Salinity of deep groundwater in California: Water quantity, quality, and protection

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Deep groundwater aquifers are poorly characterized but could yield important sources of water in California and elsewhere. Deep aquifers have been developed for oil and gas extraction, and this activity has created both valuable data and risks to groundwater quality. Assessing groundwater quantity and quality requires baseline data and a monitoring framework for evaluating impacts. We analyze 938 chemical, geological, and depth data points from 360 oil/gas fields across eight counties in California and depth data from 34,392 oil and gas wells. By expanding previous groundwater volume estimates from depths of 305 m to 3,000 m in California's Central Valley, an important agricultural region with growing groundwater demands, fresh [<3,000 ppm total dissolved solids (TDS)] groundwater volume is almost tripled to 2,700 km^3, most of it found shallower than 1,000 m. The 3,000-m depth zone also provides 3,900 km^3 of fresh and saline water, not previously estimated, that can be categorized as underground sources of drinking water (USDWs; <10,000 ppm TDS). Up to 19% and 35% of oil/gas activities have occurred directly in freshwater zones and USDWs, respectively, in the eight counties. Deeper activities, such as wastewater injection, may also pose a potential threat to groundwater, especially USDWs. Our findings indicate that California's Central Valley alone has close to three times the volume of fresh groundwater and four times the volume of USDWs than previous estimates suggest. Therefore, efforts to monitor and protect deeper, saline groundwater resources are needed in California and beyond.

groundwater quantity | salinity | contamination | California | oil and gas development

Deep groundwater aquifers are rarely studied compared with freshwater zones (1) but can be important groundwater resources. Estimating the quantity of useable groundwater and assessing the risk of groundwater contamination by human activities, such as oil and gas development, require baseline data and an appropriate monitoring framework (2–7). In this paper, we (*i*) characterize salinity of deep groundwater aquifers in eight counties across California, (*ii*) estimate useable groundwater volumes in California's Central Valley, and (*iii*) evaluate potential saline water migration into freshwater zones and underground sources of drinking water (USDWs) in eight counties in California.

USDWs as defined by the US Environmental Protection Agency include groundwater aquifers with concentrations of total dissolved solids (TDS) $\leq$10,000 mg/L, consistent with US Bureau of Land Management's definition for "usable" water (43 Code of Federal Regulation 3160), that have not been exempted and allow other subsurface activities, such as mineral, oil, and geothermal energy production. Depending on the state or federal agency, freshwater is defined as having <1,000 (8, 9), $\sim<$2,000 (10, 11), and <3,000 mg/L TDS (7, 12), including in California (7). The National Ground Water Association defines slightly saline water as having TDS concentrations of 1,000–3,000 ppm and moderately saline water as having TDS concentrations between 3,000 and 10,000 ppm (9). Water with TDS concentrations >10,000 ppm (upper limit for USDWs) and up to 35,000 ppm (seawater) is considered highly saline (9). Seawater is currently being desalinated to provide drinking water in California (7) as well as other parts of the United States and internationally (13). The billion dollar Carlsbad desalination plant in San Diego County, CA opened in December of 2015 and is desalinating $\sim$0.14 km^3 (37 billion gallons) of seawater annually (14) at a cost of $>\$1.70/\mathrm{m}^3$ ($>\$2,100$/acre ft) (15), far above the cost of most other freshwater sources in the state. Moderately saline groundwater aquifers, containing lower TDS concentrations than seawater, require less desalination and are useable for drinking water.

Under what circumstances could deep, useable groundwater serve as a feasible alternative resource for drinking water or agriculture? To answer this question about groundwater quantity and quality, we first need to understand the depths and locations of useable drinking water and characterize the resource. Typically, groundwater salinity increases with depth (16). Fresh groundwater resources occurring at relatively shallow depths ($\ll$ 1,000 m) have been studied extensively in terms of groundwater availability (17–22) and quality (23–26). In California, water quality data from over 200,000 groundwater wells are available from the State Water Resources Control Board Groundwater Ambient Monitoring and Assessment Program (27). Depth information for these samples is not publicly available, but depths are unlikely to be deeper than a few hundred meters in most cases. Information on deeper, more saline aquifers are limited, and most of the available information comes from oil and gas production. The California Department of Conservation, Division of Oil, Gas, and Geothermal Resources (DOGGR) provides data on formation water salinity and TDS from oil and gas pools (28–30) and records of wells (31) drilled to depths of a several thousand meters (*SI Appendix* and Dataset S1).

