradates	64	64	64
Noble gases and tritium[2]	7	7	7
Stable isotopes of hydrogen and oxygen	2	2	2
Potential waste-water indicators[3]		48	48
Pharmaceuticals[4]		16	16
Perchlorate and NDMA		2	2
Chromium species		2	2
Tritium[5]		1	1
pH, dissolved oxygen, alkalinity, turbidity			4
Polar pesticides and degradates[6]			59
1,4-Dioxane			1
Nutrients and dissolved organic carbon			6
Major and minor ions, and trace elements			36
Arsenic and iron species			4
Carbon isotopes			2
Radon-222			1
Radium isotopes			2
Gross alpha and beta radioactivity			4
Microbial constituents			4
Sum of constituents for each schedule:	163	232	355

[1]Not all analyte groups or analytes are discussed in the report.

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

[3]Counts do not include analytes in common with VOCs, pesticides and degradates, pharmaceuticals or polar pesticides and degradates. Wastewater data is not used for assessment of status or understanding in this report.

[4]Pharmaceutical data is not used for assessment of status or understanding in this report.

[5]Analyzed at USGS Stable Isotope and Tritium Laboratory, Menlo Park, California.

[6]Counts do not include analytes in common with pesticides and degradates.

CDPH Grid Wells

The four study areas were divided into 60 grid cells, out of which no USGS-grid wells were available for 13 cells; USGS-grid wells were available for 28 cells but no USGS data for major ions, trace elements, nutrients, and radiochemical constituents were available. Data from the CDPH database were used to provide missing inorganic and radiochemical data. CDPH wells with data for the most recent 3 years available at the time of sampling (July 30, 2001 through July 29, 2004) were considered. If more than one analysis for a constituent was available in the 3-year interval for a well, then the most recent data were selected.

The decision tree used to identify suitable data from CDPH wells is described in appendix A. 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 whose data were supplemented from the CDPH database (fig.A1*A–C*; table A1). If all the needed data for the DG well were not available, then 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. The combination of the USGS-grid wells and the CDPH-grid wells produced a grid-well network covering 54 of the 60 grid cells in the San Diego study unit.

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 grid-based 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 64 pesticides and pesticide degradates at every well in the San Diego study unit (table 1). In addition, method detection limits for USGS-GAMA analyses of organic constituents typically were one to two orders of magnitude lower than the reporting limits for analyses compiled by CDPH (table 3).

Table 2. Inorganic constituents and number of grid wells per constituent, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, May–July 2004.

[CDPH, California Department of Public Health; N, nitrogen; SMCL, Secondary Maximum Contaminant Level; HBB, Health Based Benchmark (including all benchmark types except SMCL); USGS, U.S. Geological Survey]

Constituent type	Constituent	Number of grid wells	
		Sampled by USGS GAMA	Selected from CDPH
Major element—SMCL			
	Chloride	19	14
	Sulfate	19	14
	Total dissolved solids	19	16
Minor element—HBB			
	Fluoride	19	14
Nutrient—HBB			
	Nitrite-N	19	15
	Ammonia-N	19	0
	Nitrate-N	19	18
Radioactive—HBB			
	Gross alpha radioactivity	19	16
	Gross beta radioactivity	19	4
	Ra226+228	19	0
	Rn222	19	0
	Uranium	19	8
Trace element—HBB			
	Aluminum	19	15
	Antimony	19	14
	Arsenic	19	15
	Barium	19	15
	Beryllium	19	14
	Boron	19	15
	Cadmium	19	15
	Chromium	19	14
	Copper	19	16
	Lead	19	14
	Mercury	19	15
	Nickel	19	14
	Selenium	19	15
	Strontium	19	0
	Thallium	19	14
	Vanadium	19	14
Trace element—SMCL			
	Iron	19	15
	Manganese	19	15
	Silver	19	15
	Zinc	19	15

Table 3.   Comparison of number of compounds and median method detection limit or laboratory reporting levels by type of constituent for data stored in the California Department of Public Health database and data collected for the San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May 17–July 29, 2004.

[CDPH, California Department of Public Health; MDL, method detection limit; LRL, laboratory reporting level; MRL, method reporting level; mg/L, milligrams per liter; µg/L, micrograms per liter; nc, not collected; pCi/L, picocuries per liter]

Constituent type	CDPH		GAMA	
	Number of compounds	MDL	Number of compounds	Median LRL/MRL
Volatile organic compounds (µg/L)	61	0.5	88	0.06
Pesticides and degradates (µg/L)	27	2	123	0.019
Nutrients, major and minor ions (mg/L)	4	0.4	17	0.06
Trace elements (µg/L)	20	8	25	0.12
Radioactive constituents (SSMDC)[1] (pCi/L)	5	1	8	0.54
Perchlorate (µg/L)	1	4	1	0.5
1,4-Dioxane (µg/L)	1	3	1	2
N-Nitrosodimethylamine (NDMA) (µg/L)	nc	nc	1	0.002
Pharmaceutical constituents (µg/L)	nc	nc	16	0.021

[1] Value reported for the median LRL/MRL is a median sample-specific critical level for eight radioactive constituents collected and analyzed by GAMA.

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 (understanding wells), and all wells in the CDPH database with water-quality data during the 3-year interval July 30, 2001, through July 29, 2004. For wells with both USGS and CDPH data, only the USGS data were used.

Identification of Constituents for Status Assessment

Three criteria were used to identify constituents for additional evaluation in the status assessment of groundwater in the San Diego study:

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 well;

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

These criteria identified 11 organic and special-interest constituents and 26 inorganic constituents for additional evaluation in the *status assessment* (table 4). An additional 23 organic constituents and 20 inorganic constituents were detected by USGS-GAMA, and are not included for further analysis in the *status assessment* because they either have no established benchmarks (table 5), or were only detected at low relative-concentrations.

The CDPH database also was used to identify constituents that have been reported at high relative-concentrations historically, but not at the time of this study. The historical period was defined as from the earliest record maintained in the CDPH electronic database within the period May 1983 to June, 2001. Constituents may be historically high, but not currently high, because of improvement in groundwater quality with time or abandonment of wells with high relative-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 San Diego study unit, there were six historically high constituents (table 6).

Table 4. Aquifer proportions from grid-based and spatially weighted methods for constituents detected in the Alluvial Fill study areas (Temecula Valley, Warner Valley, and Alluvial Basins) (1) with high relative-concentrations reported in the California Department of Public Health (CDPH) database during July 30, 2001–July 29 2004, or (2) with moderate or high relative-concentrations in samples collected from grid wells during May–July 2004, or (3) with organic or special-interest constituents detected in more than 10 percent of samples collected from grid wells during May–July 2004, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California.

[Grid-based aquifer-scale proportions for organic constituents are based on samples collected by the U.S. Geological Survey from 47 grid wells during May–July 2004. Spatially weighted aquifer-scale proportions are based on CDPH data for July 30, 2001–July 29, 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 inorganic constituents or 0.5 of benchmark for organic constituents; low, concentrations less than 0.1 of benchmark for organic constituents or 0.5 of benchmark for inorganic constituents. HAL–US, USEPA lifetime health advisory level; MCL–US, USEPA maximum contaminant level; MCL–CA, CDPH maximum contaminant level; NL–CA, CDPH notification level; SMCL–CA, CDPH secondary maximum contaminant level; USEPA, U.S. Environmental Protection Agency; CDPH, California Department of Public Health; µg/L, microgram per liter; ns, not sampled; mg/L, milligram per liter; pCi/L, picocurie per liter]

Constituent	Threshold type	Threshold value	Threshold units	Grid-based aquifer-scale proportion[1]				Raw detection frequency[2]			Spatially weighted aquifer-scale proportion[1,2]	
				Number of wells	High (percent)	Moderate (percent)	Low (percent)	Number of wells	Number of wells with high values	Raw detection frequency (percent)	Number of cells	High (percent)
Trace elements												
Vanadium	NL–CA	50	µg/L	28	7.5	28.5	64.0	117	12	10.3	32	9.8
Arsenic	MCL–US	10	µg/L	29	4.1	2.8	93.1	117	4	3.4	32	3.8
Boron	NL–CA	1,000	µg/L	28	4.1	0.0	95.9	117	2	1.7	32	1.3
Antimony	MCL–US	6	µg/L	28	3.4	0.0	96.6	106	1	0.9	31	3.2
Selenium	MCL–US	50	µg/L	29	0.0	3.2	96.8	117	0	0.0	32	0.0
Fluoride	MCL–CA	2	mg/L	28	[3]0.7	2.8	97.2	115	1	0.9	31	0.7
Aluminum	MCL–CA	1,000	µg/L	29	0.0	0.0	100.0	117	0	0.0	32	0.0
Thallium	MCL–US	2	µg/L	28	0.0	0.0	100.0	106	0	0.0	32	0.0
Chromium	MCL–CA	50	µg/L	28	0.0	0.0	100.0	109	0	0.0	32	0.0
Lead	AL–US	15	µg/L	28	0.0	0.0	100.0	114	0	0.0	31	0.0
Nickel	MCL–CA	100	µg/L	28	0.0	0.0	100.0	105	0	0.0	32	0.0
Cadmium	MCL–US	5	µg/L	29	0.0	0.0	100.0	117	0	0.0	32	0.0
Mercury	MCL–US	2	µg/L	29	0.0	0.0	100.0	117	0	0.0	32	0.0
Radioactive constituents												
Gross-alpha radioactivity	MCL–US	15	pCi/L	29	3.2	10.5	86.3	115	4	3.5	30	3.4
Uranium	MCL–US	30	µg/L	22	0.0	13.1	86.9	53	1	1.9	26	0.9
Radon-222	Proposed AMCL–US	4,000	pCi/L	15	0.0	0.0	100.0	21	0	0.0	18	0.0
Radium-228	MCL–US	5	pCi/L	14	0.0	0.0	100.0	34	0	0.0	20	0.0
Gross-beta radioactivity	MCL–CA	50	pCi/L	19	0.0	0.0	100.0	47	0	0.0	22	0.0
Nutrients												
Nitrate as nitrogen	MCL–US	10	mg/L	31	3.4	6.8	89.8	148	7	4.7	36	3.4
Nitrite, as nitrogen	MCL–US	1	mg/L	28	0.0	0.0	100.0	127	0	0.0	33	0.0

Table 4. Aquifer proportions from grid-based and spatially weighted methods for constituents detected in the Alluvial Fill study areas (Temecula Valley, Warner Valley, and Alluvial Basins) (1) with high relative-concentrations reported in the California Department of Public Health (CDPH) database during July 30, 2001–July 29 2004, or (2) with moderate or high relative-concentrations in samples collected from grid wells during May–July 2004, or (3) with organic or special-interest constituents detected in more than 10 percent of samples collected from grid wells during May–July 2004, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California.—Continued.

