

Metrics for Assessing the Quality of Groundwater Used for Public Supply, CA, USA: Equivalent-Population and Area

Kenneth Belitz,^{*,†} Miranda S. Fram,[‡] and Tyler D. Johnson[§]

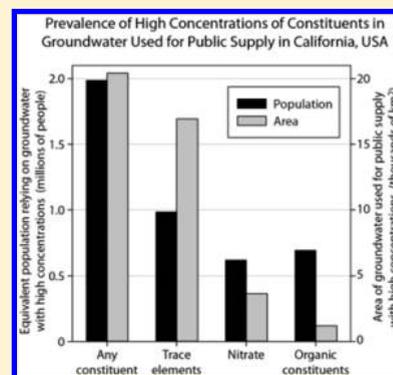
[†]U.S. Geological Survey, National Water Quality Assessment Program, Northborough 01532, Massachusetts, United States

[‡]U.S. Geological Survey, California Water Science Center, Sacramento, California 95819, United States

[§]U.S. Geological Survey, California Water Science Center, San Diego, California 92101, United States

Supporting Information

ABSTRACT: Data from 11 000 public supply wells in 87 study areas were used to assess the quality of nearly all of the groundwater used for public supply in California. Two metrics were developed for quantifying groundwater quality: area with high concentrations (km² or proportion) and equivalent-population relying upon groundwater with high concentrations (number of people or proportion). Concentrations are considered high if they are above a human-health benchmark. When expressed as proportions, the metrics are area-weighted and population-weighted detection frequencies. On a statewide-scale, about 20% of the groundwater used for public supply has high concentrations for one or more constituents (23% by area and 18% by equivalent-population). On the basis of both area and equivalent-population, trace elements are more prevalent at high concentrations than either nitrate or organic compounds at the statewide-scale, in eight of nine hydrogeologic provinces, and in about three-quarters of the study areas. At a statewide-scale, nitrate is more prevalent than organic compounds based on area, but not on the basis of equivalent-population. The approach developed for this paper, unlike many studies, recognizes the importance of appropriately weighting information when changing scales, and is broadly applicable to other areas.



INTRODUCTION

Groundwater provides about 50% of the global drinking water supply,¹ and about 45% of the United States drinking water supply.² Given the importance of groundwater, ambient groundwater quality monitoring programs have been established at national and regional scales across North America, South America, Europe, Africa, Asia, and the Pacific.^{3–10} These programs typically include synoptic sampling for the purposes of assessing the quality of groundwater resources. Often, these programs are based on a targeted design where certain areas are selected for monitoring based on a given set of priorities or criteria.^{11–13} In California, the State Water Resources Control Board (SWRCB) implemented the Groundwater Ambient Monitoring and Assessment (GAMA) program in 2000, which was expanded in 2001 by California Assembly Bill 599 (AB599). The GAMA Priority Basin Project (GAMA-PBP) is one component of the GAMA program.¹⁴ In a typical year, about one-third of California's drinking water supply is provided by groundwater from public supply wells.

The GAMA-PBP was designed as a 10-year comprehensive study to monitor and assess the quality of California groundwater at the depth zone used for public supply (Figure 1).^{15,16} The GAMA-PBP implemented a stratified, random sampling design.^{15,17} The fundamental scale of analysis was the study area. Study areas generally consist of a single alluvial groundwater basin,¹⁸ multiple alluvial groundwater basins that share common characteristics, or areas outside of basins (areas

of hard rock) that share common characteristics. Eighty-seven study areas were identified statewide, with each study area represented by a single grid consisting of equal-area cells (Figure 2; Figures S1–S8, SI).^{17,19} The 87 study areas account for nearly all of the groundwater used for public supply in California. The GAMA-PBP is a comprehensive, rather than a targeted, assessment.

Equal-area grids provide a basis for obtaining a spatially unbiased assessment of groundwater quality at the scale of a study area.¹⁷ Equal-area grids can be used for the design of stratified sampling programs (one well per cell), or for the declustering of previously collected regulatory-compliance data (multiple wells per cell). In the case of stratified sampling, each well is given equal weight, and in the case of declustering, wells are generally not given equal weight. In both cases, inference is drawn for the study area as a whole; inference is not drawn at the scale of a single cell. Hence, the approach presented in this paper represents a focus on the groundwater resource rather than a focus on small areas or on wells.

Field methods, laboratory analytical methods, quality assurance, and data for samples collected by the USGS at the study area scale have been presented in 35 U.S. Geological

Received: January 15, 2015

Revised: June 22, 2015

Accepted: June 26, 2015

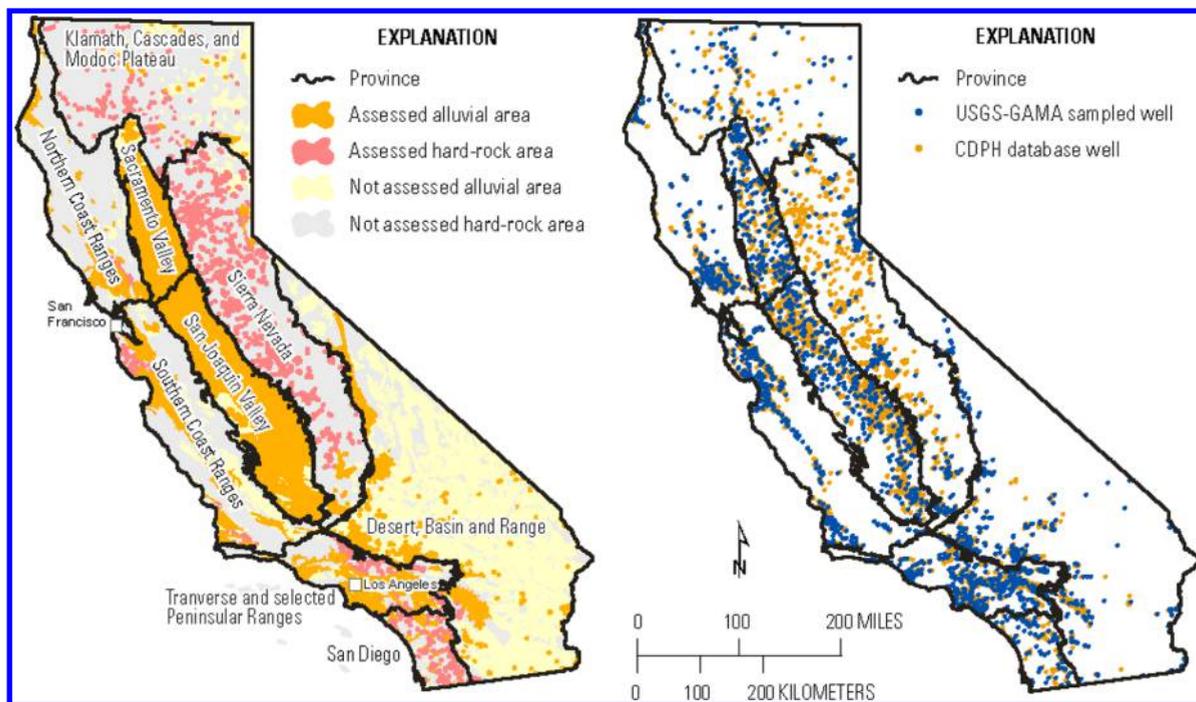


Figure 1. (A) Map of California showing boundaries of the nine hydrogeologic provinces and alluvial basin and hard-rock areas of the state assessed in this study. (B) Map showing locations of 11 000 wells used for assessing groundwater quality at the depth zone used for public supply.

