Geostatistical analysis of tritium, groundwater age and other noble gas derived parameters in California

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Abstract

Key characteristics of California groundwater systems related to aquifer vulnerability, sustainability, recharge locations and mechanisms, and anthropogenic impact on recharge are revealed in a spatial geostatistical analysis of a unique data set of tritium, noble gases and other isotopic analyses unprecedented in size at nearly 4000 samples.

The correlation length of key groundwater residence time parameters varies between tens of kilometers (³H; age) to the order of a hundred kilometers (⁴He_{ter}; ¹⁴C; ³He_{trit}). The correlation length of parameters related to climate, topography and atmospheric processes is on the order of several hundred kilometers (recharge temperature; δ¹⁸O). Young groundwater ages that highlight regional recharge areas are located in the eastern San Joaquin Valley, in the southern Santa Clara Valley Basin, in the upper LA basin and along unlined canals carrying Colorado River water, showing that much of the recent recharge in central and southern California is dominated by river recharge and managed aquifer recharge. Modern groundwater is found in wells with the top open intervals below 60 m depth in the southeastern San Joaquin Valley, Santa Clara Valley and Los Angeles basin, as the result of intensive pumping and/or managed aquifer recharge operations.

1 INTRODUCTION

Water is a limited resource in California. While some areas receive over 3000 mm of precipitation per year, a large proportion of the population is located in areas receiving less than 500 mm per year (Figure 1b). Most precipitation falls in winter and a large proportion of precipitation falls as snow in the Sierra Nevada mountain range. Snowmelt contribution to rivers draining the Sierra Nevada causes peak discharge to occur in late spring. Reservoirs mitigate flood risk and store snowmelt, to be released gradually in summer. The groundwater system acts as a natural buffer for seasonal and inter-annual precipitation variability. Historically, groundwater has been exploited at a rate higher than the natural recharge rate, leading to depletion of fresh groundwater resources (Famiglietti et al. 2011). At present, groundwater recharge is enhanced by managed aquifer recharge (MAR), mainly in urban areas, to replenish overdrafted aquifers and utilize the storage capacity (Bouwer 2002, Massmann and Sültenfuß 2008). For optimal use and protection of groundwater, knowledge of the key characteristics of the groundwater system, such as recharge locations and mechanisms, groundwater flow patterns and subsurface residence times, are essential.

The Groundwater Ambient Monitoring and Assessment (GAMA) program (Belitz et al. 2010, Belitz et al. 2003) aims to assess the quality and vulnerability of groundwater resources in California. A large proportion of the monitoring effort is dedicated to the collection and analysis of water quality samples (Deeds et al. 2012, Fram and Belitz 2011a, Jurgens et al. 2009, Fram and Belitz 2011b, Landon et al. 2011). Simultaneous collection and analysis of environmental tracers, including tritium, stable isotopes of the water molecule and dissolved noble gases and the helium isotope ratio, has allowed assemblage of an unprecedented database containing valuable information regarding key

groundwater characteristics, allowing assessment of contamination vulnerability and sustainability of groundwater abstraction.

Tritium is a tracer for modern groundwater that has recharged since the start of the nuclear era in 1945 (Nir 1964, Vogel et al. 1974). Residence time distributions of groundwater and surface water have been derived by matching observed concentration time series to outflow concentrations of a mixing model, with the historical concentrations of tritium in precipitation as input (Stewart et al. 2010, Robert 2004, Plummer et al. 2001, Izbicki et al. 2000, Michel 1992, Rose 2007, Kluge et al. 2010, Eastoe et al. 2011, Blavoux et al. 2013). When combined with the analysis of helium-3, the “ $^3\text{H}/^3\text{He}$ age” of groundwater recharged after about 1950 can be calculated from the ratio of tritium and its decay product (Takaoka and Mizutani 1987, Poreda et al. 1988, Schlosser et al. 1988). Accumulation of helium-4 in groundwater, from the decay of naturally occurring uranium and thorium, provides a qualitative age tracer over the 500 year to million year time scale (Solomon et al. 1996, Schlosser et al. 1989). Well water samples almost invariably comprise a mixture of different ages, which should be characterized by an age distribution, ideally derived from a number of different age tracers. References to “groundwater age” in this paper are limited to the (apparent) $^3\text{H}/^3\text{He}$ age, which represents the initial-tritium weighted mean age of the modern groundwater component. This is a useful metric of groundwater age for studying the vulnerability of groundwater and identifying areas of active recharge, despite the bias towards time periods of higher concentrations of tritium in recharging groundwater.

Dissolved noble gas concentrations in groundwater reflect the climatic and hydrological conditions at the time of recharge, such as temperature and water table fluctuations (Stute et al. 1992, Stute et al. 1995a, Aeschbach-Hertig et al. 2000a, Wilson and McNeill 1997). Stable isotopes of the water molecule (represented by $\delta^2\text{H}$ and $\delta^{18}\text{O}$), vary spatially in precipitation in California due to

continental and orographic effects, as illustrated by the variation in river water (serving as a proxy for precipitation) (Kendall and Coplen 2001). Rivers generally maintain the signal of their source region (Dutton et al. 2005) and the stable isotope signature in groundwater acts as a fingerprint of the origin of precipitation if recharge occurs aerially or by river bank infiltration downstream of the source area. These analyses, taken together and interpreted in a physiographic context, allow us to address the following questions:

- Which aquifers contain modern groundwater, indicating areas of active recharge that are vulnerable to surface contamination?
- Where is pre-modern or fossil groundwater abstracted and over what time scale is the abstraction sustainable considering the reservoir volume and the rates of recharge and abstraction?

To answer these questions, a unique data set of nearly four thousand tritium and noble gas and isotopic analyses was subjected to geostatistical analysis. The size ($n=3895$), spatial extent (spanning over 1300 km) and density (2.3 analyses in every 10×10 km area on average) present an unprecedented opportunity for a spatial analysis of groundwater age and recharge characteristics. The spatial correlation structure of the data was analyzed by means of variogram analyses and the variables of interest were mapped by kriging prediction. To our knowledge, these techniques have never before been applied to groundwater age tracer data. Previous studies have focused on many other features such as contaminants and the risk to human health, rather than gathering information about the hydrological functioning of the groundwater system using travel time tracers. Geochemical and isotopic data and signatures have been the subject of variogram analysis and kriging in the past (Samper and Neuman 1989, Myers et al. 1982, Subyani and Şen 1989). More

recent work focused on soil water content (Snepvangers et al. 2003) and contaminants such as nitrate (Mendes and Ribeiro 2010, Chica-Olmo et al. 2014) and arsenic (Gong et al. 2014, Antunes and Albuquerque 2013, Goovaerts et al. 2005, Lee et al. 2007, James et al. 2014) The geostatistical analyses in this study were performed on the state-wide data set, which was divided into subsets according to depth in order to address the vertical structure of the data. Besides addressing the research questions presented above, the purpose of this paper is to present the data set to the scientific community to solicit further research. Future research opportunities include calibration of numerical groundwater models (Castro et al. 1998, Ivey et al. 2008, Murphy et al. 2010, Sanford 2010, Sheets et al. 1998), paleoclimate reconstruction (Stute et al. 1992, Aeschbach-Hertig et al. 2000b, Hall et al. 2005, Castro et al. 2007, Klump et al. 2008, Stute et al. 1995b, Corcho Alvarado et al. 2009), water quality vulnerability in relation to groundwater age (Wright et al. 2004, Johnston et al. 1998, Tesoriero et al. 2007, Visser et al. 2007), and identification of regions where mantle fluids are transported into shallow aquifers (Boles et al. 2015, Kulongoski et al. 2013, Castro 2004, Kulongoski et al. 2003, Jenden et al. 1988, Poreda et al. 1986). The geostatistical analysis presented here is a first step in disseminating and visualizing the data set.