[Grid-based aquifer-scale proportions for organic constituents are based on samples collected by the U.S. Geological Survey from 47 grid wells during May–July 2004. Spatially weighted aquifer-scale proportions are based on CDPH data for July 30, 2001–July 29, 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. HAL-US, USEPA lifetime health advisory level; MCL-US, USEPA maximum contaminant level; MCL-CA, CDPH maximum contaminant level; NL-CA, CDPH notification level; SMCL-CA, CDPH secondary maximum contaminant level; USEPA, U.S. Environmental Protection Agency; CDPH, California Department of Public Health; µg/L, microgram per liter; ns, not sampled; mg/L, milligram per liter; pCi/L, picocurie per liter]

Constituent	Threshold type	Threshold value	Threshold units	Grid-based aquifer-scale proportion[1]				Raw detection frequency[2]			Spatially weighted aquifer-scale proportion[1,2]	
				Number of wells	High (percent)	Moderate (percent)	Low (percent)	Number of wells	Number of wells with high values	Raw detection frequency (percent)	Number of cells	High (percent)
Major and minor elements (SMCLs)												
Total dissolved solids (TDS)	SMCL-CA	1,000	mg/L	29	13.7	31.2	55.1	119	15	12.6	34	13.0
Manganese	SMCL-CA	50	µg/L	28	13.7	3.4	82.9	120	32	26.7	32	21.2
Iron	SMCL-CA	300	µg/L	28	6.9	0.0	93.1	120	10	8.3	32	6.5
Chloride	SMCL-CA	500	mg/L	28	3.4	10.3	86.3	117	5	4.3	32	2.7
Sulfate	SMCL-CA	500	mg/L	28	3.4	6.9	89.7	117	2	1.7	32	3.7
Zinc	SMCL-CA	5,000	µg/L	29	0.0	0.0	100.0	114	0	0.0	32	0.0
Gasoline components												
MTBE	MCL-CA	13	µg/L	37	3.0	0.0	97.0	113	2	1.8	39	1.4
Benzene	MCL-CA	1	µg/L	37	0.0	0.0	100.0	113	0	0.0	39	0.0
Trihalomethanes												
Chloroform	MCL-US	480	µg/L	37	0.0	0.0	100.0	112	0	0.0	38	0.0
Solvents												
Tetrachloroethylene	MCL-US	5	µg/L	37	0.0	0.0	100.0	113	0	0.0	39	0.0
Carbon tetrachloride	MCL-CA	0.5	µg/L	37	0.0	0.0	100.0	113	0	0.0	39	0.0
Trichloroethylene	MCL-US	5	µg/L	37	0.0	0.0	100.0	113	0	0.0	39	0.0
1,2-Dichloropropane	MCL-US	5	µg/L	37	0.0	3.0	97.0	113	0	0.0	39	0.0
Herbicides												
Prometon	HAL-US	100	µg/L	37	0.0	0.0	100.0	38	0	0.0	37	0.0
Simazine	MCL-US	4	µg/L	37	0.0	0.0	100.0	101	0	0.0	37	0.0
Atrazine	MCL-CA	1	µg/L	37	0.0	0.0	100.0	101	0	0.0	37	0.0

Table 4. Aquifer proportions from grid-based and spatially weighted methods for constituents detected in the Alluvial Fill study areas (Temecula Valley, Warner Valley, and Alluvial Basins) (1) with high relative-concentrations reported in the California Department of Public Health (CDPH) database during July 30, 2001–July 29 2004, or (2) with moderate or high relative-concentrations in samples collected from grid wells during May–July 2004, or (3) with organic or special-interest constituents detected in more than 10 percent of samples collected from grid wells during May–July 2004, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California.—Continued.

[Grid-based aquifer-scale proportions for organic constituents are based on samples collected by the U.S. Geological Survey from 47 grid wells during May–July 2004. Spatially weighted aquifer-scale proportions are based on CDPH data for July 30, 2001–July 29, 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 inorganic constituents; low, concentrations less than 0.1 of benchmark for organic constituents or 0.5 of benchmark for inorganic constituents. HAL–US, USEPA lifetime health advisory level; MCL–US, USEPA maximum contaminant level; MCL–CA, CDPH maximum contaminant level; NL–CA, CDPH notification level; SMCL–CA, CDPH secondary maximum contaminant level; USEPA, U.S. Environmental Protection Agency; CDPH, California Department of Public Health; µg/L, microgram per liter; ns, not sampled; mg/L, milligram per liter; pCi/L, picocurie per liter]

Constituent	Threshold type	Threshold value	Threshold units	Grid-based aquifer-scale proportion[1]				Raw detection frequency[2]			Spatially weighted aquifer-scale proportion[1,2]	
				Number of wells	High (percent)	Moderate (percent)	Low (percent)	Number of wells	Number of wells with high values	Raw detection frequency (percent)	Number of cells	High (percent)
Constituent of special interest												
Perchlorate	MCL–CA	6	µg/L	32	[3]0.2	36.3	63.7	103	1	0.9	38	0.2

[1] Alluvial Fill study area aquifer-scale proportion is calculated by summing the area weighted average for each individual study area except the Hard Rock. Area-weighted values for each study area are: Temecula Valley = 0.41, Warner Valley = 0.11, Alluvial Basins = 0.48. Aquifer-scale proportions will not sum to 100 if a spatially-weighted value is used.

[2] Based on most recent analysis for each CDPH well during July 30, 2001–July 29, 2004, combined with GAMA grid-based data.

[3] Spatially-weighted value. Aquifer-scale proportions will not sum to 100 if a spatially-weighted value is used.

[4] The MCL–US threshold for trihalomethanes is the sum of chloroform, bromoform, bromodichloromethane, and dibromochloromethane.

Table 5. Number of constituents analyzed and detected by benchmark and constituent type, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit grid wells, California, May 17 to July 29, 2004.

[VOCs, volatile organic compounds; NWQL, National Water Quality Laboratory; USEPA, U.S. Environmental Protection Agency; CDPH, California Department of Public Health; MCL, USEPA or CDPH Maximum Contaminant Level; HAL, USEPA Health Advisory Level; NL, CDPH Notification Level; RSD5, USEPA Risk Specific Dose at 10^{-5}; AL, USEPA Action Level; SMCL, USEPA or CDPH Secondary Maximum Contaminant Level]

Groups of organic constituents

Benchmark type	Sum organic and special-interest constituents		VOCs + gasoline oxygenates		Pesticides and degradates (NWQL Schedule 2003)[1]		Polar pesticides and degradates (NWQL Schedule 2060)[1]		Special-interest constituents	
	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected
MCL	46	16	32	12	3	2	10	1	1	1
HAL	31	6	7	0	14	5	10	1	0	0
NL	16	0	14	0	0	0	0	0	2	0
RSD5	8	1	4	0	3	0	1	1	0	0
AL	0	0	0	0	0	0	0	0	0	0
SMCL	0	0	0	0	0	0	0	0	0	0
None	117	11	31	0	44	10	42	1	0	0
Total	218	34	88	12	64	17	63	4	3	1

Groups of inorganic constituents

Benchmark type	Sum of inorganic constituents		Major and minor ion		Nutrients		Trace elements		Radioactive constituents	
	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected	Analyzed	Detected
MCL	23	21	1	1	2	2	12	10	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	6	6	3	3	3	3	1	1
Total	50	48	10	10	6	6	25	23	9	9

Organic, special interest, inorganic total	
Analyzed	Detected
268	82

[1]There are four overlapping compounds between NWQL Schedules 2003 and 2060.

Table 6.   Constituents with one or more concentrations above health-based benchmarks for the period of May 1983 to June 2001, based on the California Department of Public Health data for public-supply wells in the San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California.

Constituent	Number of wells with analyses	Total number of analyses	Total number of analyses above threshold	Number of wells with at least one high analysis	Date of most recent concentration above a health-based benchmark
Trace elements					
Chromium	230	843	1	1	11-29-1989
Cadmium	246	843	3	3	05-22-1990
Mercury	248	859	1	1	02-26-1992
Radioactive constituents					
Gross-beta radioactivity	77	80	1	1	07-05-1995
Radium 226	41	109	4	3	06-26-1996
Solvents					
Tetrachloroethylene	269	1,173	19	2	10-10-2000
Trichloroethylene	270	1,173	25	2	07-10-2000
1,2-Dichloropropane	243	1,108	2	1	03-27-1995

Calculation of Aquifer-Scale Proportions

The *status assessment* is intended to characterize the quality of groundwater resources within the primary aquifers of the San Diego 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 a discrete aquifer unit. In most groundwater basins, municipal and community supply wells generally are perforated at greater depths than are domestic wells. Thus, because domestic wells are not listed in the CDPH database, the primary aquifers generally correspond to the portion of the aquifer system tapped by municipal and community supply wells. All wells used in the *status assessment* in the San Diego study unit are listed in the CDPH database, and are therefore classified as municipal and community drinking-water supply wells.

Two statistical approaches, grid-based and spatially weighted (Belitz and others, 2010), were applied to evaluate the proportions of the primary aquifers in the San Diego 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 additional evaluation in the *status assessment* and for classes of constituents. Classes of constituents with health-based benchmarks included: trace elements, radioactive constituents, nutrients, VOCs, and pesticides. Aquifer-scale proportions were also calculated for the following constituents having aesthetic (SMCL) benchmarks: manganese, total dissolved solids, iron, chloride, sulfate, and zinc.

The grid-based calculation uses the grid-well dataset assembled from the USGS- and CDPH-grid wells. For each constituent the high aquifer-scale proportion for a study area was calculated by dividing the number of cells (wells) represented by a high value for that constituent by the total number of grid cells with data for that constituent. The high aquifer-scale proportions at the study-unit scale were then calculated by first multiplying the study-area aquifer-scale proportion by an area-weighted correction factor, and then summing the high aquifer-scale proportions for all the study areas. An area-weighted correction factor was needed because the study areas are not the same size (fig. 6A–C). Moderate and low aquifer-scale proportions were calculated using the same approach as the calculations for the high aquifer-scale proportions. A more detailed discussion of the calculation used for aquifer-scale proportion is located in appendix B.

The grid-based estimate is spatially unbiased; however, this approach may not detect constituents that are present at high relative-concentrations in small proportions of the primary aquifers. The spatially weighted calculation uses all CDPH wells in the study unit (most recent analysis during the current period from July 30, 2001–July 29, 2004), USGS-grid wells, and USGS-understanding wells to represent the primary aquifers. By using the spatially weighted approach, the proportion of high relative-concentrations for the primary aquifers for each constituent was computed by (1) computing the proportion of wells with high relative-concentrations in each grid cell and (2) averaging together the grid-cell proportions computed in step (1) (Isaaks and Srivastava, 1989; Belitz and others, 2010). Similar procedures were used to calculate the proportions of the aquifer with moderate and low relative-concentrations of constituents. The resulting proportions are spatially unbiased (Isaaks and Srivastava, 1989; Belitz and others, 2010). Confidence intervals for spatially weighted detection frequencies of high relative-concentrations are not described in this report.

In addition, for each constituent, the raw detection frequencies of high and moderate values for individual constituents were calculated by 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. For example, if a constituent were present at high relative-concentrations in a small region of the aquifer with a high density of wells, then 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 B for details of statistical methods).