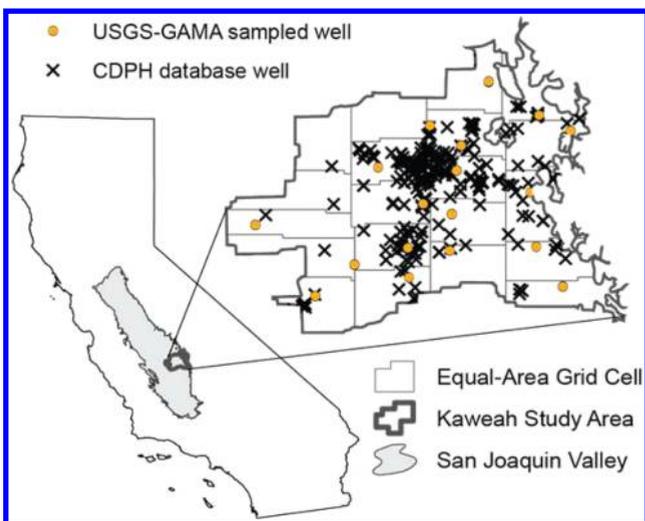


Figure 2. Example of a grid for the Kaweah study area, one of 87 study areas. Study area grids are presented in Figures S1–S8 (SI).

Survey (USGS) Data Series Reports (DSRs; Table S1, SI).²⁰ Data collected for the purposes of regulatory compliance have not been previously published. Evaluation of groundwater quality, and the factors affecting groundwater quality, have been presented in 25 USGS Scientific Investigations Reports (SIRs) and 35 USGS Fact Sheets (FSs; Table S1, SI).²⁰ Important results for selected individual constituents have also been presented at statewide and regional scales.^{21–29} The data for this assessment are provided in the supplement to this paper (Table S2, SI).

The purpose of this paper is to present an approach for the systematic and quantitative assessment of groundwater quality at multiple scales, and to apply that approach to groundwater used for public supply in California. The systematic approach relies upon the use of two metrics, one for area and one for

population, as indicators of groundwater quality. Previously, aquifer-scale proportion was introduced as a metric for basin-scale groundwater quality; aquifer-scale proportion is the proportion of an aquifer, on an areal basis, with concentrations above a specified threshold.¹⁷ Aquifer-scale proportion is nondimensional, spatially unbiased, and can be applied to an individual constituent or class of constituents. Consequently, aquifer-scale proportion allows for comparison of basins that may vary in size and which may be affected by different contaminants. In this paper, we extend the previous approach to include population as well as area. In addition, the area metric is expressed in terms of square kilometers (km²) as well as proportion. Likewise, the population metric is expressed as number of people as well as proportion.

The use of area and population as metrics for evaluating groundwater quality differs from the metrics typically used in other regional assessments.^{11–13} In other regional assessments, results are often presented as box-plots or detection frequencies with each well given equal weight. To the extent that wells are sampled using equal-area grids or comparable methods, then the unweighted results for the ensemble of wells can be taken as representative of the study area. If, however, the wells are clustered, then a box-plot or detection frequency may or may not provide a spatially unbiased representation of a study area. Also, if data from different study areas are combined without accounting for differences in the size of the study areas (area or population), then it may be difficult to know what the combined results are representing. The approach presented in this paper yields metrics that are representative of the specified region and is applicable at multiple scales.

For the purposes of assessment, high concentrations are defined as values above a human health benchmark (HHB; Table S3, SI). HHB's can be regulatory maximum contaminant levels (MCLs)^{30,31} or nonregulatory health-based screening levels.^{32,33} For constituents with an MCL, the HHB is equal to the MCL. In this context, the area metric provides an

Table 1. Area, Population (in the year 2000), and Number of Wells

province ^a	area (thousands of sq km)		population (millions of people)		equiv population density	no. of wells with data		
	total ^b	assessed ^c	total ^b	equiv population ^c		trace elements	nitrate	organic compd
state	410	89	33.7	11.1	125	8772	10 875	8733
KCM	62	5	0.2	0.05	9	234	385	193
NCR	38	4	1.4	0.2	39	601	770	571
SCR	42	6	6.6	1.4	231	1063	1231	1115
SAC	17	13	2.0	0.9	66	904	1196	951
SJV	36	26	3.3	2.0	78	2230	2755	2409
SNR	66	16	0.7	0.1	6	761	1308	601
TSPR	22	7	14.9	5.6	804	1802	1924	1829
SAN	10	4	3.4	0.2	41	271	321	223
DBR	117	8	1.3	0.7	91	906	985	841

^aProvince names: KCM, Klamath Mountains–Cascade Range and Modoc Plateau; DBR, Desert–Basin and Range; NCR, Northern Coast Ranges; SAC, Sacramento Valley; SCR, Southern Coast Ranges; SAN, San Diego Drainages; SNR, Sierra Nevada; SJV, San Joaquin Valley; TSPR, Transverse and Selected Peninsular Ranges. Equivalent-population density based on assessed area. ^bTotal area and total population for hydrogeologic provinces from Belitz and others.¹⁵ ^cAssessed area and equivalent population for hydrogeologic provinces are a summation of values computed at the scale of study areas (Table S3, SI).

assessment of the lateral extent of an aquifer with high concentrations; the area metric is spatially unbiased. The population metric provides an assessment of the number of people relying on groundwater with high concentrations, and may have utility as an indicator of human exposure; the issue of spatial bias does not arise directly for the population metric.

This paper distinguishes between area and assessed area (Table 1) because not all areas of the state are served by public supply wells. This paper also distinguishes between population and equivalent-population (Table 1) because public drinking water supplies can be a mix of surface water and groundwater.² Assessed area and equivalent-population were evaluated at the scale of study areas (Table S4, SI),¹⁵ and then aggregated at the scale of hydrogeologic provinces and the state (Table S5, SI). In 2000, California had a population of 33.7 million people and an equivalent-population of 11.1 million people.

Hydrogeologic provinces are regions with relatively similar geologic and climatic characteristics. In general, California's hydrogeologic provinces include relatively undeveloped highland areas underlain by hard rock and relatively flat-lying alluvial-filled basins that support urban and (or) agricultural land uses. In many parts of California, areas that are currently urban were previously characterized by agricultural land use. The Transverse and Selected Peninsular Ranges (TSPR) is the most densely populated province and includes Los Angeles and Orange Counties. The Southern Coast Ranges (SCR) province extends northward from the TSPR and includes the San Francisco–San Jose region. The TSPR and SCR provinces account for about two-thirds of California's equivalent-population. Two of the provinces—the San Joaquin Valley (SJV) and the Sacramento Valley (SAC)—are primarily agricultural, but do include sizable urban areas that rely upon groundwater. The Desert–Basin and Range (DBR) province is generally undeveloped due to the arid climate, but does include some urbanized areas, particularly along the western margin of the province. The remaining four provinces account for less than 5% of California's equivalent-population, while comprising about 40% of the total area (and one-third of the assessed area).