2 METHODS

2.1 Study Area

The state of California covers 424 thousand square kilometers between 33 and 42 degrees North on the west coast of the United States (Figure 1b inset). Physiographic features include the Coastal

Range, the Central Valley, the Sierra Nevada and Cascade mountain ranges and the Mojave Desert. Elevation and 30-year normal temperature and precipitation data were retrieved at 800 meter resolution from the PRISM Climate Group at Oregon State University (<http://prism.oregonstate.edu>, maps created July 2012). Elevation (Figure 1a) varies from below sea level in Death Valley and the San Joaquin-Sacramento Delta to 4421 m above sea level on top of Mt Whitney. The large latitudinal and elevational span leads to a wide range in mean annual air temperatures, from 2°C in the Sierra Nevada to 24°C in the Mojave Desert (Figure 1d). Central California has a Mediterranean climate and, as a consequence, nearly all of the annual precipitation occurs during winter and early spring (Lundquist et al. 2005). The spatial distribution of precipitation (Figure 1b) ranges from less than 100 mm in the southeast to over 3000 mm in the northwest. Nearly 80% of precipitation in the Sierra Nevada is deposited as snow (Natural Resources Conservation Service 2013). Snowmelt is drained from the Cascade Range and Sierra Nevada by large, perennial rivers like the Sacramento, Tuolumne, Kings and Kern, which experience peak flow in late spring (Lundquist et al. 2005). While nearly all rivers are dammed, reservoir capacity is insufficient to capture peak flow entirely. Groundwater basins (Department of Water Resources 2003) cover about 170 thousand square kilometers of land surface, mostly in the Central Valley (Figure 1c). A groundwater basin is defined in DWR Bulletin 118 as an alluvial aquifer or a stacked series of alluvial aquifers with reasonably well-defined boundaries in a lateral direction and a definable bottom (Department of Water Resources 2003). The Mediterranean climate and snowmelt discharge cause natural recharge of groundwater to occur seasonally. Additional recharge comes from irrigation return flow, making up the majority of recharge in intensively farmed regions such as the southern Central Valley and the Salinas Valley. Water districts in highly populated areas with little precipitation employ managed aquifer recharge operations to replenish aquifer reserves, using storm water runoff, imported water or treated wastewater. While dams, reservoirs and canals control most surface water flows, abstraction,

irrigation and artificial recharge dictate groundwater flow patterns over much of the state. As such, some California groundwater systems are part of an engineered hydrologic cycle.

2.2 Data Collection

The data analyzed here were collected as part of a number of large and small research projects. The majority of the samples was collected by United States Geological Survey (USGS) staff as part of the GAMA Priority Basin monitoring program (Belitz et al. 2003). Tritium and noble gas data for selected study units are published in USGS Data Series Reports (<http://ca.water.usgs.gov/gama/>) and available on GeoTracker GAMA (http://geotracker.waterboards.ca.gov/gama/data_download.asp). The Priority Basin program applied well selection on an irregular grid, to provide a spatially unbiased data set. The Priority Basin data set was supplemented with localized studies of groundwater systems, collected by Lawrence Livermore National Laboratory (LLNL) and local water district staff, as part of the California Aquifer Susceptibility (CAS) program (Moran and Halliwell 2002, Moran et al. 2002a, Eaton et al. 2003, Moran and Halliwell 2003, Moran et al. 2004, Moran et al. 2002b, Moran et al. 2005a, Moran et al. 2005b, Moran et al. 2005c, Carle et al. 2006) and GAMA Special Studies (McNab et al. 2007, Singleton et al. 2007, Moran et al. 2009, McNab Jr et al. 2010, Singleton and Moran 2010, Singleton et al. 2010, Moran et al. 2011, Visser et al. 2012).

Samples were collected for tritium in 1 L glass bottles. Tritium analyses were performed at LLNL by helium-3 accumulation (Surano et al. 1992, Clarke et al. 1976) and at the USGS in Menlo Park by enriched liquid scintillation counting (Thatcher et al. 1977). Both techniques are capable of achieving a detection limit of 1 pCi/L (0.3 TU) and have a typical accuracy of 5%.

Noble gas and helium isotope samples were collected in 10 mL copper tubes and were analyzed at the LLNL noble gas mass spectrometry facility (Rademacher et al. 2001, Cey et al. 2008, Visser et al. 2013a). Measurement uncertainty of the helium isotope ratio and dissolved concentrations of helium, neon, and argon is 2% and is 3% for krypton and xenon concentrations. The total number of analyses is presented in Table 1.

Besides tritium and noble gas concentrations and derived parameters, a spatial analysis of nitrate concentrations and stable isotopes of water is included for comparison. Data were obtained from the GAMA Priority Basin GeoTracker data base. Results are presented for $\delta^{18}\text{O}$ and deuterium excess, defined as $D_{\text{exc}} = \delta^2\text{H} - 8 \cdot \delta^{18}\text{O}$, which represents the deviation of stable isotope pairs from the global meteoric water line.

2.3 Data Reduction

Noble gas derived parameters (recharge temperature, excess air, terrigenic helium-4, terrigenic helium isotope ratio and tritiogenic helium-3) were calculated using the unfractionated excess air (UA) model (Heaton and Vogel 1981). This single, simplest excess air model was used in order to avoid bias in derived parameters resulting from the choice of the excess air model (Cey et al. 2008, Visser et al. 2014). The recharge elevation was assumed to be the well head elevation, extracted from the digital elevation model. The two free parameters of the UA model (noble gas recharge temperature (NGT) and excess air (EA, expressed as $\Delta\text{Ne} = (\text{Ne}_{\text{sample}}/\text{Ne}_{\text{equilibrium}} - 1) \times 100\%$) were estimated by minimizing the uncertainty-weighted squared differences between modeled and observed concentrations (Ballentine and Hall 1999), denoted by χ^2 (Eq. 1), using a bound

constrained quasi-Newton method (Byrd et al. 1995). $C_{i,m}$ are the modeled noble gas concentrations;
 $C_{i,o}$ and σ_i^2 are the observed noble gas concentrations and their uncertainties.

$$\chi^2 = \sum_i \frac{(C_{i,o} - C_{i,m})^2}{\sigma_i^2} \quad (i=\text{Ne, Ar, Kr, Xe}) \quad [\text{Eq. 1}]$$

The probability of the model parameters was obtained from the χ^2 distribution if the degrees of freedom were greater than zero (Johnson et al. 1995). The χ^2 distribution has an expected value equal to the number of degrees of freedom. Parameter sets with a χ^2 probability ($P\chi^2$) of less than 1% were rejected. The UA model was initially fitted to the dissolved concentrations of all five noble gases, including helium, leaving 3 degrees of freedom. Samples containing significant terrigenous helium yielded large χ^2 values resulting in low parameter probability. The UA model was then fitted to the dissolved concentrations of the four atmospheric noble gases (Ne, Ar, Kr, Xe), leaving 2 degrees of freedom. If no acceptable fit was obtained, the UA model was fitted to all 4 combinations of 3 atmospheric noble gases. The parameter set with the highest probability was selected, if it exceeded 1%. The UA model was fitted successfully to 3743 samples (>95% of samples, Table 1). The propagated uncertainty of the estimated parameters (NGT and EA) was calculated according to Ballentine and Hall (1999). For approximately 300 samples, no acceptable fit was obtained. For the calculation of terrigenous and tritogenic helium components in these samples, the recharge temperature was assumed to be equal to the mean annual air temperature at the well location. Excess air amount was derived from the measured neon concentration in these samples. The terrigenous helium concentration and isotopic ratio and tritogenic helium component were calculated after subtracting the atmospheric helium components derived from the neon excess air amount.

