

# Impact of Artificial Recharge on Dissolved Noble Gases in Groundwater in California

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Dissolved noble gas concentrations in groundwater can provide valuable information on recharge temperatures and enable  $^3\text{H}$ – $^3\text{He}$  age-dating with the use of physically based interpretive models. This study presents a large (905 samples) data set of dissolved noble gas concentrations from drinking water supply wells throughout California, representing a range of physiographic, climatic, and water management conditions. Three common interpretive models (unfractionated air, UA; partial re-equilibration, PR; and closed system equilibrium, CE) produce systematically different recharge temperatures or ages; however, the ability of the different models to fit measured data within measurement uncertainty indicates that goodness-of-fit is not a robust indicator for model appropriateness. Therefore caution is necessary when interpreting model results. Samples from multiple locations contained significantly higher Ne and excess air concentrations than reported in the literature, with maximum excess air tending toward 0.05  $\text{cm}^3$  STP  $\text{g}^{-1}$  ( $\Delta\text{Ne} \sim 400\%$ ). Artificial recharge is the most plausible cause of the high excess air concentrations. The ability of artificial recharge to dissolve greater amounts of atmospheric gases has important implications for oxidation–reduction dependent chemical reactions. Measured gas concentration ratios suggest that diffusive degassing may have occurred. Understanding the physical processes controlling gas dissolution during groundwater recharge is critical for optimal management of artificial recharge and for predicting changes in water quality that can occur following artificial recharge.

## Introduction

Concentrations of atmospherically derived noble gases dissolved in groundwater are used to determine recharge temperatures which are useful for paleoclimatic studies of glacial–interglacial temperature variation (1–5). Concentra-

tions of dissolved noble gases in groundwater are virtually always greater than equilibrium solubility. The portion of gas in excess of equilibrium solubility is referred to as “excess air” because of its compositional similarity to air, although it is commonly fractionated relative to air (heavy gases more enriched than light gases) (6). Because determinations of recharge temperature and  $^3\text{H}$ – $^3\text{He}$  age are based on equilibrium gas solubility, total measured gas must be corrected for excess air. Entrapped soil air near the water table is generally considered to be the source of excess air (6). These bubbles dissolve during downward water flux and during water table fluctuations. Early interpretations of dissolved gas data assumed excess air resulted from complete dissolution of entrapped air (4, 7). Subsequent research suggested that the commonly observed elemental fractionation of excess air was caused by complete dissolution of entrapped air and subsequent diffusive degassing (2) or by incomplete dissolution of entrapped air (8).

Three physically based models are used to interpret dissolved noble gas concentration data in groundwater: (1) unfractionated air, UA, model based on complete dissolution of entrapped air (7), (2) partial re-equilibration, PR, model based on complete dissolution of entrapped air bubbles followed by diffusive degassing (2), and (3) closed system equilibrium, CE, model based on incomplete dissolution of entrapped air (8). The PR and CE models both simulate excess air elemental fractionation, but PR fractionation is controlled by diffusivity whereas CE fractionation is controlled by gas solubility.

It is generally believed that the CE model best represents physical processes occurring during recharge (6), although few studies have systematically compared all three models. Aeschbach-Hertig et al. (8) showed that the CE model provided the best fit when comparing models using dissolved noble gas data from four diverse sites. Peeters et al. (9) used data from an aquifer in Niger to compare the three models and found that the CE and PR models both adequately fit elemental data; however, only the CE model fit isotopic data.

The process interpreted to control gas dissolution during groundwater recharge can have a significant impact on calculated recharge temperatures and  $^3\text{H}$ – $^3\text{He}$  groundwater ages (6, 8, 9). For example, incorrectly assuming complete dissolution of entrapped air (unfractionated excess air) results in erroneously low  $^3\text{H}$ – $^3\text{He}$  ages. Accurate determination of  $^3\text{H}$ – $^3\text{He}$  ages require an understanding of the processes affecting gas dissolution during groundwater recharge.