For the purposes of assessment, individual constituents were grouped into classes and subclasses. Three primary constituent classes were identified: trace elements, nitrate, and organic compounds. Within the organic compounds class, seven

subclasses were identified: solvents, gasoline-related compounds, fumigants, miscellaneous volatile organic compounds, insecticides, herbicides, and fungicides. The identification of classes and subclasses generally reflect the source of these constituents in groundwater. Trace elements are generally associated with geologic sources, nitrate with agricultural sources, and organic compounds with either agricultural or urban sources. The grouping of constituents into classes and subclasses allowed for the systematic assessment of a large number of constituents in a large number of study areas, and for the aggregation of results from smaller to larger scales.

The assessment for California presented in this paper is for in situ groundwater rather than delivered supply because groundwater can be blended or treated prior to delivery to consumers. Results are reported primarily on a state-wide scale. It is beyond the scope of this study to present detailed results at the study area scale or to assess quantitatively the factors affecting groundwater quality. Study area results are provided in the SI (Table S4).

METHODS

Study areas were the fundamental unit of organization for the GAMA-PBP, and the delineation of a study area depended on whether the area was an alluvial groundwater basin or a hard rock area. In alluvial basins with broadly distributed public supply wells, the entire basin was defined as a study area and represented by a grid of equal-area cells. In basins that contain relatively large areas without wells, and in hard-rock areas, a “buffered” approach was used.¹⁷ In the buffered approach, the study area was defined as the collective area within 3 km of any given public supply well; the collective area was then represented by a grid of equal-area cells. For basins that were buffered, the size of the study area was smaller than the size of the basin. For hard-rock areas, the study area is for “selected” areas of hard rock.

The number and size of cells varied from one study area grid to another (Table S4, SI). The target cell size was 25 km², but was modified in small study areas to obtain a minimum number of samples, and in large study areas to avoid collecting too many samples. The median number of cells in a grid was 20, with a range (1st and 3rd quartiles) of 15 to 30. The median cell size was 25 km², with a range of 20 km² to 54 km². The

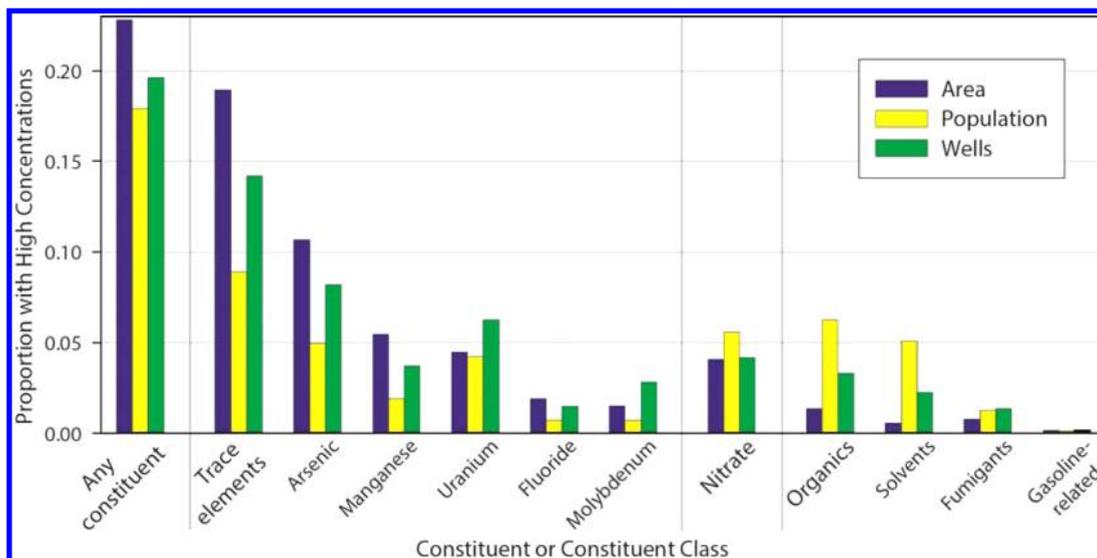


Figure 3. Bar charts summarizing groundwater quality (selected constituents and classes of constituents) for California. Tabular information is provided in the Supporting Information (Table S5).

buffer radius of 3 km was selected because the area of a circle of that radius is close to the target cell size.

Within each study area, the USGS generally sampled one public supply well per cell for the GAMA-PBP, but additional wells were also sampled for the purposes of understanding the factors affecting groundwater quality. From May 2004 through March 2012, the USGS sampled 2400 wells.²⁰ Samples from most wells were analyzed for several hundred water-quality constituents, including volatile organic compounds, pesticides and pesticide degradates, nutrients, major and minor ions, and trace elements by the USGS National Water Quality Laboratory (NWQL). Samples from some wells were not analyzed for inorganic constituents because of the availability of data from the California Department of Public Health Drinking Water Program (CDPH). (Note: The Drinking Water Program moved from CDPH to the SWRCB on July 1, 2014; the term CDPH is used in this paper for consistency with previous GAMA-PBP reports.) The USGS also sampled wells for geochemical indicators and age-tracers, but evaluation of those data is beyond the scope of this paper.

For each study area, additional data were obtained from the CDPH database. A “current” period was defined for each study area as the three-year period prior to the initiation of sampling by the USGS for that study area. In turn, the most recent analysis of a water quality parameter within the current period was obtained for each well. For those wells with data available from both the USGS and CDPH data sets, and given the definition of the current period, data collected by the USGS was the most recent value at any well. Relative to laboratories used for regulatory compliance, the NWQL generally analyzed samples for a larger suite of constituents and used laboratory methods with lower detection limits (for example^{34,35}). The use of methods with lower detection limits can provide additional insight into the distribution and occurrence of constituents, and may help to explain the factors affecting groundwater quality (for example^{36,37}). The methods used for regulatory compliance do allow for detection of constituents at concentrations at or above HHBs. The resulting data set for the current period (2004–2012) allowed for a synoptic assessment of groundwater quality.

About 11 000 wells have water quality data available, but not all wells have a full suite of analytical results (Table 1; Tables S2 and S4, SI). At the scale of hydrogeologic provinces, the numbers range from 200 wells with results for organic compounds in the Klamath-Cascades-Modoc Plateau (KCM) province to 2800 wells with results for nitrate in the SJV.

A sample from a well can be coded as a high value (greater than an HHB) or a low value for an individual constituent, for a class of constituents, or for any constituent. About 180 constituents have an HHB (Table S3, SI). A sample was coded as high for a class if it was high for any constituent in the class. Many constituents, particularly organic compounds, do not have an HHB, and were not considered in the assessment.

Each well, whether sampled by the USGS or obtained from the CDPH database, was geo-located and assigned membership in a study area grid and a grid cell (Table S2, SI). A total of 1800 grid cells (in 87 study areas), covering a total of 89 000 km², contained at least one well with water-quality data. Although the area assessed in this study is about 20% of the total area of the State, it accounts for more than 99% of the equivalent-population and about 90% of the public supply wells.