2.4 Groundwater Age Calculation

For samples without significant terrigenous helium-4 ($< 2 \times 10^{-9} \text{ cm}^3 \text{STP/g}$, $n=1947$), the tritiogenic helium concentration ($^3\text{He}_{\text{trit,He}}$) is calculated from the measured sample helium isotope ratio (R_s) and concentration (He_s), the atmospheric helium isotope ratio ($R_a = 1.384 \times 10^{-6}$), the equilibrium helium concentration ($^4\text{He}_{\text{eq}}$) and the helium isotope dissolution fractionation factor ($\alpha = 0.983$, Eq. 2).

$$^3\text{He}_{\text{trit}} = (R_s - R_a) \times ^4\text{He}_s + (1 - \alpha) \times R_a \times ^4\text{He}_{\text{eq}} \quad [\text{Eq. 2}]$$

The uncertainty associated with the tritiogenic helium is derived from the measurement uncertainties of the measured helium isotope ratio and helium concentration, assuming these are uncorrelated, and the uncertainty of the equilibrium helium concentration:

$$\sigma_{^3\text{He}_{\text{trit}}} = \left([(R_s - R_a) \times \sigma_{^4\text{He}_s}]^2 + [\sigma_{R_s} \times ^4\text{He}_s]^2 + [\sigma_{^4\text{He}_s} \times \sigma_{R_s}]^2 + [(1 - \alpha) \times R_a \times \sigma_{^4\text{He}_{\text{eq}}}]^2 \right)^{1/2} \quad [\text{Eq. 3}]$$

Terrigenous helium-4 ($^4\text{He}_{\text{ter}}$, Eq. 4) and non-atmospheric helium-3 ($^3\text{He}_{\text{na}}$, terrigenous + tritiogenic) (Eq. 5) were calculated from the measured helium isotope ratio, the measured helium concentration and the modeled atmospheric (equilibrium and excess air) helium components (He_a). Associated uncertainties with measured and modeled concentrations were propagated accordingly.

$$^4\text{He}_{\text{ter}} = ^4\text{He}_s - ^4\text{He}_a \quad [\text{Eq. 4}]$$

237

$$^{3}\text{He}_{\text{na}} = ^{3}\text{He}_{\text{ter}} + ^{3}\text{He}_{\text{trit}} = ^{3}\text{He}_s - ^{3}\text{He}_a \quad [\text{Eq. 5}]$$

239

240 For samples containing terrigenous helium, the tritiogenic and terrigenous helium-3 components need
241 to be separated. A critical variable is the local terrigenous helium isotope ratio (R_{ter}), which can vary
242 over three orders of magnitude, from radiogenic ($R_{\text{rad}} = 2 \times 10^{-8}$, (Torgersen 1980)) to mantle derived
243 ($R_{\text{man}} = 1 \times 10^{-5}$, (Craig et al. 1978)). Locations where mantle helium is found in groundwater often
244 coincide with locations where significant radiogenic helium has accumulated. The local terrigenous
245 helium isotope ratio was derived from a geostatistical analysis and interpolation. First, the maximum
246 tritiogenic helium-3 component was calculated (Eq. 6) under the assumption that all tritium
247 measured in the sample originated from the initial test period (1953). The maximum tritiogenic
248 helium-3 component was subtracted from the non-atmospheric helium-3 component to calculate
249 the non-atmospheric tritiogenic-corrected helium-3 component (Eq. 7), which was divided by the
250 terrigenous helium-4 concentration to derive a representative terrigenous helium isotope ratio (Eq. 8):

251

$$^{3}\text{He}_{\text{trit,max}} = ^{3}\text{H} \times (e^{[\lambda \times (ts - 1953)]} - 1) \quad [\text{Eq. 6}]$$

253

$$^{3}\text{He}_{\text{na,tc}} = ^{3}\text{He}_{\text{na}} - ^{3}\text{He}_{\text{trit,max}} \quad [\text{Eq. 7}]$$

255

$$R_{\text{ter}} = ^{3}\text{He}_{\text{na,tc}} / ^{4}\text{He}_{\text{ter}} \quad [\text{Eq. 8}]$$

257

258 To incorporate the uncertainty in the age of the tritium, the uncertainty of the maximum tritium
259 component was set equal to the tritiogenic-corrected ^{3}He value (Eq. 9), and integrated into the
260 uncertainty calculation of the terrigenous helium isotope ratio (Eq. 10 and 11).

261

$$\sigma_{3Hetc} = {}^3He_{tc} \quad [Eq. 9]$$

263

$$\sigma_{3Hena,tc} = (\sigma_{3Hena}^2 + \sigma_{3Hetc}^2)^{1/2} \quad [Eq. 10]$$

265

$$\sigma_{Rter} = R_{ter} \times [(\sigma_{3Hena,tc} / {}^3He_{na,tc})^2 + (\sigma_{4Heter} / {}^4He_{ter})^2]^{1/2} \quad [Eq. 11]$$

267

268 The impact of the tritiogenic correction on the uncertainty of the terrigenous helium isotope estimate
269 depends on the concentrations of tritium and terrigenous helium. For samples with a large terrigenous
270 helium component, the tritiogenic correction is negligible. For the geostatistical analysis, only
271 samples which contained a significant component of terrigenous helium (${}^4He_{ter} \geq 1.645 \times \sigma_{4Heter}$,
272 $n=1890$) and with a propagated uncertainty of the terrigenous helium isotope ratio of less than 10% of
273 the estimated value plus the atmospheric helium isotope ratio ($R_a = 1.384 \times 10^{-6}$) were included. Our
274 analysis thus includes a total of 897 samples. Because of the high variability between terrigenous
275 helium isotope ratios in regions impacted by mantle helium (e.g. northern volcanic provinces, areas
276 in proximity to major faults), the geostatistical analysis was performed for each groundwater
277 province separately on the base-10 logarithm of the terrigenous helium isotope ratio.

278

279 The local terrigenous helium isotope ratio ($R_{ter,loc}$) was predicted for each sample location using
280 kriging. To avoid circular logic (prediction based on previous assumptions), the sample location for
281 which the prediction was made was excluded from the data upon which the kriging prediction was
282 based, in a process known as cross-validation. The cross-validation process results in residuals
283 between the cross-validated kriging predictions and the calculated terrigenous helium isotope ratio.
284 The root mean square error of residuals was used as the uncertainty of the local terrigenous helium

isotope ratio for each of the groundwater provinces separately, for further propagation in the $^3\text{H}/^3\text{He}$ age uncertainty.

Tritogenic helium was then calculated by subtracting atmospheric and terrigenic components from the measured helium concentration (Eq. 12), and the uncertainty in the underlying estimates was propagated (Eq. 13).

$$^3\text{He}_{\text{trit}} = ^3\text{He}_s - ^3\text{He}_m - R_{\text{ter},\text{loc}} \times ^4\text{He}_{\text{ter}} \quad [\text{Eq. 12}]$$

$$\sigma_{^3\text{He}_{\text{trit}}} = (\sigma_{^3\text{He}_s}^2 + \sigma_{^3\text{He}_m}^2 + (\sigma_{R_{\text{ter},\text{loc}}} \times ^4\text{He}_{\text{ter}})^2 + (R_{\text{rad}} \times \sigma_{^4\text{He}_{\text{ter}}})^2)^{1/2} \quad [\text{Eq. 13}]$$

Negative estimates of terrigenic and tritogenic helium were set to zero. From the measured tritium concentration and estimated tritogenic helium-3 concentration, the tritium-helium age was calculated using the decay constant of ^3H ($\lambda = \ln(2)/\tau_{1/2} = 0.05626$) (Eq. 14):

$$\tau = \ln(1 + [^3\text{He}_{\text{trit}}] / [^3\text{H}]) \lambda^{-1} \quad [\text{Eq. 14}]$$