Understanding gas dissolution during groundwater recharge has broad implications for water resources management. Regions suffering from water shortages and poor water quality increasingly rely on (1) reclaimed municipal wastewater as a source of water, and (2) artificial recharge to store surface water for later reuse and to improve water quality (10) (herein we limit the definition of artificial recharge to recharge from surface sources actively managed to maximize recharge). Water quality improvement by artificial recharge largely results from microbially mediated, oxidation–reduction (redox) dependent degradation of organic compounds (e.g., trihalomethanes and endocrine-disrupting compounds) (11). Because of the importance of dissolved oxygen as a terminal electron acceptor, understanding gas dissolution processes is especially important for artificially recharged treated wastewater.

Objectives of this study were as follows: (1) quantify variability in observed dissolved noble gas concentrations across the study area, (2) compare measured data to previously published data, (3) examine possible causes of

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observed variability in dissolved noble gas concentrations, (4) evaluate ability of interpretive models to fit measured gas data, and (5) assess implications of these results for groundwater age-dating and groundwater management. This study is based on dissolved noble gas data from groundwater basins throughout California. Unique aspects of the study include the following: (1) the size of study area which is nearly twice that of any previous study of dissolved noble gases in groundwater, (2) the large range of physiographic (Coastal Plain, Central Valley, Sierra Nevada) and climatic (arid to humid) regimes, (3) the range of water management regimes (artificial recharge versus natural recharge), and (4) application of various interpretive models to a large and highly variable data set. The size of this study provides a unique opportunity to assess factors controlling excess air generation during groundwater recharge.

## Materials and Methods

**Overview of Study.** Samples evaluated in this study were collected as part of a statewide, comprehensive assessment of groundwater contamination vulnerability in California ([www.swrcb.ca.gov/gama](http://www.swrcb.ca.gov/gama)).  $^3\text{H}$ – $^3\text{He}$  groundwater age was used in combination with analyses of ubiquitous contaminants at ultralow levels to assess the relative probability that drinking water aquifers will become contaminated with anthropogenic pollutants. Dissolved noble gas analyses were used to calculate  $^3\text{H}$ – $^3\text{He}$  groundwater ages (12).

Nearly all of the wells in this study are public drinking water supply wells. There are ~16,000 public supply wells in California; wells sampled for this study are a subset from large metropolitan areas (Los Angeles, San Jose, and Sacramento), as well as several smaller population centers (e.g., Bakersfield, Chico, Stockton) and rural areas that rely on groundwater for drinking water supply (see Supporting Information for sample locations). Wells were selected according to the following criteria: (1) spatial distribution for the groundwater basin, including depth distribution that represents the exploited aquifers, (2) availability of well information such as total depth, open intervals, typical pumping rate, and year of construction, and (3) availability for sampling during the study period. The sample set almost exclusively comprises deep (>50 m total depth below ground surface), long-screened/perforated (>50 m open interval), high production (>  $10^{-2}$  m<sup>3</sup> s<sup>-1</sup>) wells actively used for drinking water supply.

**Sampling and Analysis.** Dissolved noble gas samples were collected using standard sampling techniques. Samples were collected by connecting the sample vessel (8 mm i.d. copper tubing, 250 mm long) to the wellhead of operating (pumping) wells with clear tygon tubing at full wellhead pressure. Water flowed for several minutes to purge air bubbles. The copper tubing was tapped lightly to dislodge bubbles and a visual inspection for bubbles was made. Steel clamps pinched the copper tubing flat in two locations to secure the water sample. Tritium samples were collected in 1 L glass bottles.

Sample analyses were performed at Lawrence Livermore National Laboratory (LLNL). Reactive gases were removed with multiple reactive metal getters. Known quantities of isotopically enriched  $^{22}\text{Ne}$ ,  $^{86}\text{Kr}$ , and  $^{136}\text{Xe}$  were added to provide internal standards. The isotope dilution protocol used for measuring noble gas concentrations is insensitive to potential isotopic composition variation in dissolved gases (especially Ne) from diffusive gas exchange. Noble gases were separated from one another using cryogenic adsorption. Helium was analyzed using a VG-5400 noble gas mass spectrometer. Other noble gas isotopic compositions were measured using a quadrupole mass spectrometer. The Ar abundance was determined by measuring the total noble gas sample pressure using a high-sensitivity capacitive manometer. The procedure was calibrated using water

samples equilibrated with the atmosphere at a known temperature and pressure. Tritium concentrations were determined on 500 g subsamples by the  $^3\text{He}$  in-growth method (approximately 15 day accumulation time). Analytical uncertainties are approximately 1% for  $^3\text{He}/^4\text{He}$ , 2% for He, Ne, and Ar, and 3% for Kr and Xe.