At the scale of study areas, the area of the resource with high concentrations was computed through the use of cell-declustering.^{17,38,39} For an individual study area, a cell-declustering proportion was obtained in two steps: (1) for each grid cell, compute the detection frequency (number of wells coded high for a constituent [or class] divided by total number of wells with a measurement for that constituent [or class]), and (2) compute the average of the cell-based detection frequencies. The resulting proportion, defined here as the areal-proportion, is a measure of groundwater quality for the study area. In turn, the size of the area with high concentrations is computed by multiplying the areal-proportion by the size of the study area grid (km²). Cells without wells were not included in the computation of the size of the area with high concentrations.

At the scale of provinces, the size of the area with high concentrations was computed as a sum of the values for the individual study areas located within the given province. The areal-proportion at the province scale (Table S5, SI) was then

computed by dividing the sum of the study area values by the sum of the assessed areas for those study areas. In turn, area and areal-proportion were computed at the statewide scale.

The equivalent-population relying upon groundwater with high concentrations was computed somewhat differently than the size of the area with high concentrations. At the scale of study areas, we used detection frequency for the entire study area, rather than areal-proportion, under the assumption that the population in a study area draws equally upon each well, rather than the assumption that drinking water is drawn uniformly across the aquifer. An assumption about the distribution of pumping needs to be made because pumping rates at individual wells are not generally available. The number of equivalent-people relying upon groundwater with high concentrations was computed as the product of the equivalent-population in the study area times the detection frequency. For buffered study areas, the population for the entire study area was used under the assumption that the equivalent-population relies upon the available wells (which by definition are located in the buffered areas).

At the scale of provinces and the state, the equivalent-population relying upon groundwater with high concentrations was computed as a sum, in a manner analogous to the computation for area. When the equivalent-population relying upon groundwater with high concentrations is divided by the equivalent-population (at the scale of study areas, provinces, or the state), the result is defined as the population-proportion (Table S5, SI).

RESULTS AND DISCUSSION

Identification of an Appropriate Metric. Detection frequency (proportion of wells) has often been used as a basis for assessing groundwater quality at regional scales. However, detection frequencies can provide misleading results. For example, the detection frequency for the occurrence of high concentrations of organic compounds in California's public supply wells is greater than the areal-proportion and lower than the population-proportion (Figure 3). This discrepancy arises because organic-compound concentrations are high in a group of wells located in a few small study areas in which a large number of people rely upon groundwater; these study areas are located in the TSPR province (Figure 4). This example illustrates the value of using area and equivalent-population as metrics, rather than detection frequency, for assessing groundwater quality.

The area and population metrics can be expressed with or without units, and it is important to consider which formulation might be better. Identification of an appropriate formulation depends on the question that one is trying to answer. At a statewide scale, if the question is which constituent or constituent class is most prevalent at high concentrations, then either formulation provides a direct answer. If, however, the question is which province (or study area) contributes to the statewide prevalence, then the formulation with units provides a more direct answer. Alternatively, if the question is what process or processes control the occurrence of high concentrations, then the unitless formulation is better. There are other important questions, and an appropriate formulation—with or without units—should be selected to address that question.

Which Constituents and Constituent Classes are Most Prevalent at High Concentrations? At a statewide scale (Figures 3 and 4), the area with high concentrations of any

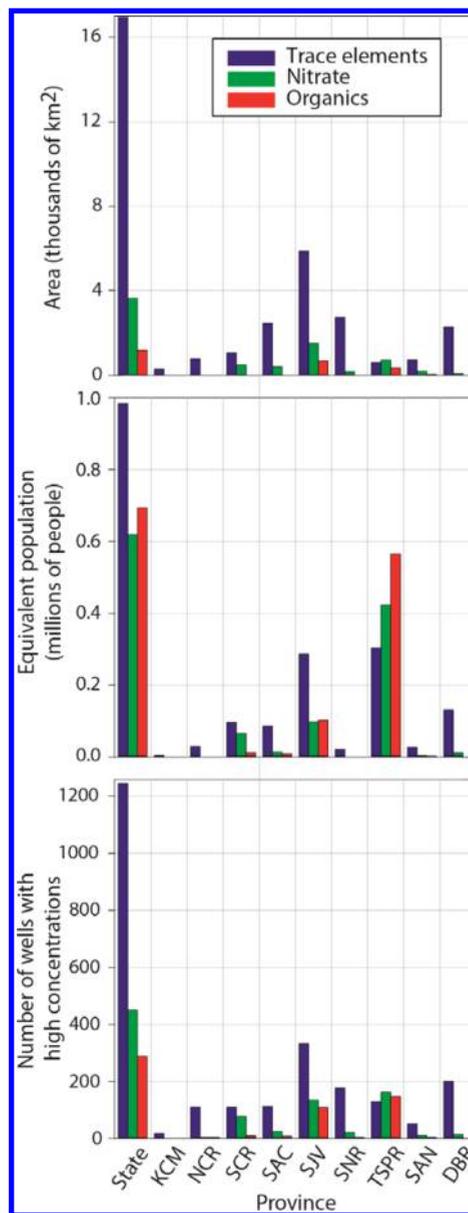


Figure 4. Bar charts summarizing groundwater quality (constituent classes) at the scale of hydrogeologic provinces, with statewide results shown for reference. Province name abbreviations are provided in Table 1. Tabular information is provided in the Supporting Information (Table S5).

constituent is 20 000 km² (23% of the assessed area) and the equivalent-population relying on groundwater with high concentrations of any constituent is 2.0 million people (18% of the equivalent-population). With respect to constituent classes, trace elements are more prevalent at high concentrations than either nitrate or organic compounds, whether the metric is area or population. Nitrate is more prevalent than organic compounds with respect to area, but not with respect to equivalent-population.

The results observed at the statewide-scale are recapitulated at the scale of hydrogeologic provinces and study areas. Trace elements are more prevalent than nitrate or organic compounds in eight of the nine provinces (Figure 4), and in 67 of the 87 study areas (compare Tables S4c–e, SI).

At a statewide scale, the trace elements that are most prevalent at high concentrations are arsenic, manganese, and uranium (Figure 3). For each of the three constituents, the area metric is larger than the value for nitrate. In contrast, the population metrics for the three constituents are smaller than the value for nitrate. Two additional trace elements—fluoride and molybdenum—are relatively prevalent with respect to area (>1%; Table S5a, SI) but not with respect to equivalent-population (<1%, Table S5b, SI). About 980 000 equivalent-people rely upon groundwater with high concentrations of one or more trace elements.

The organic subclasses that are most prevalent at high concentrations are solvents, fumigants, and gasoline-related constituents (Figure 3). Trichloroethylene (TCE) and perchloroethylene (PCE) are the constituents primarily accounting for the prevalence of solvents at high concentrations, and dibromochloropropane (DBCP) is the primary fumigant. Herbicides and insecticides were not detected at high concentrations. About 690 000 equivalent-people rely on groundwater with high concentrations of one or more organic compounds.