The uncertainty of the apparent $^3\text{H}/^3\text{He}$ age (σ_τ) depends on the analytical precision of the ^3H measurement ($\sigma_{^3\text{H}}$) and uncertainty in the tritogenic ^3He component ($\sigma_{^3\text{He}_{\text{trit}}}$) derived from the propagation of the noble gas measurement uncertainty (Solomon et al. 1993). A linear approximation of the age uncertainty is given by Eq. 15.

$$\sigma_\tau = \lambda^{-1} ([^3\text{H}] + [^3\text{He}_{\text{trit}}])^{-1} (\sigma_{^3\text{He}_{\text{trit}}}^2 + ([^3\text{He}_{\text{trit}}]/[^3\text{H}])^2 \sigma_{^3\text{H}}^2)^{1/2} \quad [\text{Eq. 15}]$$

Samples containing less than 1 pCi/L of tritium (n=977, Table 2) must have recharged before the start of atmospheric testing of nuclear fission devices (1950) and were assigned an age of 60 years for the purposes of binning the age data (see (Visser et al. 2013b) for a discussion of ‘tritium dead’ results for a subset of this data set). Two acceptance criteria (Table 3) were evaluated for the calculated $^3\text{H}/^3\text{He}$ ages: (1) the calculated recharge year must be after 1950 and (2) the propagated uncertainty must be less than 5 years plus 10% of the estimated age. $^3\text{H}/^3\text{He}$ ages that corresponded to a recharge year before 1950 were discarded (n=221). Tritium-helium ages with an associated uncertainty of more than 5 years plus 10% of the estimated age (n=718) were also discarded. In total, 1630 $^3\text{H}/^3\text{He}$ ages were accepted, in addition to 977 samples with less than 1 pCi/L that were assigned an age of 60 years. The influence of terrigenous helium on the ability to calculate an acceptable $^3\text{H}/^3\text{He}$ age using these criteria (Table 4) is demonstrated by comparing the acceptance rate of samples with terrigenous helium (216/996 = 22%) to that of samples without terrigenous helium (1414/1573 = 90%).

2.5 Geostatistical analysis

To create maps of noble gas derived parameters and groundwater age, the spatial structure of the data was analyzed geostatistically, in particular by kriging, using the gstat package (Pebesma 2004) of the statistical software R (R Core Team 2013, Bivand et al. 2013). Prior to the analysis, the statistical distribution of the data was evaluated by histogram analysis and a Shapiro-Wilks test for normality (Shapiro and Francia 1972). While the distributions of all variables in the data set were significantly different from normal, the distributions of tritium, terrigenous helium and excess air were visibly skewed. A log-transformation was applied to these variables before analysis, and predicted

values were back-transformed. The detection limit of tritium causes a high number of data points to occur at the 1 pCi/L level and the distribution of the log-transformed tritium concentration lacks a left tail.

Figure 2a shows an example variogram. The variogram represents the variance within the data for sample pairs at a certain distance. If the data are spatially correlated, the variance at shorter distances is smaller than the variance at large distances. The variance extrapolated to a zero distance is called the “nugget effect”, representing measurement error, short range variability, or in this case, differences in sample depth. A small nugget relative to the variance at long distances, indicates little short scale variability and high predictability of the variable at short distances. The distance at which the variance increases to the maximum variance (“range”) reflects the distance over which points in space are still correlated. For distances beyond the range, points are no longer correlated.

For each variable (Z), the variogram (γ) was calculated from all sample pairs with lag distance h between locations (s) as:

$$\gamma(h) = \frac{1}{2} E(Z(s) - Z(s+h))^2 \quad [\text{Eq. 16}]$$

under the assumption that the spatial correlation of Z does not depend on location s , but only on separation distance h . Under the assumption of isotropy (i.e., the correlation does not depend on the direction of the lag distance), the sample variogram $\hat{\gamma}$ was estimated from N_h sample pairs for binned distance intervals $\tilde{h}_j$:

$$\hat{\gamma}(\tilde{h}_j) = \frac{1}{2N_h} \sum_{i=1}^{N_h} (Z(s_i) - Z(s_i + h))^2, \forall h \in \tilde{h}_j \quad [\text{Eq. 17}]$$

357

358 For state-wide geostatistical analyses, the bin width was 1 km. A variogram model defined by the
 359 nugget n , the partial sill s , and the range r , was fitted to the sample variogram for each variable. Two
 360 model shapes were used, spherical (Eq. 18) and exponential (Eq. 19). Variogram analysis was
 361 performed on the entire data set for each variable, as well as on subsets of the data.

362

$$\gamma(h) = \begin{cases} n + s \left(\frac{3h}{2r} - \frac{h^3}{2r^3} \right) & 0 < h < r \\ n + s & h \geq r \end{cases} \quad [\text{Eq. 18}]$$

$$\gamma(h) = n + s \left(1 - e^{-\frac{h}{a}} \right) \quad [\text{Eq. 19}]$$

365 The exponential model reaches the sill asymptotically. The 'effective range' of the exponential
 366 model is the distance where the variogram reaches 95% of its maximum, which is at 3 times the
 367 range parameter, a .

368

369 In Figure 2, blue circles represent the distance-binned Sample Variogram. The Sample Variogram is
 370 represented by a Spherical Variogram Model (blue line). The parameters of the Spherical Variogram
 371 Model are (in this case) a nugget, n , of 0.25, a range, r , of 100 km and a partial sill, s , of 0.5. The total
 372 variance in the data is the sum of the nugget and partial sill (0.75). The example variogram shows
 373 that variance between samples is very close to one third (0.25/0.75) of the variance of the entire
 374 data set, due to the spatial correlation. The variance of a set of samples collected at greater
 375 distances increases as the spatial correlation decreases. Samples collected more than 100 km apart
 376 are no longer correlated.

377

378 As noted above, the nugget parameter of the variogram is found by extrapolating the short range
379 variability to a lag distance of zero. To better visualize this part of the variogram, the lag distance of
380 the variogram is plotted on a logarithmic horizontal scale (Figure 2b). The fitted variogram model
381 reaches the nugget asymptotically when the lag distance decreases to zero. Because the variogram
382 is calculated by the squared differences between measurements, the square root of the variogram
383 represents the spatial correlation structure in the same units as the variable of interest, allowing
384 direct interpretation of the parameter values for the nugget and the sill. In the resulting figures,
385 both the nugget and range parameters of the fitted model can be evaluated visually.

386

387 The concentrations of the noble gases neon, argon, krypton and xenon are divided by the mean
388 concentration, resulting in relative variations. A nugget parameter of 0.02 then represents a
389 variation of 2% of the mean concentration, allowing direct comparison between the different noble
390 gases. Because of the skewed distributions of the helium concentration and helium isotope ratio,
391 variograms are calculated on base-10 log transformed data.

392

393 Maps of variables were obtained by ordinary kriging prediction, yielding linear unbiased predictions
394 of variables at gridded locations, at a 0.005 degree resolution for the statewide maps, corresponding
395 to distances of 0.5 km. It should be noted that after prediction, log-transformed variables were back
396 transformed. Variables related to groundwater properties (e.g. tritium concentration, age) were
397 predicted only for grid cells within a California Department of Water Resources-defined
398 groundwater basin. It should be noted that the kriging prediction does not include a spatial
399 connectivity analysis. Samples in disconnected groundwater basins can therefore impact predictions
400 across groundwater divides.