Groundwater volume estimates in California are uncertain and require additional studies. As an example, the groundwater estimate for the well-studied Central Valley Aquifer of 1,000 km^3 (830 million acre-ft) is more than 20 y old (32) and still widely

Significance

Groundwater withdrawals are increasing across the United States, particularly in California, which faces a growing population and prolonged drought. Deep groundwater aquifers provide an alternative source of fresh and saline water that can be useable with desalination and/or treatment. In the Central Valley alone, fresh groundwater volumes can be increased almost threefold, and useable groundwater volumes can be increased fourfold if we extend depths to 3,000 m. However, some of these deep groundwater resources are vulnerable to contamination from oil/gas and other human activities. Our findings provide the first estimates, to our knowledge, of underground sources of drinking water depths and volumes in California and show the need to better characterize and protect deep groundwater aquifers.

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used as a reference (18). The volume estimate is based on the shallower of either the base of freshwater (BFW) or 1,000 ft (305 m) (32). Current technologies and growing water demands have made water wells deeper than 1,000 ft more common. Thus, groundwater volumes reflecting this change and including deeper and saline groundwater resources are needed.

As deeper groundwater resources become increasingly important, additional studies are needed for evaluating subsurface activities that could contaminate these resources. Fluid injections, an integral part of a wide range of applications, including wastewater disposal, CO_2 storage, and enhanced oil/gas recovery, will cause formation pressures to increase, and this increase will propagate horizontally. If the horizontally propagated pressure increase is sufficiently large, upward water migration and groundwater contamination can occur through permeable vertical pathways, such as abandoned wells (33) or geologic faults (34). Upward migration of resident brine or fracturing fluids requires pressure gradients that can overcome gravity forces and is controlled by subsurface conditions and various fluid and porous media properties (34–37). Salinity has been identified as a key variable controlling brine/saline water densities (38). Threshold critical pressure increases based on salinities and migration depths coupled with semianalytic solutions provide a useful framework for evaluating upward water migration as applied previously to the case of geologic storage of CO_2 (38).

Here, we characterize deep groundwater salinities, expand groundwater volume estimates to include deeper and more saline waters, and estimate the potential for groundwater contamination for water-stressed California. We focus on eight counties across California: Los Angeles, Ventura, Santa Barbara, Kern, Fresno, Solano, Yolo, and Colusa (Fig. 1). For each county, we compile and analyze trends in available salinity, TDS, BFW, and depth data and estimate the previously unavailable base of USDWs. We use the depth-based salinity and TDS information to revise fresh groundwater volume estimates and provide the first estimates, to our knowledge, of USDW volumes for California's Central Valley. To evaluate contamination potential, we estimate the threshold critical pressure increases for saline water to migrate upward into fresh groundwater zones and USDWs in eight counties. Finally, we discuss the implications of our findings for California's water resources and oil and gas development.