The grid-based high aquifer-scale proportions were used to represent proportions in the primary aquifers unless the grid-base high aquifer-scale proportion was zero and the spatially weighted proportion was non-zero, and then the spatially weighted result was used. This situation can arise when the relative-concentration of a constituent is high in a small fraction of the primary aquifers. 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 non-zero, then the spatially weighed value was used..

Understanding-Assessment Methods

Explanatory factors, including land use, well depth, depth to the top of the uppermost open interval, classified groundwater age, and redox conditions (see appendix C 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. Statistical tests were used to identify significant correlations between the constituents of interest and potential explanatory factors. Significant correlations for explanatory factors influencing water quality are shown in the figures.

The wells included in the *understanding assessment* include USGS-grid and CDPH-grid well and USGS-understanding wells. CDPH-other wells were not used in the *understanding assessment* because age tracer, dissolved oxygen, and sometimes well construction data were not available. For different potential explanatory variables, correlations were tested by 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 variables (land use) to avoid areal-clustering bias. However, USGS-understanding wells were included in analyses of relations between constituents and the vertically distributed

explanatory variables depth, classified groundwater age, and oxidation-reduction characteristics in order to have data spanning a sufficient range of variables to identify relations.

For inorganic constituents to be discussed in the *understanding assessment*, they must have been detected at high relative-concentrations in greater than or equal to 2 percent of the aquifer (based on non area-weighted detections for all study areas) For organic and special-interest constituents to be discussed in the understanding assessment, a constituent needs to be detected at a high or moderate relative-concentration, or detected in greater than or equal to 10 percent of grid wells (based on detections that were not area-weighted) regardless of concentration

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 generally are 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

Explanatory factors that potentially affect water quality include land use, depth (well depth and the depth to the top of the uppermost open interval), groundwater age, and geochemical conditions. Sources and methodologies for obtaining data for these factors are discussed in the following sections. Potential correlations within these factors also were evaluated to identify which factors are likely to relate directly to water quality and could result in higher relative-concentrations or detection frequencies, and which factors may be coincidental and not directly affecting water-quality.

Land Use

Land use around wells sampled in the San Diego study unit generally indicated the composition of land use in the respective study areas as a whole. This also was true of the land use around PSWs in the CDPH database that was used in this study. The majority of land use around PSWs used in this study was natural, with lesser amounts of urban and agricultural (fig. 3A–B). The most urbanized areas around PSWs was in the Alluvial Basins study area (28 percent), followed by the Temecula Valley (23 percent), and then the Hard Rock study areas (8 percent). The Warner Valley study unit did not have wells located in any urban land-use settings. Agricultural land-use around PSWs most often was in the Temecula Valley (29 percent) study area, followed by the Alluvial Basins (17 percent), Hard Rock (1 percent) and Warner Valley (1 percent) study areas.

Well Depth

Well-construction information, including well depths, depths to the tops of the uppermost open interval, and lengths of the perforated intervals, where available, is reported in table A1. Depths for the PSWs sampled in the San Diego study unit (grid and understanding) ranged from 46 to 2,500 ft, with a median of 450 ft (fig. 7). Depth to the top of the uppermost open interval ranged from 20 to 690 feet, with a median of 96 feet. The open length ranged from 23 to 1913 feet with a median of 325 feet. These values represent different sets of wells because the total well depth was not known for as many wells as depth to the top of the uppermost open interval.
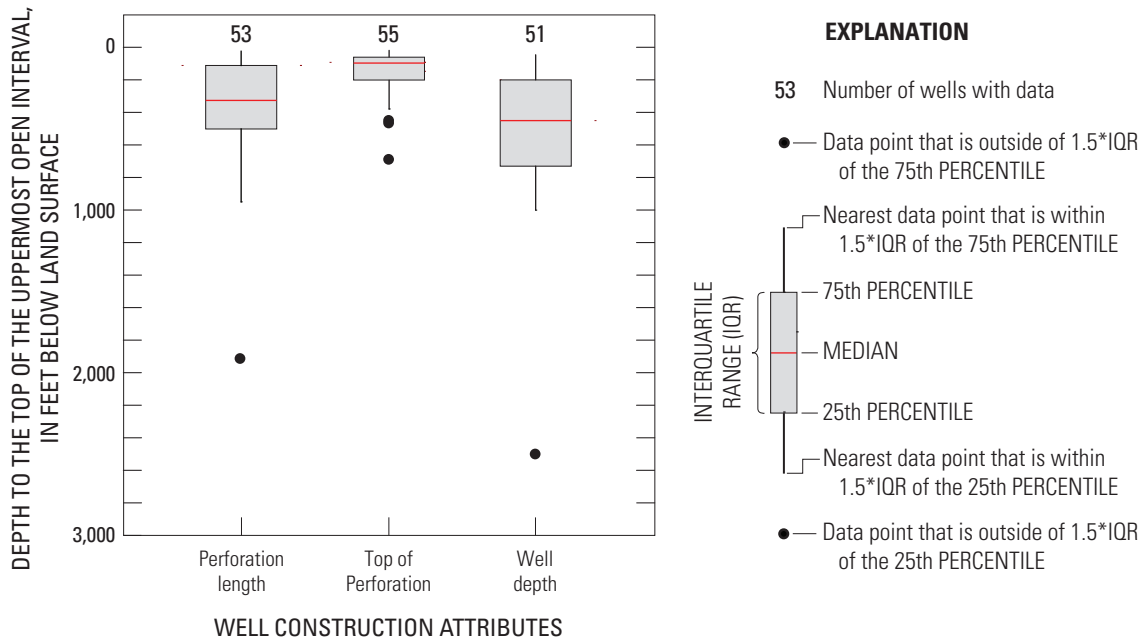
Figure 7.   Boxplots of construction attributes for grid and understanding wells, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004.

Groundwater Age Classification

Of the 58 groundwater samples collected by the USGS in the San Diego study unit, 8 were modern, 29 were mixed, and 19 were pre-modern (see table C1). Samples from two wells could not be classified because the age-tracer data was incomplete or did not meet all quality-assurance checks. Classified groundwater ages generally were older with increased depth to the top of the uppermost open interval (fig. 8A). The depth to the top of uppermost open interval was significantly less for wells with modern and mixed age distributions than for wells with pre-modern age distributions. Relative to well depth, wells classified as modern and mixed were significantly shallower than wells classified as pre-modern (fig. 8B).
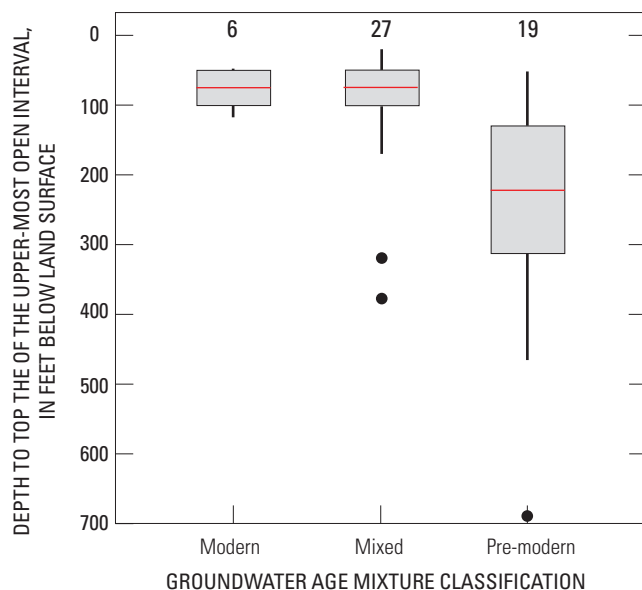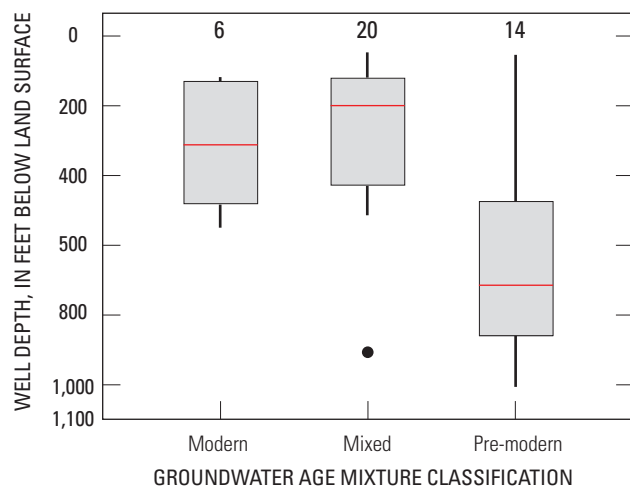
Figure 8A–B. Boxplots of relation of classified groundwater age to (A) depth to top of the uppermost open interval below land surface and (B) well depth below land surface, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004.

Geochemical Condition

Geochemical information collected for the San Diego study unit included pH, dissolved oxygen (DO), and concentrations of nitrate, manganese, and iron. Concentrations of DO, nitrate, manganese, and iron were used to determine the "redox" (oxidation-reduction) condition for the wells, using techniques described in appendix C. In the San Diego study unit, data was sufficient to classify the redox condition for 45 grid and understanding wells. Wells were either classified as oxic or anoxic; wells tapping groundwater with a mixed redox condition were not used this analysis. Sixty-two percent of the wells were classified as anoxic and 38 percent as oxic. pH values in the study unit ranged from 6.6 to 9.5 with a median value of 7.4.

Correlations between Explanatory Variables

Apparent correlations between an explanatory variable and a water-quality constituent actually could indicate correlations between explanatory factors. For example, detections of VOCs may be inversely correlated to urban land-use in a given area because the uppermost open interval of wells tend to be deep, and the water being tapped is pre-modern, not because VOCs are not used in urban settings. Therefore, it is important to identify statistically significant correlations between explanatory variables

The majority of explanatory variables used in this report are not significantly related (table 7). The strongest correlation is between well depth and depth to the top of the uppermost open interval. Because of the significance of this correlation only depth to the top of the uppermost open interval will be used in this report. Positive correlations of well depth to groundwater classified as pre-modern and pH were significant. The only other significant correlations were positive correlations between pH and groundwater classified as pre-modern and between anoxic groundwater and urban land-use; there was a negative correlation between natural land-use and depth to the top of the uppermost open interval.

Table 7.   Results of non-parametric analysis of correlations between selected potential explanatory variables, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004.