2.6 Depth Evaluation

All geostatistical analyses are initially performed in two horizontal dimensions. To investigate the vertical age stratification and the depth of modern groundwater penetration, the tritium and terrigenic helium data sets were split into three depth categories, based on the top of the well screen. The top of the screen was chosen (as opposed to the bottom or center) as an indicator of the depth of the boundary between modern and pre-modern under the assumption that modern groundwater generally overlies pre-modern groundwater. If tritium is not detected in a well, the boundary between modern and pre-modern groundwater lies above the top of the well screen. If tritium is detected in a well, the bottom of a screen can be far below the boundary between modern and pre-modern groundwater if the tritiated water enters the well at the top of the screen. Therefore, the top of the screen was chosen to estimate the pre-modern –modern boundary, even while the tritiated waters may enter the well near the bottom of the screen. Screen depth thresholds were chosen at 61 m (200 ft.) and 122 m (400 ft.), resulting in nearly equally sized data sets. However, the statistical distribution of data in each subset was distinctly different, because the proportion of pre-modern groundwater was larger at greater depths. Also, the spatial distribution of wells within each category was no longer unbiased. The subsets were subject to geostatistical analysis and kriging prediction to create depth specific maps of these two tracers.

421

422

3 RESULTS

423

3.1 Variogram Analysis

425 The variograms of the logarithm of the helium isotope ratio and the helium concentration have a
426 range of approximately 80 km (Figure 3). The exponential model is better at capturing the shape of
427 the variograms of the concentrations of atmospheric noble gases than the spherical model. The
428 range of the fitted variogram model increases from 26 km for Ne to 91 km for Xe, while both the
429 nugget and the total variation are highest for Ne and decrease with increasing atomic mass (Ar, Kr,
430 Xe).

431

432 The short range variability of the derived noble gas recharge temperature and elevation corrected
433 noble gas recharge temperature is 2.1 °C. The range parameter of the noble gas recharge
434 temperature is larger than that of xenon, or any of the other noble gas concentrations, but very
435 similar to the variogram of the elevation at the well head (not shown), which has a range of 240 km
436 but a negligible nugget. The elevation corrected noble gas recharge temperature range reflects the
437 continental temperature gradient across California. The increase in the correlation length of
438 dissolved noble gas concentrations going from Ne to Xe shows that the scale of the excess air
439 forming processes (mostly influencing Ne) is shorter than the scale of the groundwater recharge
440 temperatures (mostly influencing Xe). However, neither the partial nugget nor the range of the neon
441 concentration is at all similar to those of the ΔNe .

442

As expected, the variogram of the terrigenous helium component is very similar to that of the ^4He concentration. The variogram of the terrigenous helium isotope ratio is distinctly different, however, with a much smaller nugget parameter. A spherical variogram model better fits the experimental variogram than the exponential model. The similarity of the range and partial nugget of the helium isotope ratio, the helium concentration and the terrigenous helium component suggests that terrigenous helium controls the other two parameters. In contrast, the lower nugget and shorter range of the terrigenous helium isotope ratio shows that this parameter is controlled by a different mechanism. The isotope signature of the source of the terrigenous helium, be it a fault, an intrusion or radiogenic accumulation, is retained in groundwater and shows very little short range variability. The short correlation length points to localized sources like faults or intrusions, rather than *in situ* radiogenic accumulation.

The log of the tritium concentration has the shortest range of all investigated parameters and also the lowest partial nugget, except for the $^3\text{H}/^3\text{He}$ age of shallow samples, terrigenous helium isotope ratio and $\delta^{18}\text{O}$. In contrast, the log of the tritiogenic helium component shows a very poor spatial correlation structure with a partial nugget of more than 80%. The spatial correlation length of $^3\text{H}/^3\text{He}$ ages is in between, correlating up to 50 km with a partial nugget of 60%. The range parameter of $^3\text{H}/^3\text{He}$ ages reflects the size of the groundwater flow systems that operate on that time scale. The modeled correlation length corresponds to a horizontal flow velocity on the order of 1 km per year. Groundwater flow systems in which ages accumulate several thousands of years, characterized by the carbon-14 activity, are larger, as reflected by the range of carbon-14 and helium-4. While radiogenic helium can accumulate over millions of years, far beyond the lifetime of carbon-14, the range of terrigenous helium is smaller than that of carbon-14 (Figure 5c). Notably, this

suggests that the variogram of terrigenic helium is not controlled by accumulation of radiogenic helium but rather by intrusion of helium from more localized sources.

$\delta^{18}\text{O}$ (Figure 5b) has the largest range of all parameters examined (except elevation corrected noble gas recharge temperature). $\delta^{18}\text{O}$ is a faithful recorder of surface air temperature and moisture source area, which is controlled by physiographic effects such as orographic lifting and distance inland in California. The range of D_{exc} on the other hand, is much smaller because it reflects the influence of secondary effects on the isotopic composition of precipitation and groundwater, including the relative humidity in the vapor source region, and post-depositional evaporation or, on long time scales, disparate interaction with oxygen-bearing aquifer materials for oxygen vs. hydrogen. Evaporation during irrigation, MAR, or storage in surface reservoirs is the most likely influence on D_{exc} for this data set. Finally, the partial nugget of the log nitrate concentration is over 60%, which implies that spatial predictions of nitrate concentrations will be highly uncertain, while the concentrations are correlated (albeit poorly) over a range of 130 km.

For comparison, the variogram of log nitrate concentration (Figure 5c) has a nugget of 0.6. Because of the logarithmic scale for nitrate, this corresponds to a variation within 1 km of a factor of 4. Nitrate concentrations are correlated over a distance of 130 km.

3.2 Tritium and Groundwater Age

Maps of tritium concentrations (Figure 7) and groundwater age (Figure 8) show that high tritium concentrations are generally found in areas with young groundwater ages. This is especially true in the Central Valley. The tritium concentrations in these samples are therefore largely determined by the mixing of pre-modern (^3H free) groundwater with modern groundwater (containing ^3H) and not by decay of atmospheric tritium. In contrast, in samples from short-screened monitoring wells with a distinct age, high concentrations of tritium are found in older modern groundwater, as a result of high initial tritium concentrations in water that recharged in the 1960's and 1970's, when bomb-pulse tritium was present in infiltrating precipitation. The areas with the youngest groundwater ages, like the northwestern coast and the upper Los Angeles basin, have moderately low (1-10 pCi/L) tritium concentrations.

Young $^3\text{H}/^3\text{He}$ ages, less than 30 years old, delineate the regions of groundwater recharge. These are found in particular in the following areas:

- Southern San Joaquin Valley, recharge from the Kings and Kern Rivers
- Central San Joaquin Valley, recharge from the Tuolumne, Stanislaus and Merced Rivers
- Middle Sacramento Valley
- Southern Santa Clara Valley Basin, forebay recharge
- Upper Los Angeles Basin, forebay recharge
- Along the Colorado River and in the Imperial Valley
- Along the northwestern coast, due to high precipitation rates
- Along the eastern slopes of the Sierra Nevada, recharge from the Owens River

Recent recharge reaching these aquifers makes them vulnerable to contamination from surface activities.

514

515 The San Joaquin Valley shows distinct recharge areas in the east and an age gradient towards pre-
516 modern groundwater on the west side. The general trend is more clearly visible on the tritium map,
517 where high tritium concentrations are associated with young groundwater ages. Artificial recharge
518 activities in Fresno and Bakersfield are evidenced by higher tritium concentrations and younger
519 groundwater ages than surrounding areas. Burrow et al. (2013) described a similar pattern with
520 respect to nitrate patterns, which exhibit a temporal tracer component related to the steep increase
521 in nitrogen fertilizer use in the 1970's and 1980's.