**Modeling.** The total measured concentration of dissolved noble gas is the sum of equilibrium, excess air, and radiogenic components (6). Helium may have an additional radiogenic component, tritiogenic  $^3\text{He}$  (6, 12). Addition of excess air has the greatest relative impact on He and Ne concentrations because the equilibrium component is relatively small. A common way to represent the amount of excess air is as percent Ne,  $\Delta\text{Ne}$  (excess Ne relative to equilibrium component) (6).

Helium is commonly excluded from noble gas modeling because of the presence of radiogenic or tritiogenic sources. Calculation of equilibrium and excess air components of He are required to quantify tritiogenic  $^3\text{He}$  which is used to calculate  $^3\text{H}$ – $^3\text{He}$  groundwater ages (12). Helium concentrations are impacted more by excess air than Ne; therefore, the model used to determine excess air can have a significant impact on calculated  $^3\text{H}$ – $^3\text{He}$  ages (6).

Measured Ne, Ar, Kr, and Xe concentrations were fitted by UA, PR, and CE models using NOBLE90 to solve for excess air, degree of excess air fractionation (in CE and PR models only), and recharge temperature. NOBLE90 is an error weighted, least-squares fitting, inverse modeling program (8, 13). Additional details of the modeling and goodness of fit criteria are presented in the Supporting Information.

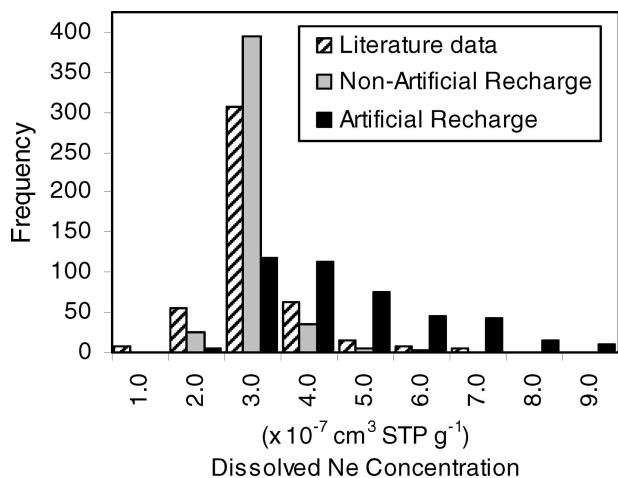
## Results and Discussion

Dissolved Ne, Ar, Kr, and Xe were measured on 905 samples. Dissolved He and  $^3\text{He}/^4\text{He}$  were measured in all but one of the samples, and  $^3\text{H}$  was measured in all but six samples (see Supporting Information for measured data and sample locations).

**Spatial Characterization.** To spatially characterize the data, samples were grouped into six geographic regions: (1) San Francisco Bay Area (SFBA), (2) Los Angeles Basin (LAB), (3) igneous/volcanic aquifers of northern California (NC), (4) Mojave Desert Basin (MDB), (5) northern portion of the Central Valley (NCV), and (6) southern portion of the Central Valley (SCV) (see Supporting Information for sample locations). All of the regions are alluvial basins with the exception of NC. Seasonal timing of precipitation is similar for all regions, with  $\geq 80\%$  of precipitation occurring from November through April. The total amount of precipitation varies greatly among the six regions (~150 mm yr<sup>-1</sup> in MDB to ~1000 mm yr<sup>-1</sup> for some NC sample locations).