[Results are shown only for those correlations with a ρ-value ≤ 0.1. Results with ρ-values ≤ 0.05 are shown in bold. Only results with ρ-values ≤ 0.05 are considered significant in this study. ρ, Spearman's correlation statistic; Z, test statistic for Wilcoxon test; negative number is inverse relation between variables; –, p >0.1; <, less than; $\leq$, less than or equal to]

Wells included in analysis	Explanatory factor	ρ: Spearman's correlation statistic			Z: Wilcoxon test statistic			
		Depth to top of the upper-most open interval, feet below land surface	Depth of well below land surface, feet	pH, pH units	Anoxic versus oxic	Mixed versus modern age class	Modern versus pre-modern age class	Mixed versus pre-modern age class
Grid wells	Percentage urban land use	–	–	–	**2.02**	–	–	–
	Percentage agricultural land use	0.27	–	–	–	1.40	–	–
	Percentage natural land use	**-0.39**	–	–	–1.65	–	–	–
Grid and understanding wells	Depth to the top of uppermost open interval below land surface, feet		**0.73**	–	–	–	**–3.10**	**–4.10**
	Depth of well below land surface, feet			**0.54**	–	–	**–2.93**	**–4.13**
	pH, pH units				–	–	**–2.77**	**–3.40**

Status and Understanding of Water Quality

As a starting point for summarizing the results of approximately 16,000 individual analytical measurements in the San Diego study unit, the maximum relative-concentrations of the individual constituents and constituent groups were calculated for all four study areas (fig. 9). Health-based benchmarks are established for all constituents shown, except for those in the group inorganic-SMCL, for which non-health-based aesthetic benchmarks are established. Aquifer proportions calculated by the grid-based approach were considered the most reliable and are used in the subsequent discussions, except where otherwise noted. In some instances, the spatially weighted approach identified constituents that could be present at moderate or high relative-concentrations in small proportions of the primary aquifers that were not identified using the grid-based approach. Results from the spatially weighted approach were used only in cases for which the grid-based approach was found to have this limitation. Non-significant relations generally are not discussed; selected significant correlations are shown graphically.

Thirty-four of the 218 organic and special-interest constituents analyzed for were detected in samples collected at grid wells (table 5). Some type of health-based benchmark has been established for most of the organic and special interest constituents detected (23 of the 34). Five of the constituents with no health-based benchmarks are pesticide degradates. Some of the parent compounds (atrazine, diuron) of these degradates with health-based benchmarks were detected in samples. In contrast to organic and special-interest constituents, inorganic constituents were nearly always detected (48 of 50, table 5). Health-based or aesthetic benchmarks were not established for just over one-quarter of inorganic constituents (13 of 48). Most of the constituents without benchmarks are major or minor ions that are naturally present in groundwater.

Table 4 shows the area-weighted aquifer-scale proportions for the Temecula Valley, Warner Valley and Alluvial Basins study areas (hereinafter referred to as the Alluvial Fill study areas because they are composed of alluvial fill aquifers), and tables B1A–D show aquifer-scale proportions for the individual study areas. Aquifer-scale proportions in these tables are calculated by using both the grid-based and spatially weighted methods, and show constituents with high relative-concentrations under the following criteria: (1) high relative-concentrations detected

during sampling for the GAMA Priority Basin Project, (2) high relative-concentrations in the CDPH database during the current period (July 30, 2001–July 29, 2004), and (3) historically high relative-concentrations in the CDPH database.

Inorganic Constituents

Sixteen inorganic constituents qualified as constituents of interest because their relative-concentrations were greater than 0.5 in the grid-based assessment (fig. 10). Inorganic constituents with health-based benchmarks (nutrients, trace elements, and radioactive constituents) were high in 17.6 percent of the primary aquifers in the Alluvial Fill study areas (table 8). The greatest proportion of the primary aquifers with high relative-concentrations is in the Temecula Valley (27.3 percent) and Alluvial Basins (13.3 percent) study areas, whereas no high relative-concentrations were detected in the Warner Valley study area (tables B2A–C). High relative-concentrations were observed in 25.0 percent of the primary aquifers in the Hard Rock study area (table B2D).
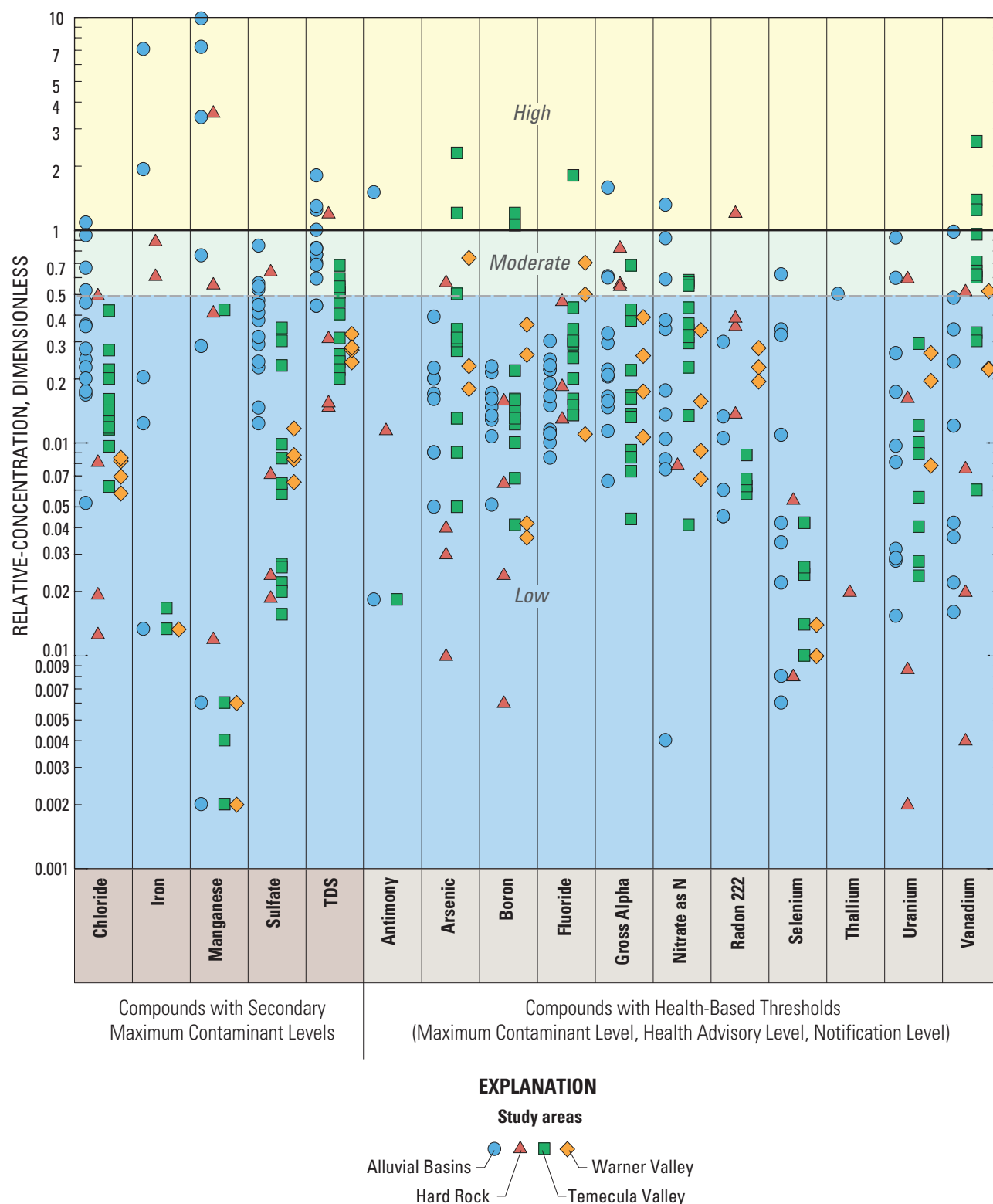
Trace Elements

The relative-concentrations of trace elements meeting the selection criteria (relative-concentration ≥ 0.5) are shown in figure 10. Trace elements were detected at high relative-concentrations in 14.4 percent of the primary aquifers in the Alluvial Fill study areas (table 8). The greatest proportion of the primary aquifers with high relative-concentrations was in the Temecula Valley (27.3 percent) and Alluvial Basins (6.7 percent) study areas (tables B2A and C). High relative-concentrations (based on spatially weighted calculations) were detected in 1.2 of the primary aquifers of the Hard Rock study area (table B2D). The three trace elements that were detected at high relative-concentrations in greater than or equal to 2 percent of the primary aquifers (based on aquifer-scale proportion that were not area-weighted for all study areas) were vanadium (2.8 percent), arsenic (2.0 percent), and boron (2.0 percent); the distribution and factors affecting distribution of these trace elements are discussed in more detail below.

The location and distribution of V, As, and B in the San Diego study unit are displayed on figures 11A–C. Of the high relative-concentrations detected for these trace elements, only a single high detection (V) was observed outside of the Temecula Valley study area. Moderate relative-concentrations for these trace elements also were most frequently detected in the Temecula Valley study area.
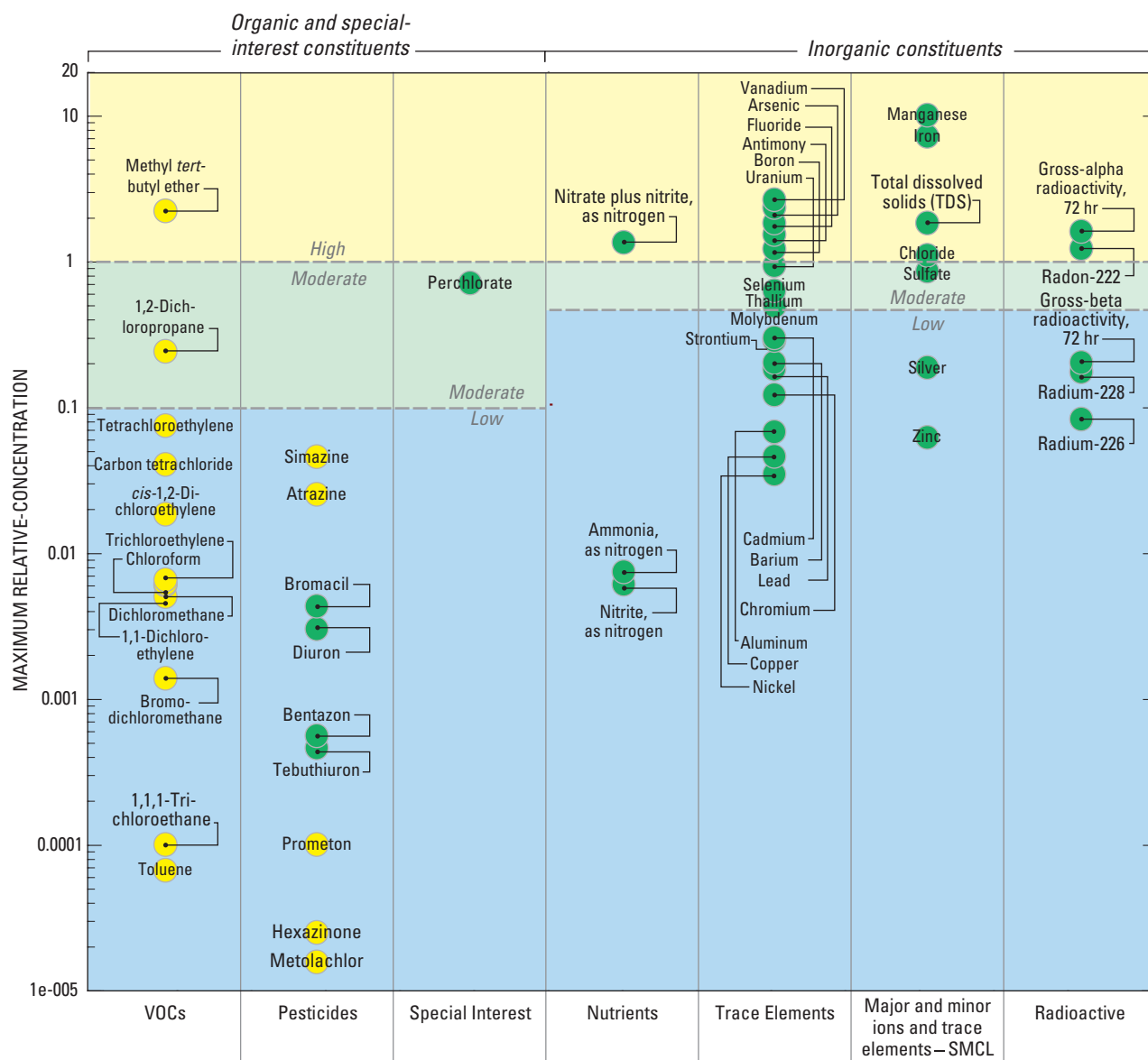
Figure 9.   Maximum relative-concentration in grid wells for constituents detected by type of constituent in the San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004.