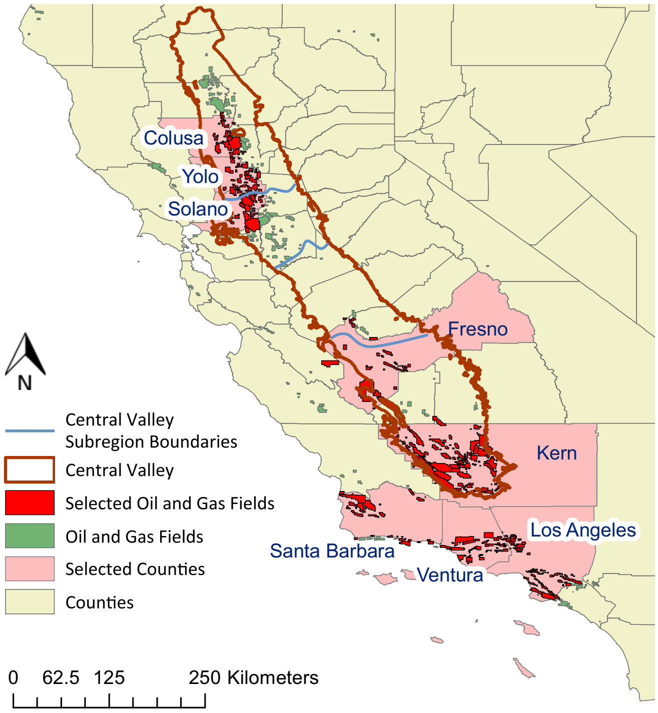

Fig. 1. Selected oil and gas fields and counties in California and the Central Valley shallow groundwater aquifer system extent (39). The Central Valley Subregions, as shown by the thicker boundary lines in blue, from north to south are Sacramento, Delta, San Joaquin, and Tulare (32).

Results

Salinity with Depth. Salinities and TDS concentrations range from 5 (Kern County) to 52,000 ppm (Fresno County) for depths of 0 (Fresno County) to 5,368 m (Kern County) (Fig. 2). [We note that salinity here refers to sodium chloride only (*SI Appendix*).] Kern County has the largest proportion and number of pools with salinities and TDS concentrations <3,000 ppm (22% for salinities and 19% for TDS concentrations considering all depths). The next largest percentages of salinities and TDS concentrations <3,000 ppm are 21% of pools for salinities (Yolo) and 8.5% of pools for TDS concentrations (Fresno). Salinities and TDS concentrations >10,000 ppm make up the majority of the pools in all counties except Yolo County. Nonetheless, both the proportion and number of data points with salinities or TDS concentrations <10,000 ppm and even in or close to the freshwater range are substantial. Furthermore, the highest salinities are still an order of magnitude less than what would typically be found at similar depths in many other North American basins (16).

The distributions of salinity and TDS concentrations vary with depth (Fig. 3). The largest observed difference is between depths shallower and deeper than 1,000 m (*SI Appendix* and Dataset S2). At depths shallower than 1,000 m, concentrations <10,000 ppm are slightly more common than concentrations >10,000 ppm, whereas at deeper depths (>1,000 m), concentrations >10,000 ppm are more frequently found. Groundwater does not become more saline on average across the dataset after depths are below 1,000 m (*SI Appendix*, Fig. S3). Finer spatial-scale variations can exist within a county. For example, cross-sections showing horizontal and vertical variations in salinity across Kern County show the abundance of fresh groundwater in up to 1,500-m depths on the east side of the Central Valley and useable groundwater in up to 1,000-m depths on the west side of the valley (Fig. 4).

Regional differences are observed between the northern counties (Yolo, Solano, Colusa, and Fresno) and most of the southern counties (Kern, Ventura, and Santa Barbara) (Fig. 2 and *SI Appendix* and Dataset S2). The southern counties have a larger proportion of fresher water (0–3,000 ppm) at depths shallower than 1,000 m (11–18% for salinities) than the northern counties (2–7% for salinities). At deeper depths, a larger proportion of fresher water (0–3,000 ppm) is found in the northern counties (10–14% for salinities) compared with the southern counties (1–4% for salinities). Overall, the data show that relatively fresh water is surprisingly abundant at deeper depths.

Oil and Gas Activities in Freshwater Zones and USDWs. The depth of the BFW across the dataset is generally shallower than 1,000 m (Fig. 5), but the mean BFWs in five Central Valley counties (Kern, Fresno, Solano, Colusa, and Yolo) are all deeper than 305 m (1,000 ft), the maximum depth used previously in groundwater estimates for the region (32). The mean BFWs for the five Central Valley counties range from 410 (Colusa) to 672 m (Kern). The mean BFWs in the coastal counties (Los Angeles, Santa Barbara, and Ventura) are shallower at 292, 368, and 226 m, respectively. The base of USDWs, z_U (Eq. **1** in *Materials and Methods*) (previously unavailable), is considerably deeper than the BFW values. The largest z_U values, found in Kern and Los Angeles Counties, are deeper than 2,500 m. The oil and gas pool depths and well depths are generally deeper than BFWs and z_U values but also, overlap with freshwater zones and USDWs (Fig. 5).