Dense population and large-scale irrigated agriculture have led to significant modification of the natural hydrologic cycle in California. Water is transferred from northern and eastern portions of California to heavily populated coastal areas (e.g., SFBA and LAB). Irrigated agriculture has considerably altered the natural groundwater and surface water flow regimes throughout the Central Valley, where many areas are severely overdrafted and recharge is dominated by net irrigation return flow (14). The current situation masks natural environmental forcing such as precipitation, temperature, and vegetative cover. Furthermore, because sampled wells all have long open intervals, samples are composites of waters recharged under various conditions. Detailed spatial characterization is therefore unrealistic, yet regional differences in dissolved gas concentrations are apparent.

High Ne concentrations are most commonly associated with locations having long-term artificial recharge. Major artificial recharge facilities in LAB, SFBA, and Bakersfield (which is in the SCV region) have been operational for decades (15–18). High Ne concentrations in areas impacted by artificial



**FIGURE 1.** Histogram of Ne concentrations for: literature data (1–5, 19–36), artificial recharge impacted areas (SFBA, LAB, and Bakersfield), and nonartificial recharge impacted areas.

recharge contrast sharply with both the remainder of this data set and also literature data (Figure 1). Literature data are from studies in a wide range of climatic and hydrogeologic settings (463 samples from 23 different studies) (1–5, 19–36). Median Ne concentration in areas impacted by artificial recharge is 50% greater than that in the literature evaluated, while in areas not impacted by artificial recharge it is 3% less than the literature value. In contrast to Ne, all Xe concentrations fall in a relatively narrow range. Spatial differences in gas concentrations decrease with increasing molecular weight.

Data from the SCV region point to artificial recharge as the cause of high Ne concentrations. The SCV region is relatively uniform in terms of land use (irrigated agriculture), geology, and climate. However, Bakersfield is the only SCV area in our study that has a history of intensive artificial recharge. The mean Ne concentration of samples from Bakersfield ( $n = 43$ ) is 49% greater than samples from the remainder of SCV ( $n = 182$ ).

As noted earlier, excess air has the greatest relative impact on the lightest gases. The unique data from areas impacted by artificial recharge indicate large amounts of excess air that cannot be attributed to sampling (e.g., trapped bubbles in sampling device) or analytical problems because many of the samples with high gas concentrations were reanalyzed and showed good replication.

**Noble Gas Models.** The UA model is a limiting case of both models incorporating fractionation; therefore, fractionation models always fit more samples than the UA model. The fractionation models fit slightly more samples than the UA model for all regions; however, the greatest difference is for areas impacted by artificial recharge (Table 1).

Correlation between measured and modeled gas concentrations for samples fit by fractionation models was greatest for Ne ( $R^2_{CE} = 0.9998$ ,  $R^2_{PR} = 0.9997$ ) and least for Kr ( $R^2_{CE} = 0.982$ ,  $R^2_{PR} = 0.984$ ) (see Supporting Information for plots of modeled versus measured gas concentrations). Model errors (relative difference between measured and modeled gas concentrations) between the gases provide additional insight. Visual inspection of model error scatter plots reveals correlations (Figure 2). Negative correlation exists between gases with similar molecular weights (e.g., Kr–Xe), which is consistent with model errors produced when modeling synthetic data.

**Excess Air.** Of samples fit by the CE model, those in artificially recharging areas had much higher median excess air (89%  $\Delta$ Ne) than samples from nonartificial recharging areas (28%  $\Delta$ Ne) (results of the other models are comparable, see Supporting Information). Samples not fit by the models

**TABLE 1.** Number of Samples Fit by Each Model for a Given Region According to Criteria Discussed in the Supporting Information (AR refers to artificial recharge impacted areas (i.e., SFBA, LAB, and Bakersfield))

area	number of samples	samples fit		
		UA	CE	PR
SFBA	221	147	148	147
LAB	170	129	147	149
NC	31	27	31	31
MDB	64	57	63	63
NCV	194	179	182	182
SCV	225	195	216	211
AR	434	305	337	338
non-AR	471	429	450	445
total	905	734	787	783

tended to have greater average Ne concentrations (by a factor of 1.6). Inability of the models to fit samples with large Ne concentrations is reflected in the lower proportion of samples from artificial recharge areas fit by the models (Table 1). The reason that models do not fit samples with large Ne concentrations may be nonequilibrium effects (e.g., gas dissolution stopping prior to attaining equilibrium between entrapped gas and dissolved gas). Kinetic factors may control dissolved gas concentrations (37), especially in locations with high recharge flux.