Figure 10. Dot plots of relative-concentrations of selected trace elements, radioactive constituents, nutrients, and major and minor elements in grid wells, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004.

Table 8.   Grid-based aquifer-scale proportions for constituent classes in the Alluvial Fill study areas, (Temecula Valley, Warner Valley, and Alluvial Basins), San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California.

[Values are grid based unless otherwise noted]

Constituent class	Aquifer-scale proportion[1] (percent)		
	High values	**Moderate values**	**Low values**
Inorganics with health-based benchmarks			
Trace elements	14.4	27.8	57.8
Radioactive	3.2	13.7	83.1
Nutrients	3.4	6.8	89.8
Any inorganic with health-based benchmarks	17.6	32.3	50.1
Inorganics with aesthetic benchmarks			
Total dissolved solids and (or) chloride and (or) sulfate	13.7	31.2	55.1
Manganese and (or) iron	13.7	3.4	82.9
Organics with health-based benchmarks			
Trihalomethanes	0.0	0.0	100.0
Solvents	0.0	3.0	97.0
Gasoline components	3.0	0.0	97.0
Pesticides	0.0	0.0	100.0
Any organic with health-based benchmarks	3.0	3.0	94.0
Constituents of special interest			
Perchlorate	[2]0.2	36.3	63.7

[1] Alluvial Fill study areas aquifer-scale proportion is calculated by summing the area-weighted average for each individual study area except the Hard Rock. Area-weighted values for each study area are: Temecula Valley = 0.41, Warner Valley = 0.11, Alluvial Basins = 0.48. Aquifer-scale proportions will not sum to 100 if a spatially weighted value is used.

[2] Spatially weighted value.

A. Vanadium

EXPLANATION

Study areas

- Alluvial Basins
- Hard Rock
- Temecula Valley
- Warner Valley

Relative-concentration	USGS-grid or -understanding well	CDPH wells
Low or not detected	■ (blue)	◆ (blue)
Moderate	■ (green)	◆ (green)
High	■ (orange)	◆ (orange)

Figure 11A–C. Values of selected inorganic constituents in USGS-grid and -understanding wells representative of the primary aquifers and the most recent analysis (July 30, 2001–July 29, 2004) for CDPH wells, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004: (A) vanadium, (B) arsenic, and (C) boron.

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

B. Arsenic

EXPLANATION

Study areas

Alluvial Basins

Hard Rock

Temecula Valley

Warner Valley

Relative-concentration	USGS-grid or -understanding well	CDPH wells
Low or not detected		
Moderate		
High		

Figure 11*A–C.*—Continued

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

C. Boron

EXPLANATION

Study areas

Alluvial Basins

Hard Rock

Temecula Valley

Warner Valley

Relative-concentration	USGS-grid or -understanding well	CDPH wells
Low or not detected		
Moderate		
High		

Figure 11*A*–*C*.**—Continued**

Factors Affecting Vanadium Distribution

Potential sources of V to groundwater are both natural and anthropogenic. Natural sources can be attributed to the dissolution of V-rich rocks, which include mafic rocks such as basalts and gabbros (Nriagu, 1998), and sedimentary rocks such as shale (Vine and Tourtelet, 1970; McKelvey and others, 1986). Anthropogenic sources of V can come from waste streams associated with the ferrous metallurgy industry (World Health Organization, 1988) and through the combustion of V-enriched fossil fuels, primarily in the form of residual crude oil and coal (Duce and Hoffman, 1976; Hope, 1997). Atmospheric V can be deposited to the land surface through wet and dry deposition and transported into to the subsurface by infiltrating surface water.

The results of a previous study by Wright and Belitz (2010) indicated that the source of moderate and high relative-concentrations of V (> 25 µg/L) in California, and in particular the Temecula Valley, likely is mafic and andesitic rock. In the San Diego study unit, correlations between land use and V concentrations in samples collected for this study did not indicate that anthropogenic activities were significant contributing sources (table 9), which implies that V-rich rocks are likely the significant contributing source of V to groundwater in the San Diego study unit.

The redox conditions of the system under considerations will influence V concentrations in groundwater. This is because V is a redox sensitive element that exists in three oxidation states in the environment: V (III), V (IV), and V (V). Thermodynamically speaking, the predominant oxidation state of V is dependent on the Eh and pH conditions of the aqueous system under consideration. Vanadium (V) and V (IV) are the most important species in natural waters, with V (V) likely the most abundant under environmental conditions (Hem, 1985). The solubility of V in groundwater is likely to be largely controlled by adsorption/desorption processes on mineral surfaces (Wehrli and Stumm, 1989; Wanty and others, 1990; Wanty and Goldhaber, 1992). Vanadium (V), an oxyanion, and V (IV), an oxycation, both adsorb to mineral surfaces. However, under most environmental conditions V is expected to be most mobile under oxic and alkaline conditions.

Vanadium concentrations were significantly higher in samples collected from oxic and alkaline (high pH) groundwater than in samples collected from anoxic groundwater (fig. 12A; table 9). Vanadium was detected at high or moderate relative-concentrations only in samples collected from oxic groundwater; concentrations were less than or equal to 10 µg/L for all samples collected from anoxic groundwater. Additionally, the four samples with the highest concentrations were collected from groundwater with a pH of at least 7.9 (fig. 12A). These results indicate that V is indeed being desorbed from, or being inhibited from adsorbing to, mineral surfaces under oxic and alkaline conditions.

The highest V concentrations tended to be detected in samples collected from deep wells with mixed and pre-modern groundwater age classifications (fig. 12B; table 9). This relation most likely is a result due in part to the fact that pH values of pre-modern groundwater generally were higher than pH values of either modern or mixed waters (table 7). In addition, 73 percent of the samples with redox indicator data that were classified as pre-modern were classified as oxic. Again, these relations highlight the relation between high V concentrations and oxic and alkaline groundwater conditions.

Factors Affecting Arsenic Distribution

Like V, potential sources of As to groundwater are both natural and anthropogenic. Natural sources may be attributed to the dissolution of relatively As-rich igneous rocks like basalts and gabbros and sedimentary marine rocks, such as shale and phosphorites (Welch and others, 1988). Anthropogenic uses of As are varied, but the dominant uses in the United States are agricultural applications, wood preservation, and glass production (Welch and others, 2000). In the San Diego study unit, the positive correlation of arsenic concentrations in groundwater samples to any land-use type was not significant, which suggests that As-rich rocks are the most significant source of arsenic concentrations to groundwater.

Arsenic also is a redox sensitive element with a behavior affected by the redox and pH conditions of the groundwater system under consideration. Arsenic is stable in two oxidation states in the environment: As (III) and As (V). Over a wide pH range and oxic conditions, the oxyanion As (V) is predicted to be the predominant species, whereas under more reducing (anoxic) conditions the oxyanion As (III) likely would be the predominant species (Welch and others, 1988). Previous investigations of As in groundwater (Belitz and others, 2003; Welch and others, 2006) and literature reviews (Welch and others, 2000; Stollenwerk, 2003) have attributed elevated As in groundwater to two mechanisms: (1) the release of As from the dissolution of iron or manganese oxyhydroxides under anoxic conditions; (2) the desorption from, or inhibition of sorption to, mineral surfaces at alkaline pH.

The distribution of sample As concentrations was not significantly correlated to either redox or pH conditions of groundwater in the San Diego study unit (fig. 13A; table 9), although concentrations were correlated to pH at the 90 percent confidence level. These results suggest that different processes, or a combination thereof, are influencing As concentrations in groundwater. Release of As from iron and (or) manganese oxyhydroxides in anoxic groundwater conditions, and (or) the desorption of As from mineral surfaces under alkaline groundwater conditions may be influencing As concentrations detected in groundwater in the San Diego study unit. Even though the statistical correlation was not significant, sample concentrations generally did increase with increasing pH, indicating that As is more available in alkaline groundwater.

Table 9. Results of non-parametric analysis of correlations between selected water-quality constituents and potential explanatory factors, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California.

[Results are shown only for those correlations with a p-value ≤ 0.1. Results with p-values ≤ 0.05 are shown in bold. Only results with p-values ≤ 0.05 are considered significant in this study. A positive value indicates positive correlations; negative values indicate negative correlations. ρ, Spearman's correlation statistic. Z, test statistic for Wilcoxon test; –, p-value > 0.1; THMs, trihalomethanes; TDS, total dissolved solids; MCL-US; U.S. Environmental Protection Agency maximum contaminant level; NL-CA, CDPH notification level; Proposed AMCL-US, U.S. Environmental Protection Agency alternative maximum contaminant level; SMCL-CA, CDPH secondary maximum contaminant level; na, not applicable; <, less than or equal to; >, greater than; ≥, greater than or equal to]

| Constituent	Benchmark type	High aquifer proportion (percent)	ρ: Spearman's correlation statistic — Depth to the top of the upper-most open interval	Z, Wilcoxon test statistic — Data analyzed: Grid and understanding wells					ρ: Spearman's correlation statistic — Data analyzed: Grid wells		
				Mixed versus modern age class	Modern versus pre-modern age class	Mixed versus pre-modern age class	Anoxic versus oxic	pH	Percent urban land use[1]	Percent agricultural land use[1]	Percent natural land use[1]
Inorganic constituents[2]											
Vanadium	NL-CA	2.8	0.33	**2.10**	–	–	**-2.50**	**0.39**	–	**-0.53**	–
Arsenic	MCL-US	2.0	**0.36**	**2.57**	–	–	–	0.40	–	–	–
Boron	NL-CA	2.0	–	1.72	–	–	–	**0.34**	**0.35**	–	–
Manganese	SMCL-CA	20.8	–	–	–	–	na	**-0.28**	–	–	–
TDS	SMCL-CA	17.2	**-0.31**	–	1.73	**4.10**	–	**-0.17**	–	**0.26**	–
Iron	SMCL-CA	2.0	–	–	–	–	na	**-0.38**	–	–	–
Radon-222	Proposed AMCL-US	5.3	–	–	–	–	–	–	–	–	–
Organic constituents and constituent classes[3]											
Trihalomethanes, sum of concentrations	MCL-US	0.0	–	**-1.99**	**1.94**	–	–	–	**0.40**	–	-0.26
Solvents, sum of concentrations	variable	0.0	–	–	–	–	–	–	**0.40**	–	**-0.30**
Gasoline, sum of concentrations	MCL-US	0.1	–	–	–	–	–	–	–	–	–
Pesticides, sum of concentrations	variable	0.0	0.23	–	2.71	**2.64**	**-2.60**	**-0.40**	–	–	–
Constituents of special interest[3]											
Perchlorate	MCL-US	0.0	–	–	–	1.70	–	–	–	0.30	**-0.36**

[1]Land-use percentages are within a circle with a radius of 500 meters around each well included in analysis.