Oil and gas activities occur in freshwater zones in seven of eight counties and USDWs in all eight counties (Table 1 and *SI Appendix*). We define the occurrence of oil and gas activity in freshwater or USDWs using salinities of oil/gas pools and well depths relative to BFWs or z_U (*SI Appendix* and *Materials and Methods*). The percentage of oil/gas activities in freshwater zones is generally small compared with the percentage of oil/gas

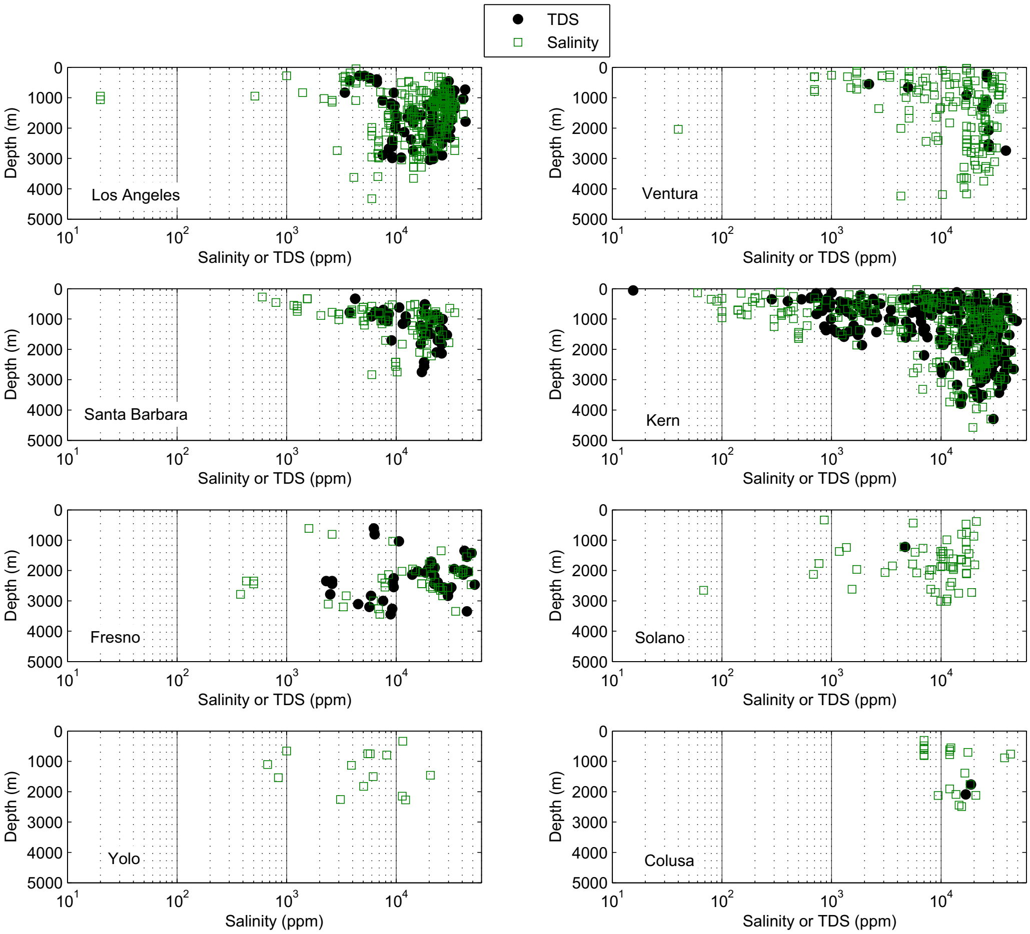

Fig. 2. Salinity and TDS data with respect to depth for each pool with data in eight counties across California. If minimum and maximum salinities or TDS concentrations are provided for a pool, we present the average of these two values.

activities in USDWs. One exception is in Kern County, where the largest percentage (15–19%) of oil/gas activities occur in freshwater zones. Kern County also has the largest number of wells at 138,958 (*SI Appendix* and Dataset S1), making the large proportion of oil/gas activity in freshwater zones substantial.