Neon, Ar, Kr, and Xe concentrations do not allow one to clearly differentiate between the CE and PR models. Peeters et al. (9) explain the benefit of isotopic data for distinguishing between the CE and PR models; however, isotopic data are not available in this study. In the absence of isotopic data, an examination of model-predicted He concentrations can help differentiate the models. Helium data were not used for modeling but NOBLE90 outputs predicted He concentrations. The range of predicted He:Ne ratios from the CE model is limited because He:Ne in the excess air component can only range from that of air (0.288) to that of air saturated water (0.230 at 10 °C), whereas the PR model has a theoretical lower limit of zero. Over 160 samples—the majority of which are fit by the PR model—have low measured He:Ne ratios that cannot be readily explained by either the UA or CE models (Figure 3). Approximately two-thirds of these samples are from areas impacted by artificial recharge. The 160 samples represent a minimum number as some samples may have had low He:Ne ratios immediately after recharge followed by addition of radiogenic He. These results are consistent with diffusive degassing; however, elemental ratios alone can not be considered conclusive evidence of diffusive degassing. The authors of the present study are unaware of any groundwater studies that present evidence of dissolved noble gas fractionation by diffusive degassing, although studies have shown degassing caused by CO<sub>2</sub>/CH<sub>4</sub> gas stripping (32, 38).

It is clear that for high excess air concentrations, excess air is less fractionated (e.g., lower CE model fractionation factor  $F$  values, where  $F = v/q$ ,  $v$  is the ratio of entrapped gas volumes in final and initial states, and  $q$  is the ratio of dry gas pressures in entrapped air to that in the atmosphere (8)) (Figure 4). This is expected because pore spaces hold a finite amount of entrapped air in bubbles and as dissolution of entrapped air continues the excess air component becomes decreasingly fractionated until the entrapped air completely dissolves. The upper bound of excess air observed in this study is 400–500%  $\Delta$ Ne or  $\sim 0.05$  cm<sup>3</sup> at standard temperature and pressure (STP) per gram of water, cm<sup>3</sup> STP g<sup>-1</sup> (as air; Figure 4). This is reasonable given that the amount of entrapped air in quasi-saturated porous media is  $> 0.05$  cm<sup>3</sup> STP g<sup>-1</sup>, as reported from laboratory pycnometer measure-

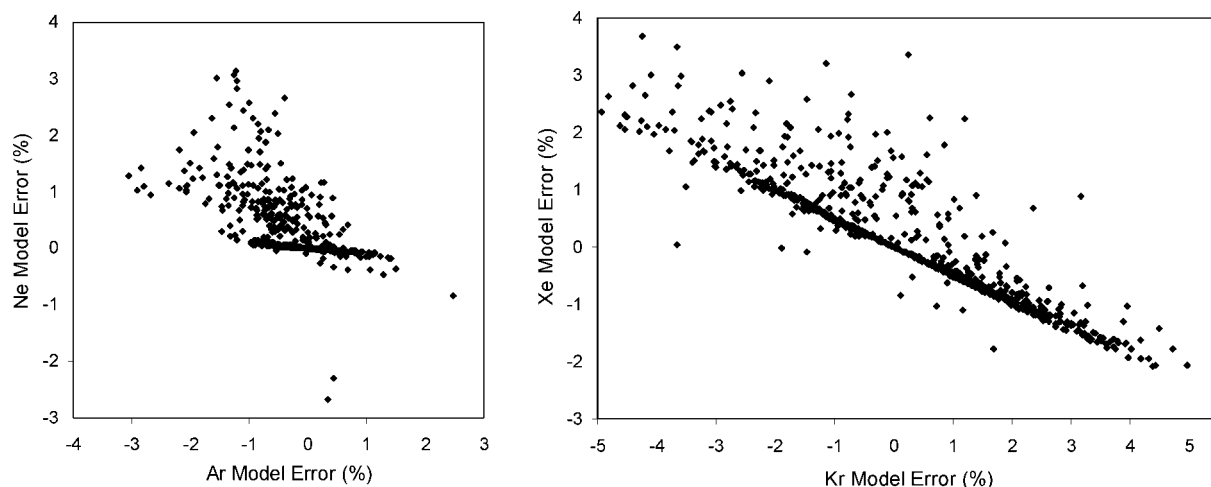


FIGURE 2. Scatter plots of model error (relative difference between modeled and measured gas concentrations) for samples fit by the CE model. Results from the other models are comparable. Note that analytical uncertainties are approximately 2% for Ne and Ar, and 3% for Kr and Xe.