[2]Constituents with ≥ 2 percent high aquifer-scale proportions based on non-area-weighted calculations for all study areas in the San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit.

[3]Classes of compounds that include constituents with high and (or) moderate values or detection frequencies at any concentration ≥ 10 percent.
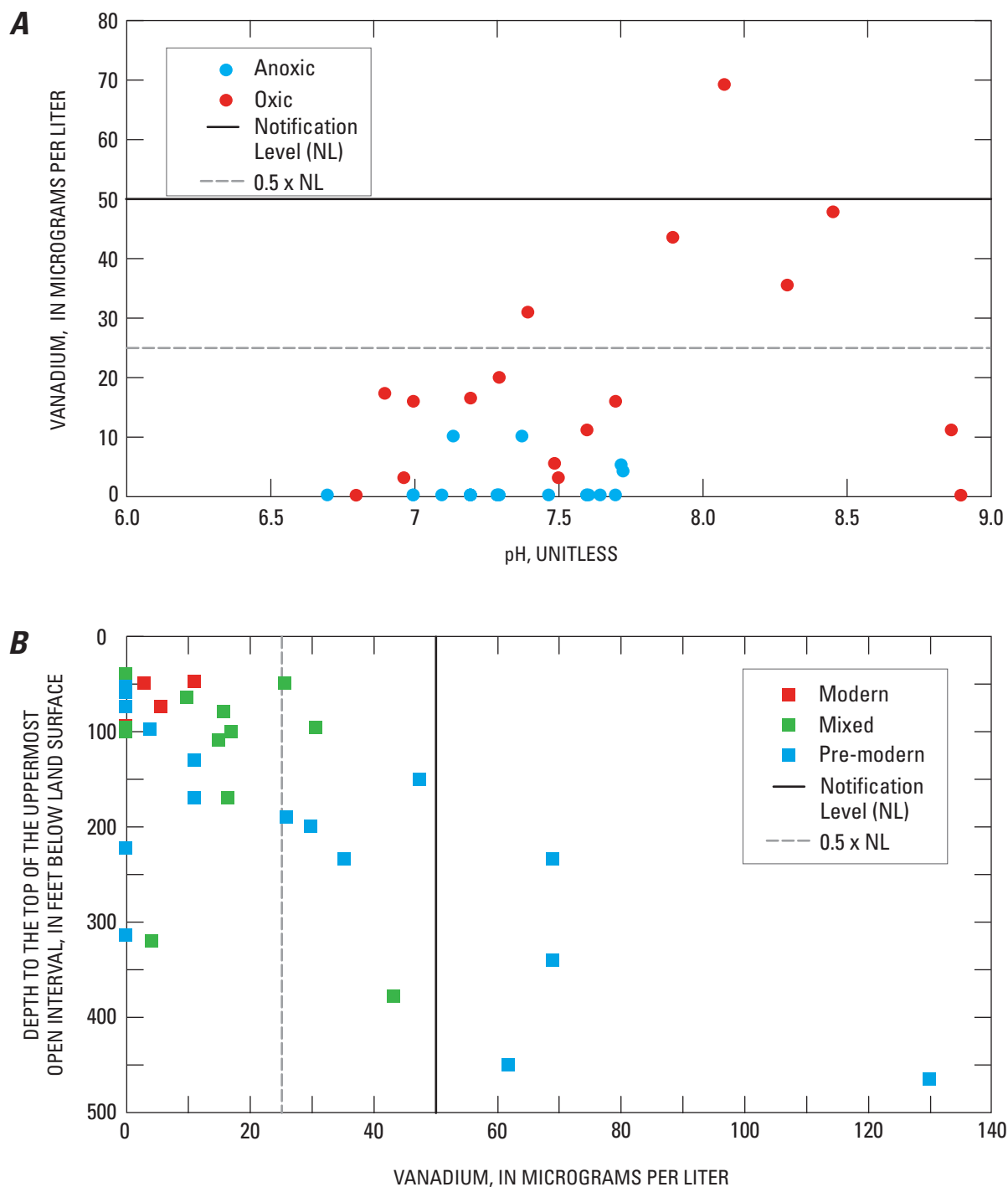
Figure 12A–B.   Relation of vanadium to explanatory variables, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California. (*A*) Relation of vanadium to redox conditions and pH and (*B*) relation of vanadium concentration to top of the uppermost open interval and groundwater age classification.
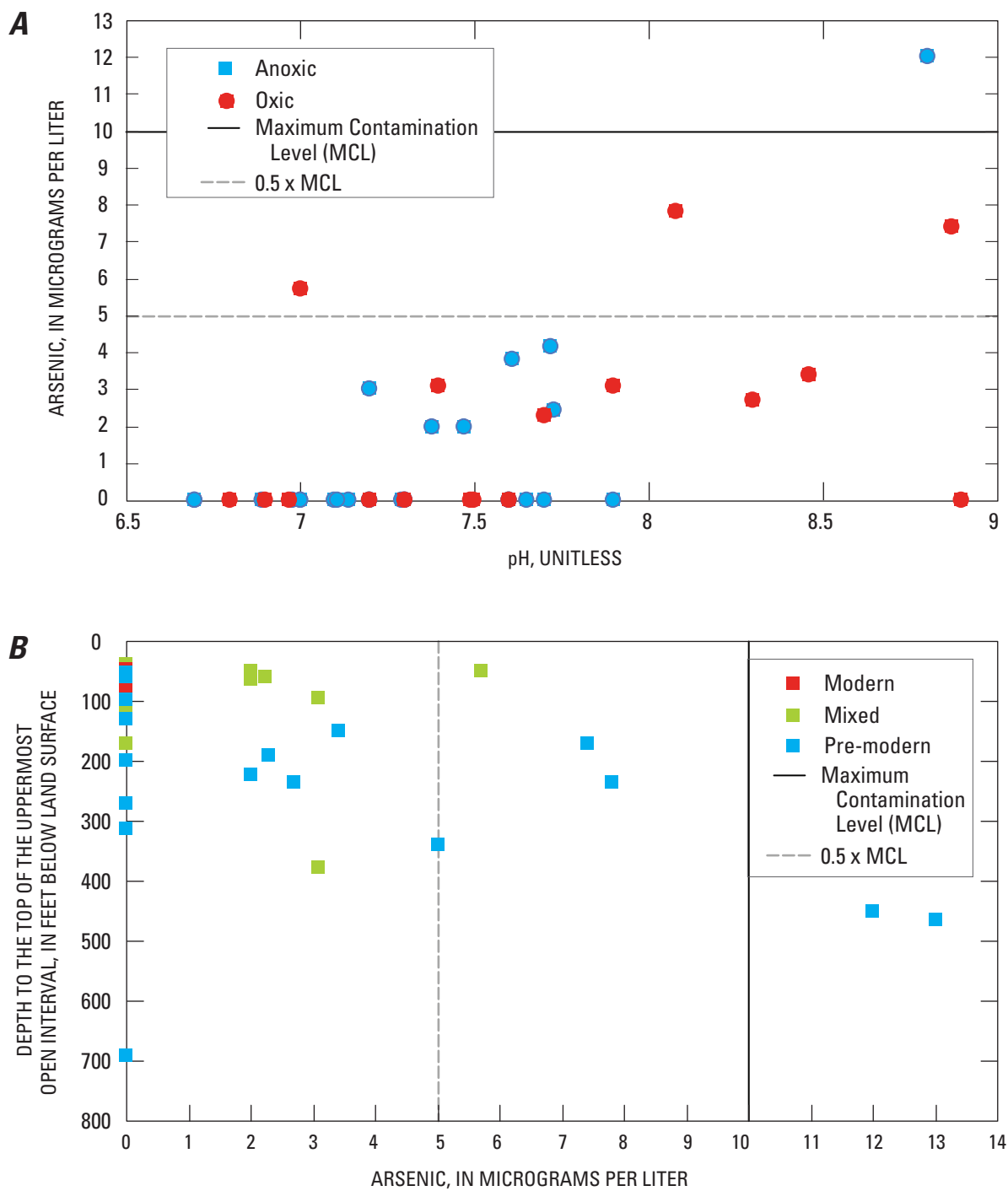
Figure 13A–B.   Relation of arsenic to explanatory variables in the San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004. (*A*) Relation of arsenic to redox conditions and pH and (*B*) relation of arsenic concentration to depth to the top of the uppermost open interval and groundwater age classification.

Correlations of samples with the highest As concentrations to depth to the top of the uppermost open interval and to mixed rather than to modern aged groundwater were significant (fig. 13*B*; table 9). Although the statistical correlation between pre-modern water and As concentrations was not significant, 83 percent of the samples with moderate and high concentrations (≥ 5 µg/L) came from samples consisting of pre-modern groundwater. The reason As concentrations tend to be highest in deep wells that are tapping mixed and pre-modern groundwater likely is a result in part that older groundwater tends to have an alkaline pH. The median pH values for samples classified as modern, mixed. and pre-modern were 7.0, 7.2, and 8.3, respectively.

Factors Affecting Boron Distribution

Natural sources of B concentrations in groundwater include the dissolution of igneous rocks like granite and pegmatites, and evaporite minerals such as kernite and colemanite (Hem, 1985; Reimann and Caritat, 1998). Borax, a B-containing evaporate mineral, is used as a cleaning agent and therefore may be present in sewage and industrial wastes. In the San Diego study unit, there was a positive correlation of B concentrations to urban land-use (table 9), indicating that

anthropogenic activities may be a source of B in groundwater. Background B concentrations are higher in seawater than in freshwater (World Health Organization 1998); therefore seawater intrusion in coastal aquifers also may increase B concentrations. Seawater intrusion does not seem to be a significant source of B in this study however, because of the relatively low concentrations of B in samples collected from the coastal alluvial aquifers (fig 11*C*).