Disparity Between Population-Proportion and Areal-Proportion. The statewide population-proportion for a constituent or class does not necessarily reflect the statewide areal-proportion (Figure 3). For example, the areal-proportion for trace elements is 19% and the population-proportion is 8.9%. In contrast, the areal-proportion for organic compounds is 1.3%, and the population-proportion is 6.3%. The disparity is even more evident for solvents that are high in about 0.5% of the area but have a population-proportion of 5.1%. The disparities arise because study areas (and provinces) with large areas do not necessarily have large equivalent-populations, and study areas with large equivalent-populations do not necessarily have large areas.

With regard to trace elements: four provinces (Figure 1)—SJV, SNR, DBR, and SAC—account for more than three-quarters of the total area with high concentrations of trace elements (Figure 4), but these provinces only account for about one-third of California's equivalent-population (Table 1). Consequently, the statewide population-proportion for trace elements (8.9%) is lower than the statewide areal-proportion (19%).

With regard to organic compounds: about 80% of the equivalent-population relying on groundwater with high concentrations of organic compounds resides in six study areas (Figure S6). The six study areas, located in the TSPR, account for 32% of California's equivalent-population, but only 3% of the assessed area (Table S4a). The six study areas do not have correspondingly large equivalent-populations relying upon groundwater with high concentrations of trace elements. Alternatively stated, a large proportion of California's equivalent-population resides in six relatively small study areas; these areas have relatively widespread contamination by organic compounds but do not have relatively widespread contamination by trace elements.

In contrast to trace elements and organic compounds (Figures 3 and 4), the statewide population-proportion for nitrate (5.6%) is comparable to the statewide areal-proportion (4.1%).

Areal-Proportion Reflects the Source of Constituents. The areal-proportions of trace elements, nitrate, and organic compounds at high concentrations at the depth zone used for public supply reflect the spatial distribution—both laterally and

vertically—of their respective sources. Trace elements naturally occur in the rocks and sediments that comprise aquifers and tend to occur at some concentration throughout the aquifer, including those parts tapped by public supply wells. In contrast, nitrate and organic compounds are generally introduced at the land surface or shallow subsurface by human activity, and are therefore relatively distal to the depth zone used for public supply. Consequently, trace elements are more spatially prevalent at high concentrations than either nitrate or organic compounds.

The areal-proportion of high concentrations of trace elements depends on a number of factors including the composition of the aquifer materials, the pH and redox conditions, and the extent of interaction between the groundwater and the aquifer materials.⁴⁰ In some cases, trace elements can be introduced or mobilized by human activity.^{24,41}

High concentrations of arsenic in California groundwater have been attributed to its release from iron and (or) manganese oxyhydroxide minerals by two mechanisms: (1) desorption under oxic, alkaline conditions, and (2) dissolution under anoxic conditions.^{42–44} Oxic, alkaline conditions are broadly prevalent in California where arid and semiarid climatic conditions prevail, but reduced conditions do occur, generally at depth and along some large rivers. Consequently, arsenic is broadly prevalent at high concentrations: there are 32 study areas in which the areal-proportion exceeds 10% (Table S4c1, SI). Additional discussion of the factors affecting the occurrence of high concentrations of arsenic is provided in several USGS SIRs.^{35,45–56} These study areas are distributed across eight of the nine hydrogeologic provinces.

Manganese is present in primary silicate minerals and in oxyhydroxide coatings, and high concentrations are associated with anoxic conditions.⁴⁰ Although oxic conditions generally prevail in California groundwater due to the climate, anoxic conditions do occur: there are 14 study areas in which the areal proportion for manganese exceeds 10% (Table S4c2, SI). The 14 study areas are distributed across seven hydrogeologic provinces, and additional discussion is provided in several USGS SIRs.^{49–54,57,58}

High concentrations of uranium in California groundwater are associated with granitic rocks and alluvium derived from granitic rocks. In the eastern SJV, uranium also has been mobilized by downward-moving irrigation water with elevated bicarbonate concentrations.²⁴ There are 10 study areas in which the areal-proportion exceeds 10% (Table S4c3, SI): they include hard-rock areas of the SNR, SD, and TSPR provinces, alluvial basins in the SJV, DBR, SNR, and KCM provinces. Additional discussion is provided in several USGS SIRs.^{35,46–48,55,56}

The DBR province is notable because the areal proportion for trace elements (30%) is the highest among the nine hydrogeologic provinces (Table S5, SI). The trace elements contributing to the high areal proportion are arsenic, boron, fluoride, molybdenum, strontium, and uranium.⁵⁴ Wright and others²⁹ evaluated the factors affecting the occurrence of these trace elements in the DBR province.

The source of nitrate is generally fertilizers applied to crops, animal manure, or septic systems. These sources are often referred to as nonpoint sources, but the landscape activities contributing nitrate to aquifers are not everywhere present. For example, the acreage for agricultural cropland in California is about 48 000 km² or 12% of the state's total area.⁵⁹ In addition, not all agricultural activities are associated with equally high

loadings of nitrate from fertilizers or animal waste.^{60,61} The areal proportion of nitrate exceeds 10% in 14 study areas (Table S4d, SI).^{45–48,50,51,62–64} They are distributed across just three provinces: SCR, TSPR, and SJV.

The occurrence of nitrate at high concentrations does not necessarily reflect current land use.⁶⁵ The four study areas with the highest values of areal-proportion (Table S4d, SI) are located in the TSPR and SCR provinces, and are primarily characterized by urban land use at the current time; the source of the nitrate is likely prior agricultural land use.^{66,67} In addition, study areas that are currently characterized by agricultural land use, including many in the SJV and SAC, are not currently characterized by high values of areal-proportion at the depth zone used for public supply. These areas could be characterized by high values in the future, as irrigation water containing elevated concentrations of nitrate moves toward the deeper parts of the aquifer tapped by public supply wells.

Organic compounds include point pollutants such as solvents, as well as nonpoint pollutants such as fumigants. The source of solvents is typically leakage from tanks or improper disposal, and the source of fumigants is generally agricultural application. In some cases, high concentrations of organic compounds can have natural sources.²⁵ In general, the sources of organic compounds at high concentrations are not as widespread as the sources of trace elements or nitrate. There are only five study areas in which the areal-proportion for organic compounds exceeds 10% (Table S4e, SI): four in the TSPR and one in the SJV.^{45,49,63,68} The occurrence of organic compounds in California groundwater is generally due to legacy activities.^{37,69–71}

Area and Equivalent-Population Provide a Basis for Comprehensive Assessment. This paper introduces two metrics—one for area and one for population—that provide a basis for quantitative assessment at multiple scales. When expressed as a proportion, they are area-weighted and population-weighted detection frequencies. An assessment based on these metrics represents an important but subtle shift from a focus on wells to a focus on study areas. The assessment also recognizes the importance of using appropriate weights when aggregating study area results at larger scales (hydrogeologic provinces and the state). The appropriate weights are the area with high concentrations and the number of equivalent-people affected by high concentrations. The GAMA-PBP assessment is comprehensive in that it has assessed nearly all of the groundwater resource used for public supply in California. Going forward, one can relate study area scale groundwater quality to potential explanatory factors that are also quantified at the scale of study areas. One might also be able to relate groundwater quality to health outcomes for a population at the scale of a study area.

■ ASSOCIATED CONTENT

● Supporting Information

Additional information as noted in the text. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b00265.