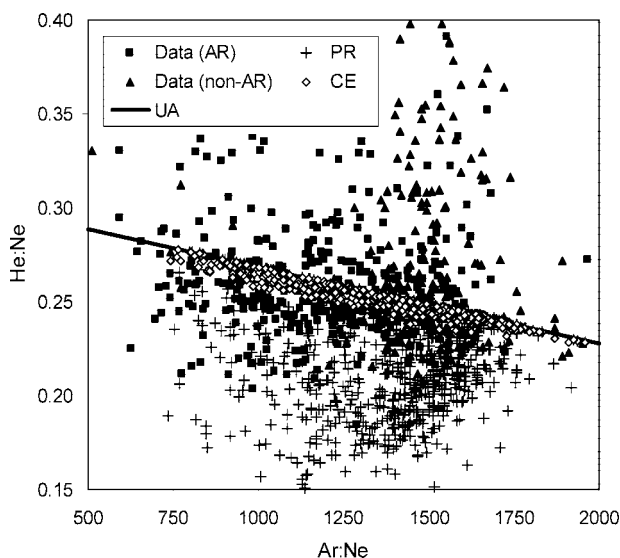


FIGURE 3. Element ratios for (1) measured gas concentrations for artificial recharge impacted areas (AR) and non-AR areas, and (2) total model-predicted gas concentrations (UA, CE, and PR). Measured ratios below the cluster of CE points cannot be explained by the UA or CE models and are consistent with diffusive degassing or other fractionating processes. The UA model-predicted ratios lie on the line shown. Not all data are shown at this scale.

ments (39) and field experiments using a neutron probe (40). Stonestrom and Rubin (39) measured entrapped air in alluvium (i.e., Oakley sand) from the NCV region and reported a range of  $0.09\text{--}0.14\text{ cm}^3\text{ g}^{-1}$  under capillary saturation at  $21^\circ\text{C}$  (STP values would be even greater because the pressure of entrapped air was unknown).

Excess air concentrations are strongly correlated with the CE model parameter  $q$  (Figure 4), consistent with results of Aeschbach-Hertig et al. (41). Aeschbach-Hertig et al. (41) and Kipfer et al. (6) assert that  $q$  is a semiquantitative measure of hydrostatic pressure exerted on entrapped air and therefore of water table fluctuations. The upper range of these data would then indicate water table fluctuations of  $>20\text{ m}$  assuming all the pressure was generated hydrostatically (interfacial tension only produces such high pressures for bubble radii  $<0.001\text{ mm}$ ). It is unlikely that such large water table fluctuations naturally occur in any of the study regions. An alternative mechanism that could generate large  $q$  values