Unlike V and As, B is not a redox sensitive element, and thus is not greatly affected by the redox conditions of groundwater. The molecular configuration of B in groundwater is dependent on pH, salinity, and specific cation content (Dotsika and others, 2006). The uncharged form of B, $B(OH)_3$, is predominant at pH less than 9.2, whereas the anionic form, $B(OH)_4^-$, is predominant at pH greater than 9.2. Most solid phases of B, for which data is available, are fairly soluble which suggests that adsorption and desorption reactions largely control the distribution of B in groundwater systems. In the San Diego study unit, the positive correlation between B concentrations and pH was significant (fig. 14; table 9), indicating that B is being desorbed, or inhibited from being adsorbed, to mineral surfaces under alkaline conditions. The correlations between boron and any other explanatory variables were not significant.
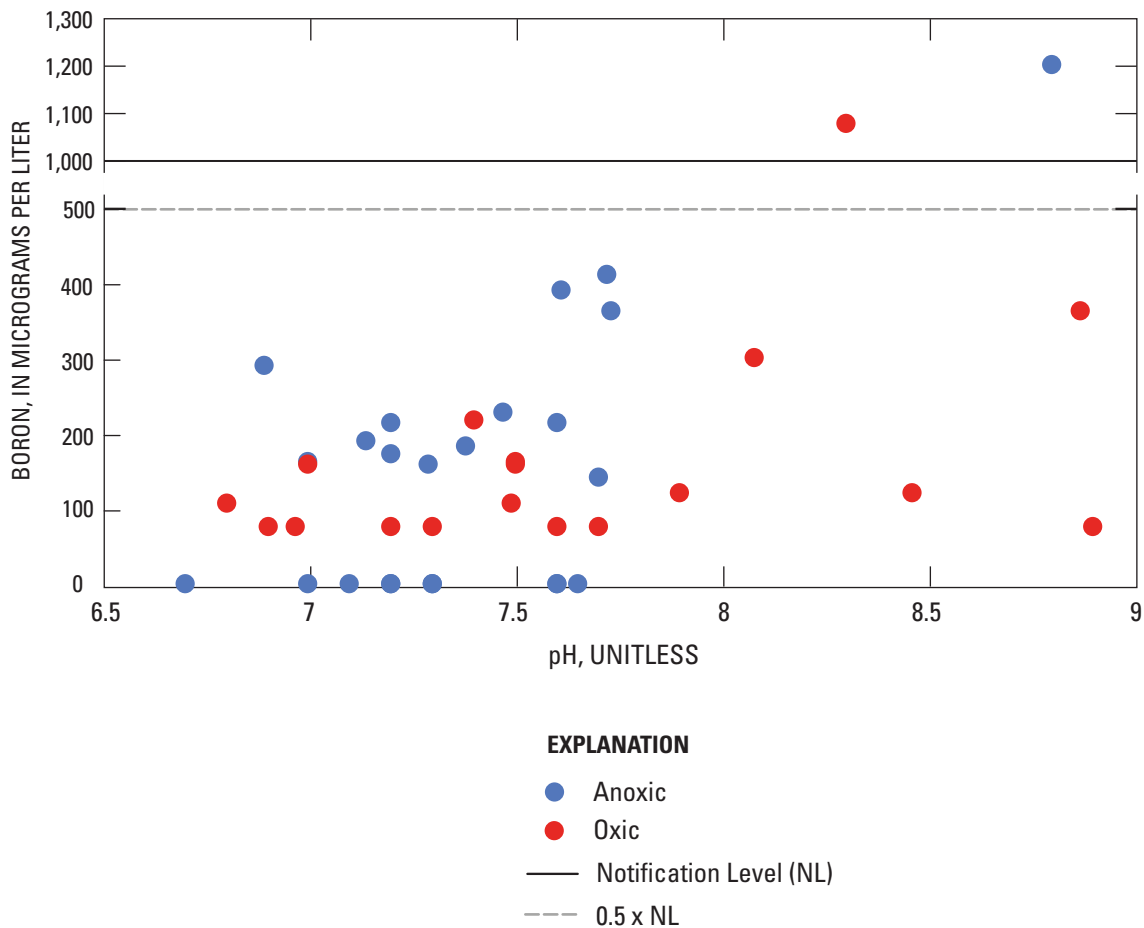

Figure 14.   Relation of boron concentrations to redox conditions and pH, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004.

Major and Minor Ions

Concentrations of some inorganic constituents can affect aesthetic properties of water, such as taste, color, and odor, and technical properties, such as scaling and staining. Although no adverse health effects are associated with these properties, consumer satisfaction with the water may be reduced or economic effects may result. For some constituents, CDPH has established non-enforceable benchmarks (SMCL-CAs) that are based on aesthetic or technical properties rather than on health-based concerns. For total dissolved solids (TDS) and the major ions chloride and sulfate, CDPH defines a "recommended" and an "upper" SMCL-CA. In this report, the "upper" SMCL-CA benchmarks were used to compute relative-concentrations. An SMCL-CA also has been established for the minor elements manganese and iron.

In the Alluvial Fill study areas, relative-concentrations of Mn and TDS were high in 13.7 percent of the primary aquifers, and relative-concentrations of Fe and fluoride (based on spatially weighted calculations) were high in 6.9 and 0.7 percent, respectively, of the primary aquifers (table 4). Manganese, TDS, and Fe were detected at high relative-concentrations in the Alluvial Basins study area at 28.6, 28.6, and 14.3 percent, respectively, and fluoride (F) was detected at high relative-concentrations (spatially weighted) in the Temecula Valley study area in 1.7 percent of the primary aquifers; major and minor ions were not detected at high relative-concentrations in the Warner Valley study area (tables B1A–C). In the Hard Rock study area Mn and TDS were detected at high relative-concentration in 33.3 and 16.7 percent of the primary aquifers, respectively, and F was detected at high relative-concentrations (spatially weighted) in 2.2 percent of the primary aquifers. Manganese (20.8 percent), TDS (17.2 percent), and Fe (2.0 percent) were the only constituents with an aesthetic benchmark that were detected at high relative-concentrations in greater than or equal to 2.0 percent of the primary aquifers for all study areas in the San Diego study unit (non area-weighted aquifer-scale proportions).

High and moderate relative-concentrations of both Mn and Fe generally occurred in the same areas of the San Diego study unit. The similar distribution of these constituents is a result of the similarities in potential sources and geochemical behavior in groundwater. High relative-concentrations of Mn and Fe were detected in every study area except for the Warner Valley (fig. 15A and 15B). High and moderate relative-concentrations most frequently were detected in the Alluvial Basins study area followed by the Hard Rock study area. In the Alluvial Basins study area, high and moderate relative-concentrations were most frequently detected in the coastal areas, whereas in the Hard Rock study area relative-concentrations were frequently highest in the most inland portions of the study area.

High relative-concentrations of TDS were detected in every study area except for the Warner Valley (fig. 15C). High relative-concentrations were most frequently detected in the Alluvial Basins study area (28.6 percent), followed by the Hard Rock study area (16.7 percent). TDS concentrations tended to be highest in the coastal and inland coastal areas of the study unit, and lowest in the most interior portions of the study unit.

Factors Affecting Manganese and Iron

Potential natural sources of Mn and Fe to groundwater include the dissolution of igneous and metamorphic rocks as well as dissolution of various secondary minerals (Hem, 1985). Rocks that contain significant amounts of Mn and Fe have a high composition of the minerals olivine, pyroxene, and amphibole. Potential anthropogenic sources of these constituents to groundwater include effluents associated with the steel and mining industries (Reimann and deCaritat, 1998). Manganese and Fe concentrations were not significantly correlated to either urban or agricultural land use (table 9), thus suggesting that natural sources are the significant contributing factor of Mn and Fe to groundwater in the San Diego study unit.

Redox and pH conditions significantly influence the concentrations of Mn and Fe in groundwater. In sediments, the oxyhydroxides of Mn and Fe are common as suspended particles and as coatings on mineral surfaces (Sparks, 1995). These oxyhydroxides are stable in oxygenated systems at neutral pH. However, under anoxic conditions, the process of reductive dissolution destabilizes these minerals which affect the mobility of Mn and Fe in aquifer systems (Sparks, 1995). Figure 16 shows the relation between DO concentrations/pH and Mn and Fe concentrations of samples collected in the San Diego study unit. The negative correlation (Spearman's rho) of both constituents to DO (Mn, rho = –0.52; Fe, rho = –0.57) and pH (table 9) was significant, indicating that reductive dissolution is a significant pathway for the mobilization of Mn and Fe in groundwater in the San Diego study unit. Manganese and Fe concentrations were not significantly correlated with any other explanatory factorss.

Factors Affecting Total Dissolved Solids

Total dissolved solids either were measured directly or calculated from specific conductance (see appendix E). Potential anthropogenic sources of TDS to groundwater in the San Diego study unit include agricultural and urban irrigation, disposal of waste water and industrial effluent, and leaking water and sewer pipes. The positive correlation of total dissolved solid concentrations to agricultural land-use in the San Diego study unit was significant (fig. 17; table 9), suggesting that agricultural irrigation practices are a significant contributing factor of TDS concentrations in groundwater.
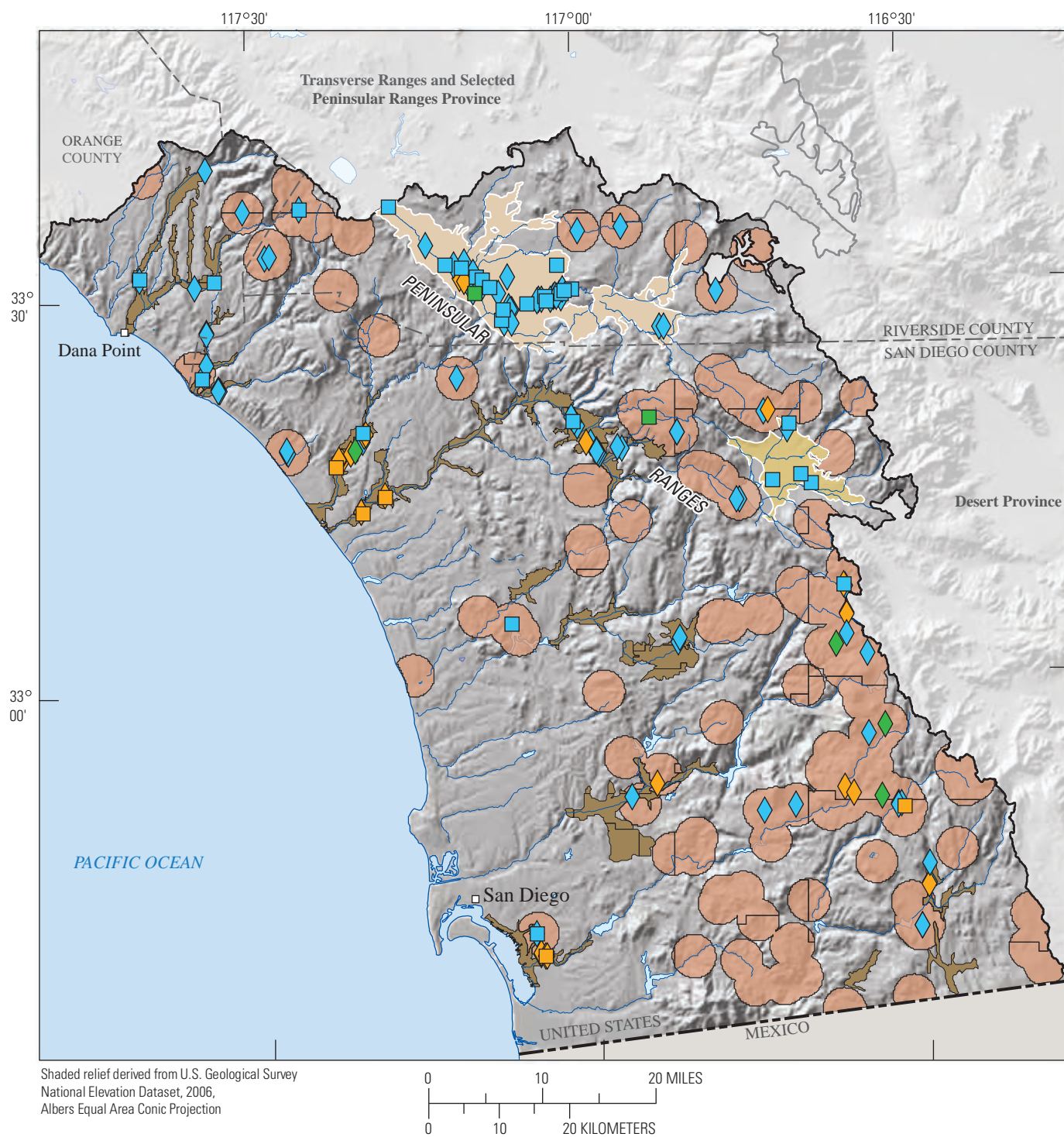
A. Manganese