■ AUTHOR INFORMATION

Corresponding Author

* E-mail: kbelitz@usgs.gov. Tel.: 978-341-6774.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the well owners who graciously allowed the USGS to collect samples, USGS personnel who collected and managed the data, and our colleagues who helped manage the effort. We are particularly indebted to Carmen Burton, Barbara Dawson, Justin Kulongoski, Matt Landon, and Elise Watson. This study was coordinated with the California GAMA program, funded by state bonds administered by the California State Water Resources Control Board; and the USGS NAWQA program. The use of brand names in the manuscript is for identification purposes only and does not imply endorsement by the U.S. Government.

■ REFERENCES

- (1) World Water Assessment Programme. *The United Nations World Water Development Report 3: Water in a Changing World*; UNESCO and Earthscan: London, 2009; <http://www.unesco.org/new/en/natural-sciences/environment/water/wwap/wwdr/wwdr3-2009/downloads-wwdr3/>.
- (2) Kenny, J. F.; Barber, N. L.; Hutson, S. S.; Linsey, K. S.; Lovelace, J. K.; Maupin, M. A. *Estimated Use of Water in the United States in 2005*; Circular 1344; U.S. Geological Survey: Reston, VA, 2009; <http://pubs.usgs.gov/circ/1344/>.
- (3) Ward, R. S.; Streetly, M. J.; Singleton, A. J.; Sears, R. A. A framework for monitoring regional groundwater quality. *Q. J. Eng. Geol. Hydrogeol.* **2004**, *37* (4), 271–280.
- (4) Mendizabal, I.; Stuyfzand, P. J. Guidelines for interpreting hydrochemical patterns in data from public supply well fields and their value for natural background groundwater quality determination. *J. Hydrol.* **2009**, *379* (1–2), 151–163.
- (5) Rosen, M. R.; Lapham, W. W. Introduction to the US Geological Survey National Water-Quality Assessment (NAWQA) of groundwater quality trends and comparison to other national programs. *J. Environ. Qual.* **2008**, *37* (5), S190–S198.
- (6) Rentier, C.; Delloye, F.; Brouyere, S.; Dassargues, A. A framework for an optimized groundwater monitoring network and aggregated indicators. *Environ. Geol.* **2006**, *50* (2), 194–201.
- (7) Lapham, W. W.; Hamilton, P. A.; Myers, D. N. *National Water Quality Assessment Program—Cycle II: Regional Assessment of Aquifers*; Fact Sheet 2005–3013; U.S. Geological Survey: Reston, VA, 2005; <http://pubs.usgs.gov/fs/2005/3013/>.
- (8) Lesage, S. Groundwater quality in Canada, a national overview. In *Bringing Groundwater Quality Research to the Watershed Scale*, IAHS Publication 297; Thomson, N. R., Ed.; IAHS Press: Wallingford, UK, 2004; pp 11–18.
- (9) Grath, J.; Ward, J.; Scheidleder, A.; Quevauviller, P. Report on EU guidance on groundwater monitoring developed under the common implementation strategy of the water framework directive. *J. Environ. Monit.* **2007**, *9*, 1162–1175.
- (10) Broers, H. P. The spatial distribution of groundwater age for different geohydrological situations in the Netherlands: implications for groundwater quality monitoring at the regional scale. *J. Hydrol.* **2004**, *299*, 84–106.
- (11) Toccalino, P. L.; Norman, J. E.; Hitt, K. J. *Quality of Source Water from Public-Supply Wells in the United States, 1993–2007*; Scientific Investigations Report 2010–5024; U.S. Geological Survey: Reston, VA, 2010; <http://pubs.usgs.gov/sir/2010/5024/>.
- (12) DeSimone, L. A. *Quality of water from domestic wells in principal aquifers of the United States, 1991–2004*; Scientific Investigations

Report 2008–5227; U.S. Geological Survey: Reston, VA, 2009; <http://pubs.usgs.gov/sir/2008/5227>.

(13) DeSimone, L. A.; McMahon, P. B.; Rosen, M. R. *Water quality in principal aquifers of the United States, 1991–2010*; Circular 1360; U.S. Geological Survey: Reston, VA, 2014; <http://pubs.usgs.gov/circ/1360/>.

(14) California State Water Resources Control Board. *Groundwater Ambient Monitoring and Assessment (GAMA) Program Home Page*; 2014, Website, accessed August 29, 2014 at: http://www.waterboards.ca.gov/water_issues/programs/gama/.

(15) Belitz, K.; Dubrovsky, N. M.; Burow, K. R.; Jurgens, B. C.; Johnson, T. D. *Framework for a ground-water quality monitoring and assessment program for California*; Water Resources Investigations Report 03–4166; U.S. Geological Survey: Reston, VA, 2003; <http://pubs.usgs.gov/wri/wri034166/>.

(16) California State Water Resources Control Board. *Report to the Governor and Legislature, A comprehensive groundwater quality monitoring program for California: Assembly Bill 599, March 2003*; California State Water Resources Control Board: Sacramento, CA, 2003; http://www.waterboards.ca.gov/gama/docs/final_ab_599_rpt_to_legis_7_31_03.pdf.

(17) Belitz, K.; Jurgens, B. C.; Landon, M. K.; Fram, M. S.; Johnson, T. D. Estimation of aquifer scale proportion using equal area grids: Assessment of regional scale groundwater quality. *Water Resour. Res.* **2010**, *46*, W11550.

(18) California Department of Water Resources. *California's Groundwater—Bulletin 118, Update 2003*; California Department of Water Resources: Sacramento, CA, 2003; <http://www.water.ca.gov/groundwater/bulletin118/index.cfm>.

(19) Scott, J. C. *Computerized stratified random site-selection approaches for design of a ground-water quality sampling network*; Water Resources Investigations Report 01–4188; U.S. Geological Survey: Reston, VA, 1990; <http://pubs.usgs.gov/wri/1990/4101/report.pdf>.

(20) U.S. Geological Survey. *California Water Science Center (CAWSC), Groundwater Ambient Monitoring and Assessment (GAMA) Program, Publications*; 2014, Website, accessed August 29, 2014 at: http://ca.water.usgs.gov/projects/gama/includes/GAMA_publications.html.

(21) Deeds, D. D.; Kulongoski, J. T.; Belitz, K. Assessing California groundwater susceptibility using trace concentrations of halogenated volatile organic compounds. *Environ. Sci. Technol.* **2012**, *46* (24), 13128–13135.

(22) Fram, M. S.; Belitz, K. Occurrence and concentrations of pharmaceutical compounds in groundwater used for public drinking-water supply in California. *Sci. Total Environ.* **2011**, *409* (18), 3409–3417.

(23) Fram, M. S.; Belitz, K. Probability of detecting perchlorate under natural conditions in deep groundwater in California and the southwestern United States. *Environ. Sci. Technol.* **2011**, *45*, 1271–1277.

(24) Jurgens, B. C.; Fram, M. S.; Belitz, K.; Burow, K. R.; Landon, M. K. Effects of groundwater development on uranium: Central Valley, California, USA. *Groundwater* **2010**, *48* (6), 913–928.

(25) Landon, M. K.; Belitz, K. Geogenic sources of benzene in aquifers used for public supply, California. *Environ. Sci. Technol.* **2012**, *46*, 8689–8697.