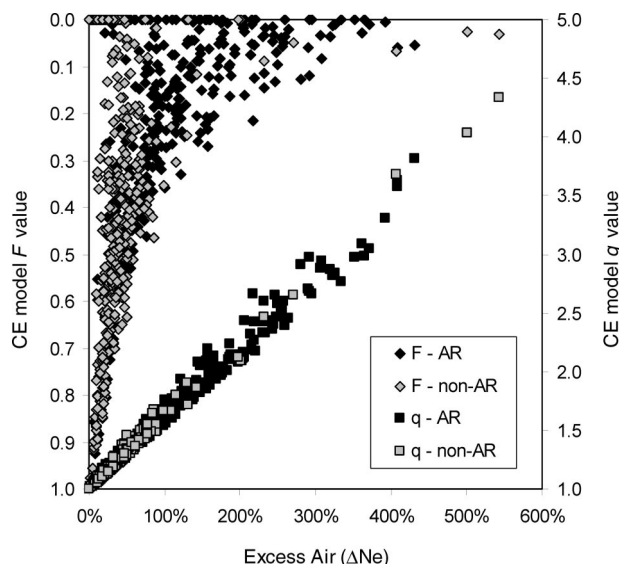
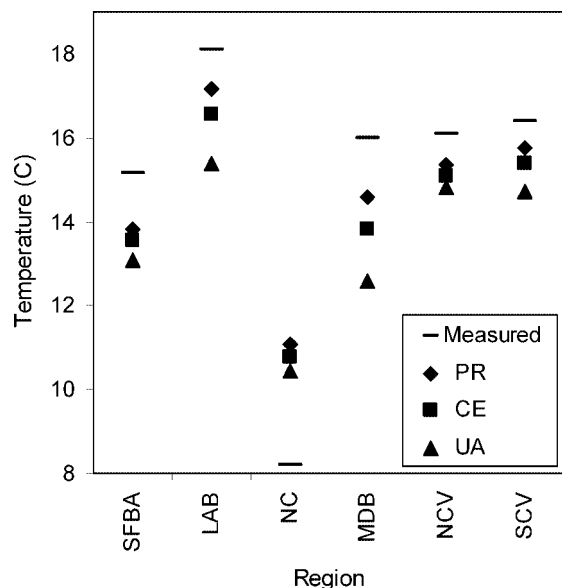


FIGURE 4. Relationship between CE model parameters and excess air. As excess air increases, the degree of fractionation decreases. Note that the CE model reduces to the UA model when  $F = 0$ . One data point is not shown at the given scale ( $\Delta\text{Ne} = 737\%$ ,  $F = 0.031$ ,  $q = 5.8$ ).

(large hydrostatic pressures) is entrainment of entrapped bubbles in areas of high recharge. Bubbles could be transported to sufficient depths to cause dissolution of large amounts of excess air.

**$^3\text{H}\text{--}^3\text{He}$  Age-Dating.** The choice of excess air model has an impact on interpreted  $^3\text{H}\text{--}^3\text{He}$  groundwater ages, especially for the youngest waters (12). Normally the excess air component of He is determined based on Ne data alone and assumes no gas fractionation (6, 12). Kipfer et al. (6) and Aeschbach-Hertig et al. (8) demonstrate that the assumption of no gas fractionation may give unreasonably low ages (even negative values of tritiogenic He).

The interpreted ages resulting from each of the three excess air models vary systematically as discussed by Peeters et al. (9). The oldest age is calculated by PR, the youngest age is calculated by UA, while the CE model yields ages between the PR and UA models (see Supporting Information for histogram of calculated  $^3\text{H}\text{--}^3\text{He}$  ages). The reason is that the interpreted excess air component of He is maximized for unfractionated conditions. A larger excess air component of He results in a lower interpreted tritiogenic He component



**FIGURE 5.** Median calculated recharge temperatures from each of the three models. The measured data are mean annual air temperatures taken from the United States Historical Climatology Network (data available at <http://www.ncdc.noaa.gov/ol/climate/research/ushcn/ushcn.html>) and are the medians of stations nearest each sample location.

for a given total measured amount of He, and a younger interpreted age. As expected the difference between PR and CE calculated ages is more pronounced for samples having higher excess air, for artificial recharge areas the mean difference is 4.1 yr ( $n = 170$ ) versus 3.6 yr for nonartificial recharge areas ( $n = 144$ ). Samples with  $^3\text{H} < 3 \text{ pCi L}^{-1}$ , negative calculated tritogenic  $^3\text{He}$ , or calculated ages  $> 55$  yr were excluded. Age-dating calculations assumed radiogenic  $^3\text{He}/^4\text{He} = 2.0 \times 10^{-8}$  and no mantle derived He.

The differences in interpreted groundwater ages were greatest for (1) younger samples, and (2) samples with fractionated excess air. These results are consistent with the literature (6) and suggest calculating groundwater age without considering gas fractionation will underestimate groundwater age, especially if diffusive degassing occurs.