Groundwater Volumes in the Central Valley. Based on our analysis, the volume of fresh (defined in California as TDS < 3,000 ppm) groundwater in the Central Valley almost triples from 1,020 to 2,700 km^3 when we scale groundwater volumes to depths of up to 3,000 m, with 59% of the additional volume found between 305 and 1,000 m (Fig. 6). The volume of fresh and saline waters that can be classified as USDWs, for which no previous estimate, to our knowledge, exists, is 3,900 km^3, with 58% in the top 1,000 m (Fig. 6). Most of the additional potential groundwater volumes, both freshwater and USDWs, are found in the southern portion of the Central Valley (San Joaquin Valley and Tulare Basin). Overall, most of the groundwater volume originates from the more accessible layers above 1,000 m, but deeper formations (1,000–3,000 m) still represent 26% of freshwater and 42% of USDWs in the top 3,000 m.

Pressure Increases. Upward saline water migration, driven by pressure increases caused by water and/or other fluid injections, can occur in extreme scenarios and is more likely to cause contamination of USDWs than shallower freshwater zones (*SI Appendix*). Threshold critical pressure increases (ΔP_{crit}), for which higher ΔP_{crit} values indicate lower groundwater contamination risk, are highly variable and range from zero to several bars (1 bar = 10^5 Pa). The highest ΔP_{crit} values are observed in Fresno County followed by Kern County. Negative ΔP_{crit} values, indicating greater potential for downward water migration, are found more frequently in southern counties, especially Los Angeles and Kern.

Discussion

Expanding California's Water Resources with Deep Groundwater. Large fresh and saline groundwater volumes of 2,200 km^3 are found in the most physically and economically accessible top 1,000 m in the Central Valley. Accounting for deep (but relatively fresh) groundwater can substantially expand California's groundwater resources, which is critical given the state's current water

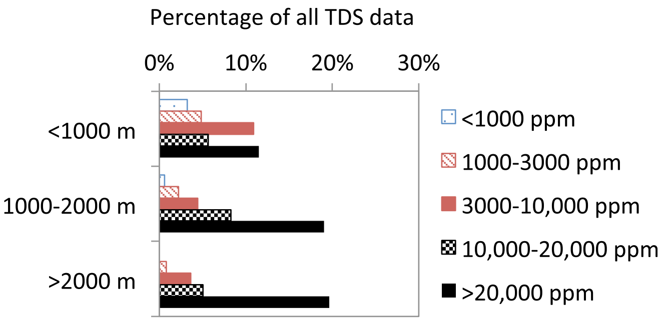

Fig. 3. Percentage of all TDS data categorized into three depth ranges (<1,000, 1,000–2,000, and >2,000 m) and five concentration ranges (0–1,000, 1,000–3,000, 5,000–10,000, 10,000–20,000, and >20,000 ppm). Note that the sum of all of the percentages is 100%.

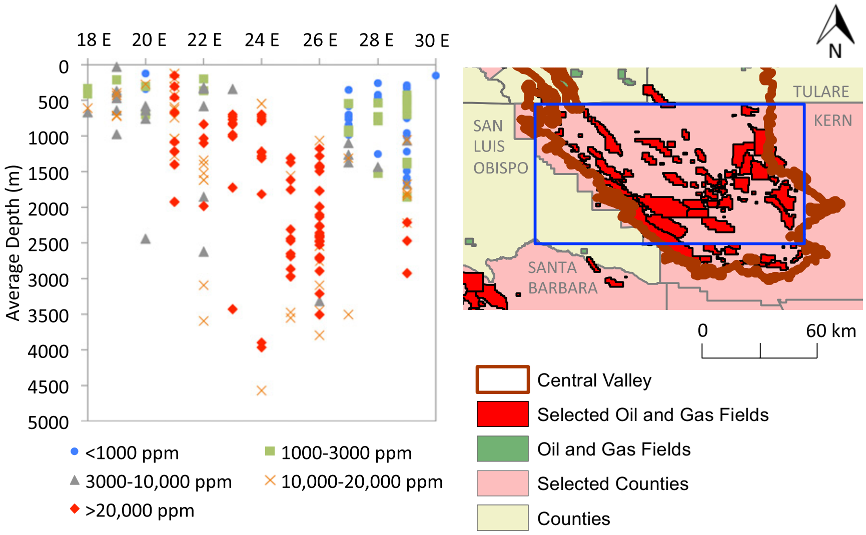

Fig. 4. Salinity data with depth categorized into ranges 18E to 30E for townships 25S to 32S following the Public Land Survey System for California. The data correspond to fields in the blue box in the map, with the western edge representing range 18E and the eastern edge representing range 30E. Cross-sections of salinity data with depth for each of these townships are shown in *SI Appendix*, Fig. S1.

shortages. Additional data collection and access to the State Water Resources Control Board's groundwater well depth data are needed to refine the first-order groundwater estimates provided in this paper. Data from oil and gas development provide a potentially large data repository on which we can analyze deep groundwater resources. Improving data collection and synthesis efforts for oil and gas development can have the cobenefit of improved characterization of deep groundwater aquifers.