522

523 Santa Clara Valley shows a clear gradient of groundwater ages from the forebay area in the south
524 towards San Francisco Bay in the north. While young ages are associated with higher tritium
525 concentrations on statewide maps, in Santa Clara Valley, high tritium concentrations are not
526 associated with young groundwater ages. In this case, the age gradient is more distinctive and
527 tritium alone is not capable of identifying the flow direction. Tritium concentrations are more
528 strongly determined by the initial tritium concentrations in specific historical recharge periods than
529 by mixing of modern and pre-modern groundwater (Moran et al. 2002a, Moran et al. 2005c).
530 Relatively high tritium concentrations in the Livermore Valley are due to historical, regulated
531 releases of tritium from Lawrence Livermore National Laboratory.

532

533 A closer look at the Los Angeles Physiographic Basin (Fig 8) shows the patterns generated by MAR
534 near the Anaheim Forebay and Montebello Forebay where groundwater ages in these engineered
535 groundwater basins increase towards the coast (Hudson et al. 2002, Clark et al. 2004). The pattern is
536 interrupted by injection of large volumes of water at seawater intrusion barriers at Dominguez Gap,
537 Alamitos Gap, and the West Coast barrier in the Los Angeles Basin and at the Talbert Gap in the

538 Orange County Basin. Pre-modern groundwater in relatively stagnant zones prevails between areas
539 affected by the major recharge areas in the forebay or the injection barriers (Clark et al. 2004).
540 Comparison between tritium and the age map shows that the highest concentrations of tritium are
541 found in groundwater with an age of 30-40 years. Here, as in Santa Clara, the tritium concentration
542 is determined by the modern age and the initial tritium during recharge, rather than by the mixing
543 of modern and pre-modern groundwater. Tritium analyses alone would not reveal the detail of age
544 gradients that are obtained from tritium-helium analysis (Hudson et al. 2002).
545
546 High precipitation rates occur in northern California and in the Sierra Nevada. However, these areas
547 have little surface alluvium to allow direct infiltration of precipitation and only transmit voluminous
548 groundwater where relatively sudden snowmelt finds extensive fractures or alpine-subalpine
549 meadows. In a pattern similar to that described above for Santa Clara Valley, regional groundwater
550 flow patterns in the central coast basins, with young groundwater ages and recharge occurring in
551 the forebay portions of the Salinas valley and Paso Robles basin, are the result of both managed
552 recharge and natural infiltration of precipitation in unconfined portions of those basins. Areas with
553 very low precipitation, like the Mojave Desert, are associated with fossil groundwater abstraction,
554 because present day precipitation rates are insufficient to contribute to substantial recharge. At
555 present, a number of areas with low precipitation rates do show young groundwater ages, indicative
556 of modern recharge, for example along the eastern San Joaquin Valley, along unlined canals in the
557 Imperial Valley, in the Los Angeles basin and in Owens valley. In these areas, the groundwater
558 reservoir is recharged by surface water imports. Surface water recharge occurs along rivers and
559 unlined canals fed by impounded Sierra Nevada snowmelt; imports and recharge of recycled
560 wastewater occur in the Los Angeles physiographic basin via managed aquifer recharge leading to

young groundwater ages in forebay areas (McDermott et al. 2008). Present day recharge is dominated by these forms of surface water infiltration, rather than precipitation.

3.3 Terrigenic helium concentration

In general, high concentrations of terrigenic helium are found in groundwater with older $^3\text{H}/^3\text{He}$ ages (Figure 9), often where the assigned age is 60 years, representing tritium-dead, pre-modern groundwater, as in the Basin and Range province and the Mojave Desert, the western San Joaquin Valley, and the eastern side of the Sacramento Valley. Fossil groundwater in the Mojave Desert coincides with very low precipitation rates and abstraction of fossil water risks depletion of a finite resource. The western side of the San Joaquin Valley lacks the river recharge from major, perennial rivers that occurs on the eastern side. Groundwater abstraction in the western San Joaquin Valley will thus draw in lateral flow from recharge occurring in the eastern San Joaquin Valley (Bolger et al. 2011). The Monterey and Santa Clara Valley Basin coastal areas are down-gradient of the forebay areas of regional groundwater flow systems and long travel times with deep flow paths allow for significant accumulation of terrigenic helium (Moran et al. 2002a, Hudson et al. 2002). Under natural conditions, this resulted in submarine groundwater discharge of old groundwater. At present, abstraction of fresh water from these aquifers has led to sea water intrusion (Werner and Simmons 2009).

3.4 Depth Evaluation

The depth to the top of the screen is available for 1919 samples. The median tritium concentrations at the three depth intervals (shallow: 0-61 m, intermediate: 61-122 m and deep: below 122 m) are

584 7.8, 3.0 and 1.6 pCi/L. Mean concentrations are higher (10.2, 7.2 and 7.3 pCi/L) due to the skewed
585 distribution of tritium concentrations.

586 Comparison of shallow with intermediate and deep groundwater shows decreasing tritium
587 concentrations with depth, as a result of age stratification. An analysis of shallow data predicts a
588 tritium concentration of more than 3 pCi/L for the entire Central Valley. When all depths are
589 considered, tritium free groundwater is predicted in the Northwestern part of the San Joaquin
590 Valley because all wells in this area had top-of-screens below 61 m. Figure 10c also shows areas
591 where modern groundwater has reached great depths in some groundwater basins. While most
592 aquifers contain less than 3 pCi/L tritium below 61 m, tritium is found in intermediate and deep
593 wells in Santa Clara Valley, the western San Joaquin Valley and the Los Angeles basin. Tritium
594 concentrations above 3 pCi/L were not found in deep wells, except in the Los Angeles basin. Here,
595 decades of intense managed aquifer recharge and deep groundwater pumping draws modern
596 groundwater down to great depths. Tritium concentrations somewhat higher than in surrounding
597 areas that are found in the southern San Joaquin Valley are also likely the result of intense pumping
598 and recharge via return flow of imported irrigation water.

599 The depth to pre-modern groundwater, illustrated in Figure 11, is an important consideration
600 because pre-modern water is less likely to be affected by anthropogenic contaminants (Fram and
601 Belitz 2011b, Moran et al. 2004, Visser et al. 2013b). Conversely, extraction of large volumes of
602 tritium-free groundwater is likely to be unsustainable unless recharge rates have been artificially
603 increased. The depth to the top of the screen is available for 470 tritium-free wells. The spatial
604 structure of the log-transformed depth to tritium free groundwater has a correlation length of 86
605 km. The sill and spherical component of the variogram are of equal size, indicating a significant short
606 lag variability. The depth to tritium-free groundwater typically varies between 30 and 120 m (Fig 10).
607 Four areas stand out as having a very deep boundary between modern and pre-modern

groundwater. In the area between Woodland, Davis and Sacramento, the boundary is as deep as 150-200 m. Similar depths to tritium-free groundwater are found in the Santa Clara River Valley, San Gabriel Basin and in the Mojave Study Unit near Hesperia. On the other hand, tritium-free groundwater is found at shallow depths in the Volcanic Highlands north of San Francisco (Moran et al. 2010) and in the Indian Wells area of the Basin and Range province.

Variograms of terrigenic ^4He concentrations in each depth category were very similar to variograms of all terrigenic helium data. Terrigenic ^4He shows the opposite pattern of ^3H , with increasing terrigenic ^4He found in deeper aquifers. The median concentrations of terrigenic helium in each of the depth classes are 1.5, 4.3 and $11.3 \times 10^{-9} \text{ cm}^3\text{STP/g}$. Mean concentrations are higher (283, 251 and $326 \times 10^{-7} \text{ cm}^3\text{STP/g}$) due to the skewed distribution of terrigenic helium concentrations. Exceptions are areas where modern water has reached deeper parts of the aquifer, as discussed above, and terrigenic helium is low or absent, even in deep-screened wells, such as in the southwestern San Joaquin Valley and LA Basin. High concentrations of terrigenic ^4He over all depths, delineate regions of low recharge and very long groundwater residence time throughout the aquifer system in the southeastern deserts and regions of magmatic influence on groundwater in the northeastern Sacramento Valley (Fig 7d, e, f).