EXPLANATION

Study areas

- Alluvial Basins
- Hard Rock
- Temecula Valley
- Warner Valley

Relative-concentration	USGS-grid or -understanding well	CDPH wells
Low or not detected		
Moderate		
High		

Shaded relief derived from U.S. Geological Survey National Elevation Dataset, 2006, Albers Equal Area Conic Projection
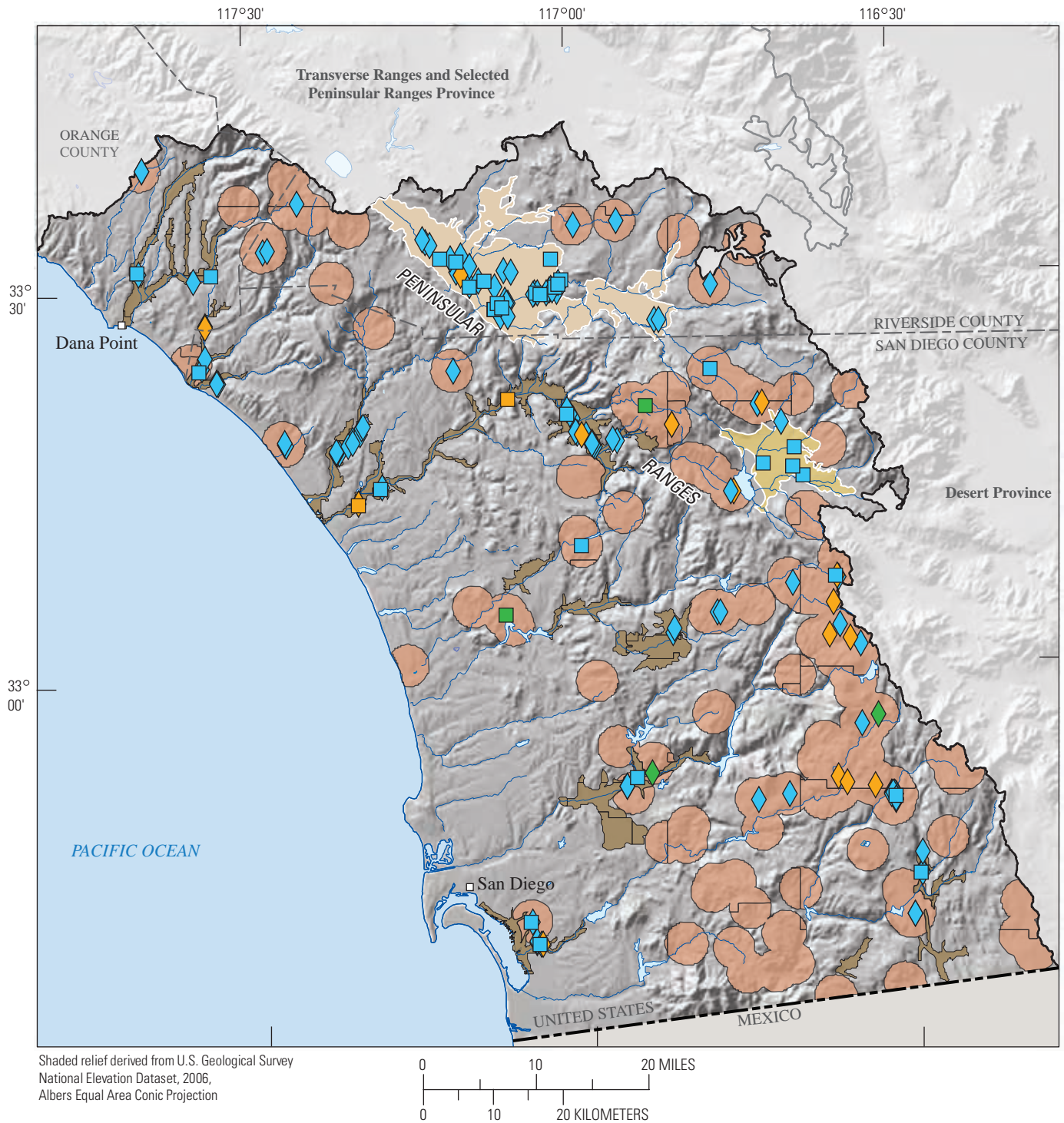
Figure 15A-C. Values of selected inorganic constituents in USGS-grid and -understanding wells representative of the primary aquifers and the most recent analysis July 30, 2001–July 29, 2004, for CDPH wells, San Diego Groundwater Ambient Monitoring and Assessment (GAMA) study unit, California, May–July 2004: (*A*) manganese, (*B*) iron, and (*C*) total dissolved solids.
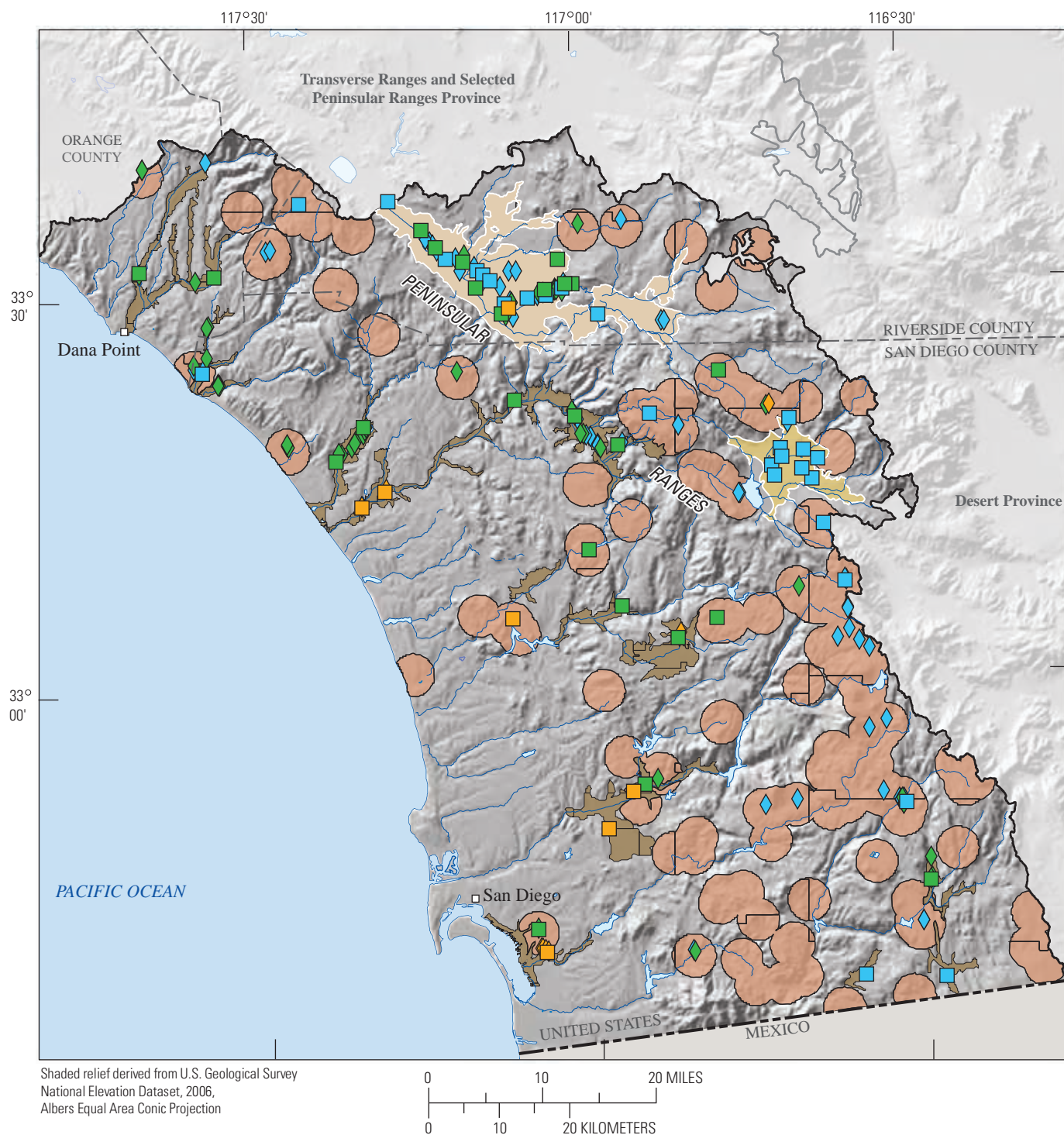
Shaded relief derived from U.S. Geological Survey
National Elevation Dataset, 2006,
Albers Equal Area Conic Projection

B. Iron

EXPLANATION

Study areas

Alluvial Basins

Hard Rock

Temecula Valley

Warner Valley

Relative-concentration	USGS-grid or -understanding well	CDPH wells
Low or not detected		
Moderate		
High		

Figure 15*A*–*C.*—**Continued**

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

C. Total dissolved solids

EXPLANATION

Study areas

▨	Alluvial Basins	▨	Temecula Valley
▨	Hard Rock	▨	Warner Valley

Relative-concentration | **USGS-grid or -understanding well** | **CDPH wells**

Low or not detected	◼	◆
Moderate	◼	◆
High	◼	◆

Figure 15*A*–*C*.—**Continued**