In addition to more data, more studies are needed to explore potential "undesirable" results caused or exacerbated by the use of deeper groundwater, such as those outlined in California's Sustainable Groundwater Management Act (39). For example, groundwater flow modeling studies can be used to explore the likelihood of "significant and unreasonable reduction of groundwater storage" (39). "Significant and unreasonable land subsidence" (39) caused by deeper groundwater extraction can be evaluated using geomechanical and fluid flow modeling and through review of related processes, including land subsidence caused by shallow groundwater withdrawals (39) and oil production (40, 41).

Moderately saline water ($\sim$7,000 ppm) desalination requires $\sim$1.3 kWh/m^3 energy, whereas seawater desalination requires 2.6–3.7 kWh/m^3 energy (13, 42). Desalination of saline groundwater from shallow aquifers ($\sim$100 ft) in coastal areas is already economically feasible as evidenced by the Richard Reynolds Groundwater Desalination Facility in Chula Vista, CA, which is expanding to double its production (43). For deeper aquifers, there may be additional costs associated with the treatment of anthropogenic or naturally occurring contaminants, such as radium (44). Nonetheless, in inland regions, such as the Central Valley, groundwater at intermediate depths, <1,000 m for instance, may be a cost-effective alternative water source for desalination or other treatment.

Oil and Gas Development. The DOGGR data that we analyzed show that oil and gas activity has occurred in USDWs in all counties and in freshwater zones in most of the southern counties (Ventura, Santa Barbara, Kern, and Fresno). The analyzed counties contain 192,925 wells out of a total 222,637 wells in California (87%) and 360 of 509 oil and gas fields (71%). The 34,392 available depths of these 192,925 wells range from 0 to 8,696 m, with many wells penetrating through different formations. Wellbore integrity issues occur in a wide variety of wells and conditions and have been linked to fluid leakage (45–50). Some of the existing wells can potentially act as leakage pathways and connect deeper, more saline formations to shallower, fresher groundwater (51, 52). Furthermore, in extreme cases, small pressure increases can drive saline water migration to useable groundwater zones. Therefore, USDWs and freshwater zones in some locations may be vulnerable to contamination caused by oil and gas development.

In contrast to concepts of vulnerability, showing direct impact to groundwater resources deeper than $\sim$100 m is rarely possible in California or elsewhere, because little or no monitoring is done below the depth of typical domestic water wells. California recently closed 56 oil/gas water disposal injection wells, because the waste water was being pumped into potentially drinkable aquifers (53). Because testing and monitoring of groundwater, especially deeper resources, are rarely undertaken, very little is known about the potential impact of such activities. The recent passage of California's well stimulation bill (State Bill 4) should provide some data from groundwater monitoring associated with hydraulic fracturing in the state. However, the requirement for monitoring only began in July of 2015.