(26) Wright, M. T.; Belitz, K. Factors controlling the regional distribution of vanadium in groundwater. *Groundwater* **2010**, *48*, 515–525.

(27) Landon, M. K.; Burton, C. A.; Davis, T. A.; Belitz, K.; Johnson, T. D. Statistical evaluation of variables affecting occurrence of hydrocarbons in aquifers used for public supply, California. *J. Am. Water Resour. Assoc.* **2014**, *50*, 179–195.

(28) Wright, M. T.; Stollenwerk, K. G.; Belitz, K. Assessing the solubility controls on vanadium in groundwater, northeastern San Joaquin Valley, CA. *Appl. Geochem.* **2014**, *48*, 41–52.

(29) Wright, M. T.; Fram, M. S.; Belitz, K. *Geochemical conditions and the occurrence of selected trace elements in groundwater basins used for*

public drinking-water supply, Desert and Basin and Range hydrogeologic provinces, 2006–11: California GAMA Priority Basin Project; Scientific Investigations Report 2014–5173; U.S. Geological Survey: Reston, VA, 2015; DOI: 10.3133/sir20145173.

(30) U.S. Environmental Protection Agency. *Drinking water contaminants: National Primary Drinking Water Regulations*; 2013, Website, accessed August 29, 2014 at: <http://www.epa.gov/drink/contaminants/index.cfm>.

(31) California State Water Resources Control Board. *Division of Drinking Water—Chemicals and contaminants in drinking water*; 2014, Website, accessed October 5, 2014 at: http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Chemicalcontaminants.shtml.

(32) Toccalino, P. L.; Nowell, L. H.; Wilber, W. G.; Zogorski, J. S.; Donohue, J. M.; Eiden, C. A.; Krietzman, S.; Post, G. B. *Development of health-based screening levels for use in state- or local-scale water-quality assessments*; Water-Resources Investigations Report 03–4054; U.S. Geological Survey: Reston, VA, 2003; <http://pubs.usgs.gov/wri/wri034054/>.

(33) Toccalino, P. L.; Norman, J. E.; Schoephoester, K. M. Health-based screening levels for evaluating water-quality data; 2014, <http://water.usgs.gov/nawqa/HBSL>, DOI: 10.5066/F71C1TWP.

(34) California State Water Resources Control Board. *Division of Drinking Water—California drinking water-related laws*; 2014, Website, accessed September 2, 2014 at: http://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/Lawbook.shtml.

(35) Fram, M. S.; Belitz, K. *Status and understanding of groundwater quality in the Tahoe-Martis, Central Sierra, and Southern Sierra study units, 2006–2007: California GAMA Priority Basin Project*; Scientific Investigations Report 2011–5216; U.S. Geological Survey: Reston, VA, 2012; <http://pubs.usgs.gov/sir/2011/5216/>.

(36) Gilliom, R. J.; Barbash, J. E.; Crawford, C. G.; Hamilton, P. A.; Martin, J. D.; Nakagaki, N.; Wolock, D. M. *Pesticides in the Nation's streams and groundwater, 1992–2001*; Circular 1291; U.S. Geological Survey: Reston, VA, 2006; <http://pubs.usgs.gov/circ/2005/1291/>.

(37) Zogorski, J. S.; Carter, J. M.; Ivahnenko, T.; Lapham, W. W.; Moran, M. J.; Rowe, B. L.; Squillace, P. J.; Toccalino, P. L. *Volatile organic compounds in the Nation's groundwater and drinking-water supply wells*; Circular 1292; U.S. Geological Survey: Reston, VA, 2006; <http://pubs.usgs.gov/circ/circ1292/>.

(38) Isaaks, E. H.; Srivastava, R. M. *An introduction to applied geostatistics*. Oxford University Press, New York, 1989.

(39) Journel, A. G. Nonparametric estimation of spatial distributions. *J. Int. Assoc. Math. Geol.* **1983**, *15* (3), 445–468.

(40) Hem, J. D. *Study and interpretation of the chemical characteristics of natural water*; Water Supply Paper 2254; U.S. Geological Survey: Reston, VA, 1985; <http://pubs.usgs.gov/wsp/wsp2254/>.

(41) Barringer, J. L.; Reilly, P. A. Arsenic in groundwater: A summary of sources and the biogeochemical and hydrogeologic factors affecting arsenic occurrence and mobility. In *Current perspectives in contaminant hydrology and water resources sustainability*; Bradley, P., Ed.; InTech: Rijeka, Croatia; 2013; pp 83–116; DOI: 10.5772/55354.

(42) Smedley, P. L.; Kinniburgh, D. G. A review of the source, behavior, and distribution of arsenic in natural waters. *Appl. Geochem.* **2002**, *17*, 517–568.

(43) Welch, A. H.; Westjohn, D. B.; Helsel, D. R.; Wanty, R. B. Arsenic in groundwater of the United States - occurrence and geochemistry. *Groundwater* **2000**, *38*, 589–604.

(44) Welch, A. H.; Stollenwerk, K. G. *Arsenic in groundwater—geochemistry and occurrence*; Kluwer Academic Publishers; Boston, MA, 2003.

(45) Kent, R.; Belitz, K. *Status of groundwater quality in the Upper Santa Ana Watershed, November 2006–March 2007 - California GAMA Priority Basin Project*; Scientific Investigations Report 2012–5052; U.S. Geological Survey: Reston, VA, 2012; <http://pubs.usgs.gov/sir/2012/5052/>.

(46) Landon, M. K.; Belitz, K.; Jurgens, B. C.; Kulongoski, J. T.; Johnson, T. D. *Status and understanding of groundwater quality in the Central-Eastside San Joaquin Basin, 2006: California GAMA Priority*