4 DISCUSSION

Decades of awareness of the challenges of providing a safe water supply for California, a state with a rapidly increasing population, high water demand by irrigated agriculture, and an uneven

distribution of naturally-supplied water, led state regulators and scientists to develop an innovative groundwater monitoring program that included chemical and isotopic tracers. In contrast to most regulatory monitoring, which involves measurement of contaminant concentrations, the parameters examined in this study reveal regional hydrologic processes, subsurface residence times, and the scale of the influence of human activity on the groundwater system. The spatial geostatistical analysis carried out here reveals key characteristics of California's groundwater systems: aquifer vulnerability, sustainability, recharge locations and mechanisms, and anthropogenic impacts on recharge. These parameters are useful for assessing vulnerability and other characteristics locally or even at individual wells (Eberts et al. 2012, Katz et al. 2009, McMahon et al. 2011), however, here we present an overview of the most obvious patterns that become clear based on regional spatial geostatistical analysis.

Analysis of variograms of groundwater tracers gives insight into the horizontal spatial variability and recharge and flow patterns of groundwater systems. Figure 6 shows that the correlation length of key groundwater residence time parameters varies between tens of kilometers (^3H : 15 km; shallow age: 20 km) to the order of a hundred kilometers ($^4\text{He}_{\text{ter}}$: ~85 km; ^{14}C : ~90 km; $^3\text{He}_{\text{trit}}$: ~110 km). The correlation lengths of parameters related to climate, topography and atmospheric processes are greater, on the order of several hundred kilometers (recharge temperature: ~200 km; $\delta^{18}\text{O}$: ~350 km). Kriging and variogram analysis allow extrapolation of derived parameters that are calculated at individual wells, along with measures of the spatial similarity of the parameters.

On the scale of California, young groundwater ages correlate with higher tritium concentrations (Figures 7 and 8). However, in some individual groundwater basins, higher tritium concentrations

are associated with groundwater with ages of 30-40 years, which are the result of higher historical concentrations of tritium (from the 'bomb pulse') in recharging groundwater. This distinction illustrates the different information drawn from tritium concentrations in mixed groundwater samples containing a large fraction of pre-modern groundwater versus samples containing mostly modern groundwater. In mixed groundwater, the tritium concentrations are mostly determined by the fraction of pre-modern groundwater, i.e. the dilution of tritium. The tritium concentration alone is then indicative of the presence of modern groundwater, although quantification of the fraction of modern water is highly uncertain, suggesting that researchers and water managers should use caution in the application of tritium alone. In areas where little pre-modern groundwater is present, the tritium-helium age is essential in identifying recharge areas and flow patterns. Tritium analyses alone would point to areas where groundwater ages are 30-40 years, while $^3\text{H}/^3\text{He}$ groundwater ages delineate areas with 0-10 year old groundwater.

The young groundwater ages observed in far northwestern California (Figure 8) are one of the few obvious imprints of the natural hydrologic system at this scale of interpretation, whereby high precipitation rates (Figure 1b) lead to high recharge rates and relatively short groundwater residence times. Other regional recharge areas, indicated by young groundwater ages, are located in the eastern San Joaquin Valley, in the southern Santa Clara Valley Basin, and in the upper LA basin and along unlined (or recently lined) canals carrying Colorado River water. These areas are not characterized by higher precipitation that might result in higher infiltration and recharge. Rather, much of the modern recharge in California is dominated by recharge via rivers (often controlled by reservoir releases, as in the San Joaquin Valley and Colorado River system), and focused managed aquifer recharge (e.g., Fremont, Santa Clara Valley, Bakersfield, Los Angeles Physiographic Basin). Wells in recharge areas are most vulnerable to surface contamination (Moran et al. 2004, Manning

et al. 2005). Managed aquifer recharge poses a smaller threat because of monitoring and regulation (California Department of Public Health 2014) and leads to more sustainable use of groundwater. Areas with young groundwater where recharge is dominated by irrigation return flow are vulnerable to contamination from non-point sources of pollution. In California, this pattern is most pronounced in portions of the San Joaquin Valley and in the upper Salinas Valley.

In the southeastern San Joaquin Valley, Santa Clara Valley and Los Angeles basin, modern groundwater is found in intermediate and deep wells. This shows that depth alone does not protect an aquifer, especially if intensive pumping and/or managed aquifer recharge operations dominate the flow pattern, since those activities generally decrease the time between recharge and discharge relative to the natural system. The great depth at which tritiated groundwater is observed in the Los Angeles Physiographic Basin (Figure 10c, Figure 11) is a testament to decades of intense pumping at deep wells and intense management to combat both seawater intrusion and groundwater overdraft. Groundwater abstracted from deep wells in the western San Joaquin Valley is better protected from surface contamination due to the presence of the Corcoran clay (Bolger et al. 2011), as evidenced by observations of old groundwater ages there (Figure 8). The presence of pre-modern groundwater does not allow prediction of a more precise time scale of vulnerability. However, the preponderance of pre-modern groundwater and high rate of extraction for irrigated agriculture combines to bring about an unsustainable condition over the southwestern San Joaquin Valley (Galloway and Riley 1999). The available age tracer data are not capable of distinguishing groundwater ages in the 60-500 year range. Additional analysis of e.g., argon-39, would potentially provide this information(Loosli 1983, Loosli et al. 1989). Modern groundwater in deeper parts of the eastern San Joaquin Valley, affected by agricultural constituents such as salts and nitrate, will be transported

laterally toward the western San Joaquin Valley, eventually threatening groundwater quality there (Burow et al. 2013).

Groundwater abstracted in the central Mojave Desert is mostly pre-modern and characterized as fossil water based on the presence of high concentrations of terrigenous helium (Figure 9). High terrigenous helium in the northeastern San Joaquin Valley is associated with magmatic He sources (Jurgens et al. 2008). The terrigenous helium age indicates a residence time of 10-50 thousand years, based on literature assumptions of the porosity and uranium and thorium contents (Kulongoski et al. 2003, Torgersen 1980). Modern groundwater abstracted in this area is found only near distributaries of the Colorado River, which recharged under distinctly different climatic and hydrologic conditions. This supports the notion that desert groundwater abstraction is depleting a finite resource because modern recharge with its distinct isotopic and noble gas signature has not been sampled in this region.

It should be noted that the kriging prediction does not include a spatial connectivity analysis. Samples in disconnected groundwater basins can therefore impact predictions across groundwater divides. Of course, tracer concentrations vary not only horizontally but also vertically. Vertical stratification of groundwater residence times due to diffuse recharge at the surface can cause strong correlations between depth and age tracers. This effect may be limited for parameters like $\delta^{18}\text{O}$, noble gas recharge temperature, or excess air, although changes in land use, water management and possibly climate could be translated into vertical trends. Nitrate is also expected to be impacted by stratification of groundwater ages because of increasing leaching of nitrate over the past 100 years. For this data set, well depth information is available for approximately 65% of the samples. The depth to top of the screen correlates significantly with tritium and log-tritium, but

the correlation coefficients are only -0.08 and -0.20 respectively, indicating that age stratification is limited. This effect of stratification was tested for tritium and age, by selecting only shallow wells. However, full 3D kriging, while in principle possible, is complicated due to a change of support problem (Truong et al. 2014, Jang et al. 2008). Kriging and variogram analysis rely on point-support observations. A large proportion of samples in this data set is collected from public supply wells, with long screens that draw groundwater from a range of depths and provide a line-support measurement. Further complications include the potential of wells to draw preferentially from high conductivity layers in the aquifer (Segal et al. 2014). Unfortunately, vertical flow profiles of long screened wells are not available for this data set. Until these challenges are overcome, vertical analysis is limited to sequential analysis of subsets of the samples which are collected from wells with screens within specific depth intervals (Figure 10).