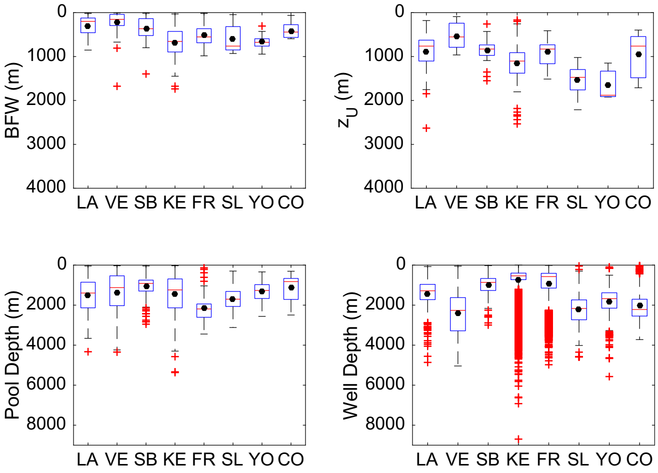

Fig. 5. Boxplots of BFW (base of fresh water) data, previously unavailable estimates of the base of USDWs (z_U) per pool, depth of oil/gas pools, and oil/gas well depths for eight counties across California: Los Angeles (LA), Ventura (VE), Santa Barbara (SB), Kern (KE), Fresno (FR), Solano (SL), Yolo (YO), and Colusa (CO) Counties. The red lines in the boxes represent the medians, and the box edges represent the 25th and 75th percentiles. The whiskers of the boxplots represent 99.3% of the data assuming a normal distribution, and the red plus signs represent data outside this range. The mean values are shown as black dots.

Table 1. Oil and gas activities in freshwater zones and USDWs

County	Freshwater, %	USDWs, %
Los Angeles	0–0.4	1.3–22
Ventura	0.8–9	0.8–18
Santa Barbara	0–2	10–31
Kern	15–19	19–35
Fresno	3–9	4–32
Solano	0	15
Yolo	0.3	13
Colusa	0.2	4

Fluid injections into deeper formations, such as water disposal and waterflooding for enhanced oil/gas recovery, are ongoing and will continue to occur in California (54, 55). In addition, geologic storage of CO_2 (56, 57) and hydraulic fracturing of shale formations involving higher pressure and volume injections (54) may be introduced in the coming decades. To detect potential contamination events, two questions arise from our analysis. To what depths should groundwater be monitored in California and elsewhere? To what extent should this monitoring include not just deeper freshwater but USDWs as well? A monitoring program that is mindful of the extents of freshwater zones and USDWs, both horizontally and vertically, is needed to protect California's abundant deeper, useable groundwater resources.

Conclusions

In conclusion, we find:

i) Estimated fresh groundwater volumes in the Central Valley are almost tripled to 2,700 km^3 with the inclusion of fresh groundwater from depths of up to 3,000 m. USDWs, for which volumes are previously unquantified, also provide additional groundwater volumes, bringing the total volume in the top 3,000 m to 3,900 km^3 in the Central Valley.

ii) In eight counties across California, up to 35% of historical oil and gas activity occurred directly in USDWs, whereas up to 19% of activity occurred within freshwater zones.

iii) Vertical saline water migration to freshwater zones and USDWs can occur in extreme scenarios but is more likely to cause contamination of deeper USDWs than shallower freshwater zones.

States, such as Texas and Florida, and countries, including China and Australia, are already desalinating brackish water to meet their growing water demands (13). Although we emphasize the importance of deep groundwater data in California, other regions and countries may also have additional useable groundwater resources that need to be characterized, monitored, and protected (58).

Materials and Methods

Data Availability. We compile and analyze available data from the DOGGR wells database (31) and the DOGGR data sheets (28–30) for eight counties in California (Fig. 1). The eight selected counties cover all six of the DOGGR districts and contain 89% of the wells in the DOGGR wells database (31) (*SI Appendix* and Dataset S1). We consider a total of 360 oil/gas fields (of 509), for which we have 938 salinity and 495 TDS data points from the DOGGR data sheets (28–30). The BFW data are available for 316 fields. For a given oil/gas field, formation water salinity, TDS, pressure, and temperature data are available for up to 22 pools, representing formations at different depths. We also use 34,392 available well depths in the DOGGR wells database (31).

Base of USDWs. We estimate the base of USDWs, z_U (length), per pool assuming a first-order approximation of increasing salinity or TDS with depth at a given location:

$$z_U = z_{\mathrm{BFW}} + \frac{z_F - z_{\mathrm{BFW}}}{s_F - s_{\mathrm{BFW}}}\left(s_U - s_{\mathrm{BFW}}\right), \tag{1}$$

where z_{BFW} is the depth of the BFW of the oil and/or gas field (length; also referred to as simply BFW), z_F is the average depth of the salinity or TDS data point and corresponds to an oil/gas pool (length), s_F is the average salinity or TDS concentration in the oil or gas formation containing saline water (ppm), s_U is the salinity or TDS concentration at the base of the USDW (ppm), and s_{BFW} is the salinity or TDS concentration at the BFW (ppm). Details on the data sources for each variable are provided in *SI Appendix*.