- Basin Project; Scientific Investigations Report 2009–5266; U.S. Geological Survey: Reston, VA, 2010; <http://pubs.usgs.gov/sir/2009/5266/>.
- (47) Burton, C. A.; Shelton, J. L.; Belitz, K. *Status and understanding of groundwater quality in the two southern San Joaquin Valley study units, 2005–2006: California GAMA Priority Basin Project*; Scientific Investigations Report 2011–5218; U.S. Geological Survey: Reston, VA, 2012; <http://pubs.usgs.gov/sir/2011/5218/>.
- (48) Shelton, J. L.; Fram, M. S.; Belitz, K.; Jurgens, B. C. *Status and understanding of groundwater quality in the Madera-Chowchilla study unit, 2008: California GAMA Priority Basin Project*; Scientific Investigations Report 2012–5094; U.S. Geological Survey: Reston, VA, 2013; <http://pubs.usgs.gov/sir/2012/5094/>.
- (49) Bennett, G. L. V.; Fram, M. S.; Belitz, K.; Jurgens, B. C. *Status and understanding of groundwater quality in the northern San Joaquin Basin, 2005 - California GAMA Priority Basin Project*; Scientific Investigations Report 2010–5175; U.S. Geological Survey: Reston, VA, 2010; <http://pubs.usgs.gov/sir/2010/5175/>.
- (50) Parsons, M. C.; Kulongoski, J. T.; Belitz, K. *Status and understanding of groundwater quality in the South Coast Interior groundwater basins, 2008 - California GAMA Priority Basin Project*; Scientific Investigations Report 2014–5023; U.S. Geological Survey: Reston, VA, 2014; DOI: 10.3133/sir20145023.
- (51) Burton, C. A.; Land, M. T.; Belitz, K. *Status and understanding of groundwater quality in the South Coast Range-Coastal study unit, 2008: California GAMA Priority Basin Project*; Scientific Investigations Report 2013–5053; U.S. Geological Survey: Reston, VA, 2013; <http://pubs.usgs.gov/sir/2013/5053/>.
- (52) Bennett, G. L. V.; Fram, M. S.; Belitz, K. *Status of groundwater quality in the Southern, Middle, and Northern Sacramento Valley study units, 2005–08: California GAMA Priority Basin Project*; Scientific Investigations Report 2011–5002; U.S. Geological Survey: Reston, VA, 2011; <http://pubs.usgs.gov/sir/2011/5002/>.
- (53) Kulongoski, J. T.; Belitz, K.; Landon, M. K.; Farrar, C. *Status and understanding of groundwater quality in the North San Francisco Bay groundwater basins, 2004 - California GAMA Priority Basin Project*; Scientific Investigations Report 2010–5089; U.S. Geological Survey: Reston, VA, 2010; <http://pubs.usgs.gov/sir/2010/5089/>.
- (54) Dawson, B. J. M.; Belitz, K. *Status of groundwater quality in the California Desert Region, 2006–2008 - California GAMA Priority Basin Project*; Scientific Investigations Report 2012–5040; U.S. Geological Survey: Reston, VA, 2012; <http://pubs.usgs.gov/sir/2012/5040/>.
- (55) Parsons, M. C.; Hancock, T. C.; Kulongoski, J. T.; Belitz, K. *Status of groundwater quality in the Borrego Valley, Central Desert, and Low-Use Basins of the Mojave and Sonoran Deserts study unit, 2008–2010 - California GAMA Priority Basin Project*; Scientific Investigations Report 2014–5001; U.S. Geological Survey: Reston, VA, 2014; DOI: 10.3133/sir20145001.
- (56) Fram, M. S.; Shelton, J. L.; *Status and understanding of groundwater quality in the Cascade Range and Modoc Plateau study unit, 2010: California GAMA Priority Basin Project*; Scientific Investigations Report 2014–5238; U.S. Geological Survey: Reston, VA, 2015; DOI: 10.3133/sir20145238.
- (57) Wright, M. T.; Belitz, K. *Status and understanding of groundwater quality in the San Diego Drainages hydrogeologic province, 2004: California GAMA Priority Basin Project*; Scientific Investigations Report 2011–5154; U.S. Geological Survey: Reston, VA, 2011; <http://pubs.usgs.gov/sir/2011/5154/>.
- (58) Mathany, T. M.; Belitz, K. *Status and understanding of groundwater quality in the North Coast Ranges study unit, 2009: California GAMA Priority Basin Project*; Scientific Investigations Report 2014–5215; U.S. Geological Survey: Reston, VA, 2015; DOI: 10.3133/sir20145215.
- (59) University of California Agricultural Issues Center. *The measure of California agriculture*; Regents of the University of California: Davis, CA, 2009; <http://aic.ucdavis.edu/publications/moca/mocamenu.htm>.
- (60) Burow, K. R.; Shelton, J. S.; Dubrovsky, N. M. *Occurrence of nitrate and pesticides in ground water beneath three agricultural land-use settings in the eastern San Joaquin Valley, California, 1993–1995*; Water-Resources Investigations Report 97–4284; U.S. Geological Survey: Reston, VA, 1998; <http://pubs.usgs.gov/wri/1997/4284/report.pdf>.
- (61) Lockhart, K. M.; King, A. M.; Harter, T. Identifying sources of groundwater nitrate contamination in a large alluvial groundwater basin with highly diversified intensive agricultural production. *J. Contam. Hydrol.* **2013**, *151*, 140–154.
- (62) Burton, C. A.; Montrella, J.; Landon, M. K.; Belitz, K. *Status and understanding of groundwater quality in the Santa Clara River Valley, 2007: California GAMA Priority Basin Project*; Scientific Investigations Report 2011–5052; U.S. Geological Survey: Reston, VA, 2011; <http://pubs.usgs.gov/sir/2011/5052/>.
- (63) Land, M.; Kulongoski, J. T.; Belitz, K. *Status of groundwater quality in the San Fernando-San Gabriel study unit, 2005: California GAMA Priority Basin Project*; Scientific Investigations Report 2011–5206; U.S. Geological Survey: Reston, VA, 2012; <http://pubs.usgs.gov/sir/2011/5206/>.
- (64) Kulongoski, J. T.; Belitz, K. *Status and understanding of groundwater quality in the Monterey Bay and Salinas Valley Basins, 2005: California GAMA Priority Basin Project*; Scientific Investigations Report 2011–5058; U.S. Geological Survey: Reston, VA, 2011; <http://pubs.usgs.gov/sir/2011/5058/>.
- (65) Puckett, L. J.; Tesoriero, A. J.; Dubrovsky, N. M. Nitrogen contamination of surficial aquifers - A growing legacy. *Environ. Sci. Technol.* **2011**, *45* (3), 839–844.
- (66) Kent, R.; Landon, M. K. Trends in concentrations of nitrate and total dissolved solids in public supply wells of the Bunker Hill, Lytle, Rialto, and Colton groundwater subbasins, San Bernardino County, California: Influence of legacy land use. *Sci. Total Environ.* **2013**, *452–453*, 125–136.
- (67) California Department of Conservation, Farmland Mapping and Monitoring Program. *Data and maps summarizing change over time*; 2014, Website, accessed August 29, 2014 at: <http://www.conservation.ca.gov/dlrp/fmmp/trends/Pages/index.aspx>.
- (68) Goldrath, D.; Fram, M. S.; Land, M.; Belitz, K. *Status of groundwater quality in the Coastal Los Angeles Basins, 2006 - California GAMA Priority Basin Project*; Scientific Investigations Report 2012–5048; U.S. Geological Survey: Reston, VA, 2012; <http://pubs.usgs.gov/sir/2012/5048/>.
- (69) Milby Dawson, B. M.; Belitz, K.; Land, M.; Danskin, W. R. *Stable isotopes and volatile organic compounds along seven ground-water flow paths in divergent and convergent flow systems, Southern California, 2000*; Water Resources Investigations Report 03–4059; U.S. Geological Survey: Reston, VA, 2003; <http://pubs.usgs.gov/wri/wri034059/>.
- (70) Shelton, J. L.; Burow, K. R.; Belitz, K.; Dubrovsky, N. M.; Land, M.; Gronberg, J. *Low-level volatile organic compounds in active public supply wells as ground-water tracers in the Los Angeles physiographic basin, California, 2000*; Water Resources Investigations Report 01–4188; U.S. Geological Survey: Reston, VA, 2001; <http://pubs.usgs.gov/wri/2001/wri014188/>.
- (71) U.S. Environmental Protection Agency. Dibromochloropropane (DBCP), suspension order and notice of intent to cancel. *Federal Register* **1979**, *44*, 65135–65176.