While previous studies have used parts of the data set for area specific studies (Deeds et al. 2012, Jurgens et al. 2009, Fram and Belitz 2011b, Landon et al. 2011, Kulongoski et al. 2013, Forrest et al. 2013, Landon and Belitz 2012, Manning et al. 2015), this was the first to analyze the entire tritium and noble gas data set from samples throughout California. Smaller scale studies combining the results reported here with more detailed geological and hydrogeological data including two dimensional delineation of near-surface permeability and three dimensional delineation of confining units and depth to basement, will enhance the understanding of key relationships between geology and groundwater residence times.

5 CONCLUSIONS

An innovative statewide groundwater monitoring program in California enabled a spatial geostatistical analysis of chemical and isotopic parameters related to regional hydrologic processes, subsurface residence times, and the scale of the influence of human activity on the groundwater

749 system. The analysis reveals young groundwater ages that highlight regional recharge areas showing
750 the importance of river recharge and managed aquifer recharge, and hydrologically vulnerable areas
751 where modern groundwater reaches deeper parts of aquifers as the result of intensive pumping
752 and/or managed aquifer recharge operations. The spatial geostatistical analysis of chemical and
753 isotopic tracers provides new information on vulnerability and sustainability, independent of
754 traditional hydrological investigations.

6 ACKNOWLEDGEMENTS

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7 TABLES

Table 1: Number of analyses and derived parameters and the number of unique wells with analyses and derived parameters available.

Variable	Number of analyses	Number of unique wells
Tritium	3895	3802
- 0-61 m deep	1281	950
- 61-122 m deep	812	651
- > 122 m deep	426	318
- $3\text{H} < 1 \text{ pCi/L}$	977	757
- $3\text{H} \geq 1 \text{ pCi/L}$	2918	2285
Oxygen-18	4772	3445
Noble gases (EA)*	3926	3926
Noble gas model fit	3743	3743
- He, Ne, Ar, Kr, Xe	1288	
- Ne, Ar, Kr, Xe	1828	
- Ne, Ar, Kr	275	
- Ne, Ar, Xe	23	
- Ne, Kr, Xe	170	
- Ar, Kr, Xe	159	
Noble gas recharge temperature	3743	3743
Terrigenous helium	3921	3921
Terrigenous helium (significant)	1886	1499
Terrigenous helium isotope ratio	1626	1626
- With significant terrigenous helium and an uncertainty of less than 10% Ra	897	897
$^3\text{H}/^3\text{He}$ age (< 60 years)	1630	1366
$^3\text{H}/^3\text{He}$ age (incl. $^3\text{H} < 1 \text{ pCi/L}$)	2589	2141

* Number of samples for which the excess air component (EA) could be derived. EA can be derived from all atmospheric noble gases (Ne, Ar, Kr and Xe) or from a subset if one or more noble gas concentrations are missing for a particular sample.

774 Table 2: Number of samples for which a $^3\text{H}/^3\text{He}$ age was calculated.

	$3\text{H} < 1 \text{ pCi/L}$	$3\text{H} \geq 1 \text{ pCi/L}$	Total
No $^3\text{H}/^3\text{He}$ age	977	1288*	2265
$^3\text{H}/^3\text{He}$ age	-	1630	1630
Total	977	2918	3895

775 * 1288 samples contain more than 1 pCi/L tritium and have no $^3\text{H}/^3\text{He}$ assigned, of which 349 lack
 776 location information or ^3He , ^4He or Ne measurements, and 939 were discarded because they did not
 777 meet the acceptance criteria.

778
 779 Table 3: Results of the $^3\text{H}/^3\text{He}$ age acceptance criteria.

	Uncertainty $\leq 5\text{y} + 10\%$	Uncertainty $> 5\text{y} + 10\%$	Total
Recharge year > 1950	1630*	718	2348
Recharge year ≤ 1950	87	134	221
Total	1717	852	2569

780 * The total number of accepted $^3\text{H}/^3\text{He}$ ages.

781
 782 Table 4: Analysis of influence of terrigenous helium on acceptance criteria results.

	No $^4\text{He}_{\text{ter}}$	Significant $^4\text{He}_{\text{ter}}$	Total
Accepted $^3\text{H}/^3\text{He}$ age	1414	216	1630
$^3\text{H}/^3\text{He}$ age not accepted	159	780	939
Total	1573	996	2569

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 784
 785

786 Table 5: Parameters of variogram models

Variable	Model ¹	Nugget <i>n</i>	Partial sill <i>s</i>	Effective Range ² [km]
$\log_{10}({}^3\text{He}/{}^4\text{He})$	Exp	0.021	0.060	86
$\log_{10}({}^4\text{Helium})$	Exp	0.092	0.163	76
Neon ³	Exp	0.045	0.116	26
Argon ³	Exp	0.009	0.024	32
Krypton ³	Exp	0.005	0.011	43
Xenon ³	Exp	0.006	0.008	91
Recharge Temperature	Exp	5.1	12.4	189
Elevation Corrected Recharge Temperature	Exp	6.5	13.2	797
$\log_{10}(\Delta\text{Ne})$	Exp	0.107	0.099	99
$\log_{10}({}^4\text{He}_{\text{ter}})$	Exp	0.535	0.934	84
• 0-61 m	Exp	0.365	1.05	76
• 61-122 m	Exp	0.266	1.26	70
• > 122 m	Exp	0.251	1.31	153
$\log_{10}(R_{\text{ter}})$	Sph	0.015	0.522	68
$\log_{10}({}^3\text{H})$	Exp	0.205	0.373	31
$\log_{10}({}^3\text{H})$ - shallow	Exp	0.007	0.376	13
• 0-61 m	Exp	0.163	0.280	161
• 61-122 m	Exp	0.102	0.498	32
• > 122 m	Exp	0.163	0.614	13
$\log_{10}({}^3\text{He}^{\text{trit}})$	Exp	0.548	0.279	110
$\log_{10}$ of depth to top of screen of tritium free wells	Exp	0.043	0.052	87
${}^3\text{H}/{}^3\text{He}$ Age	Exp	195	308	52
${}^3\text{H}/{}^3\text{He}$ Age – shallow	Exp	0	456	20
${}^{14}\text{C}$	Exp	530	535	95
$\delta^{18}\text{O}$	Sph	0.395	8.76	369
D_{excess}	Exp	4.79	4.60	181
$\log_{10}(\text{NO}_3)$	Exp	0.371	0.513	122

787 1: Exp: Exponential; Sph: Spherical.

788 2: Effective range. Parameter *r* for the Spherical model (Eq. 18) or 3×*r* for the Exponential Model.

789 3: Variogram parameters of relative concentrations: measured concentration divided by the mean
790 concentration of the entire dataset.

8 REFERENCES

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Figure 1

Figure 2

Figure 2: Example variogram, showing the nugget, partial sill and range components of the spherical variogram model (a) and the square root of the variogram on a base-10 logarithmic distance scale (b).

Figure 3

Figure 3: Variograms of concentration and isotope ratio of dissolved helium and concentrations of neon, argon, krypton and xenon with exponential model shown as blue line.

Figure 4

Figure 4: Variograms of derived parameters and tritium concentration, along with spherical or exponential model fit.

Figure 5

Figure 5: Variograms of measured carbon-14, $\delta^{18}\text{O}$ and calculated deuterium excess, and nitrate concentration, along with spherical or exponential model fit.

Figure 6

Figure 6: Summary of variogram parameters related to measured noble gas concentrations and the helium isotope ratio (black), residence times (red), physical characteristics of climate, recharge or the subsurface (blue) and nitrate (green) for comparison.

Figure 7

Figure 8

Figure 9

Figure 10

Figure 11

Variogram parameters