Oil and Gas Activities in Freshwater Zones and USDWs. To quantify the occurrence of oil or gas activity within freshwater zones or USDWs, we use two approaches: (*i*) TDS data of oil/gas pools in the DOGGR data sheets (28–30) and (*ii*) a comparison of oil/gas well depths in the DOGGR wells database (31) with the corresponding BFW or z_U values at the field area and pool level, respectively. Details on the two approaches are given in *SI Appendix*.

Groundwater Volumes. Previous groundwater volumes for four Central Valley shallow groundwater system subregions (Fig. 1) are estimated to be 210 km^3 for Sacramento Valley, 197 km^3 for San Joaquin Valley, 456 km^3 for Tulare Basin, and 160 km^3 for the Delta (32). These estimates are based on depths taken to be the shallower of the BFW and 1,000 ft (305 m) (32). We scale these groundwater volume estimates for the Central Valley based on depth, salinity, or TDS concentrations and the relative decrease in porosity with depth available in the DOGGR data sheets (28–30). We estimate the groundwater resource estimate, $W_{i,j,k}$ (length^3), for depth zone i, Central Valley region j, and water quality k as

$$W_{i,j,k} = W_{0,j}\frac{d_i}{d_0}\frac{\theta_{i,j}}{\theta_{0,j}}r_{i,j,k}, \tag{2}$$

where $W_{0,j}$ is the groundwater volume estimated for Central Valley region j in ref. 32 (length^3), d_i is the vertical depth range of zone i (length), d_0 is the vertical depth range in the volume estimates in ref. 32 (length), $\theta_{i,j}$ is the porosity in depth zone i in Central Valley region j, $\theta_{0,j}$ is the porosity in the original depth zone in Central Valley region j, and $r_{i,j,k}$ is the proportion of data with salinity or TDS concentrations that are <3,000 ppm (k = freshwater) or 3,000–10,000 ppm (k = USDW). We assume that the average of Yolo and Colusa Counties is representative of the Sacramento Valley, that Fresno County is representative of the San Joaquin Valley, that Kern County is representative of the Tulare Basin, and that Solano County is representative of the Delta. We consider three depth zones, 0–1,000, 1,000–2,000, and 2,000–3,000 km, and estimate volumes of fresh groundwater (<3,000 ppm) and USDWs (<10,000 ppm) (Dataset S3).

Pressure Increases. Pressure increases, ΔP (mass length^{-1} time^{-2}), in a geologic formation storing water, oil, and/or gas can be attributable to anthropogenic activities, such as wastewater and other fluid injections. We focus on horizontal propagations of this pressure increase within the injection formation rather than actual horizontal fluid migration. Upward water migration requires a minimum ΔP for a given vertical migration distance. This minimum ΔP is referred to here as the threshold critical pressures increase, ΔP_{crit} (mass length^{-1} time^{-2}) (38, 59). We estimate ΔP_{crit} needed for deeper saline water to reach the BFW ($\Delta P_{\mathrm{crit,BFW}}$) and the base of USDWs ($\Delta P_{\mathrm{crit,USDW}}$). Additional details are provided in *SI Appendix*.

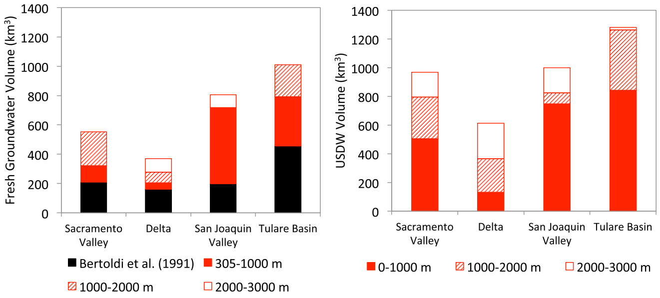

Fig. 6. Potential additional volumes of fresh groundwater (TDS < 3,000 ppm) and potential volumes of USDWs (TDS < 10,000 ppm) by depth intervals in the Central Valley of California. The mean BFWs per county are all deeper than 305 m (1,000 ft) in the Central Valley counties considered (Kern, Fresno, Yolo, Colusa, and Solano). Therefore, we assume that the depth used for the groundwater volumes estimates in ref. 32 is 305 m (1,000 ft).

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