**Recharge Temperature.** Model recharge temperatures generally range from lowest to highest in the following order; UA, CE, PR (Figure 5 and Supporting Information). Because Xe solubility increases substantially with decreasing temperature, calculated recharge temperature (which is based on the equilibrium solubility component) tends to be higher for fractionation models than for the UA model. In other words, fractionation models tend to produce higher calculated recharge temperatures than the UA model because more of the total Xe is attributed to the excess air component (and less to the equilibrium component) in fractionation models. An evaluation of the relationship between model recharge temperature differences and amount of excess air did not reveal a clear correlation.

The mean calculated recharge temperature of each region broadly tracks the measured mean annual air temperature (MAAT) for each of the three models (Figure 5). In virtually all cases soil temperatures are slightly greater (1–3 °C) than MAAT; therefore, it is common for NGTs to be greater than MAAT (6). These data show the opposite relationship, which is unusual but not unprecedented (33). There are possible reasons that NGTs are less than MAAT. Groundwater recharge may reflect winter temperatures rather than MAAT because of focused seasonal recharge. Spring snowmelt runoff from uplands (e.g., Sierra Nevada) into the alluvial basins causes focused recharge from surface channels (rivers, streams,

canals). Also, MAAT data used in this analysis are referenced to well location rather than recharge location. Detailed analyses of recharge areas for each well are beyond the scope of this study; however, it is likely that some groundwater recharged near basin edges at higher elevations and cooler temperatures than the wellhead (especially MDB). Furthermore, the assumption that the recharge elevation is the wellhead elevation may yield incorrect NGTs.

**Artificial Recharge.** The most plausible reason for the large excess air concentrations is artificial recharge. Presently LAB and SFBA artificially recharge  $\sim 4.0 \times 10^8$  and  $> 1.0 \times 10^8 \text{ m}^3 \text{ yr}^{-1}$ , respectively; which is greater than half of groundwater pumping for each area (16, 42, 43). Operational procedures of large-capacity artificial recharge facilities in LAB provide the necessary conditions to dissolve large amounts of air (18). Specifically Reichard et al. (42) present data from shallow wells near artificial recharge facilities in LAB with annual head fluctuations  $> 10 \text{ m}$  (well 2S/12W-14J1 1590F) and Mills (18) notes a sustained percolation rate of  $1.2 \text{ m s}^{-1}$  at an artificial recharge facility in LAB. Furthermore, Anders and Schroeder (17) suggest that a measured increase in redox potential of an artificially recharged groundwater plume in LAB may be caused by large amounts of excess air.

Management of artificial recharge facilities can have a major impact on the amount of dissolved gas in recharging water. Continual buildup of clogging layers on the bottom of spreading basins necessitates periodic drying to allow degradation and/or removal of clogging layers (18). Optimal management balances the effects of increased recharge flux caused by removal of low permeability clogging layers against the interruption to recharge caused by basin drying/cleaning. An additional operational consideration is reduced hydraulic conductivity following basin drying caused by the presence of newly entrapped air. Therefore, frequency and duration of basin drying strongly influence the amount of excess air in groundwater recharged from artificial recharge facilities.

The majority of samples not fit by the models (75–82% depending on model) are from areas impacted by artificial recharge (Table 1). Using such models to determine recharge parameters of samples in areas impacted by artificial recharge is challenging. Artificial recharge may occur at temperatures different from the local average water table temperature due to seasonal recharging activities and heating of water in spreading basins. For example, temperatures of surface water used for artificial recharge in LAB can vary from 10 to 35 °C annually (44). It is also likely that many well water samples are mixtures of naturally recharged and artificially recharged waters. Furthermore, it is unlikely that gas dissolution occurs under equilibrium conditions under very high recharge fluxes. Nonequilibrium gas dissolution during groundwater recharge has received relatively little attention (37), but is likely to occur during artificial recharge and other rapid infiltration scenarios (e.g., highly conductive river beds).

California, like many other regions with water supply challenges, is increasingly using reclaimed wastewater as a source for artificial recharge (17, 42). Fate and transport of organic compounds such as disinfection byproducts (e.g., trihalomethanes) and endocrine-disrupting compounds in artificially recharged wastewater is a major water quality concern in California (10, 17) and in many other areas (11). California has proposed that artificially recharged wastewater have a minimum subsurface residence time of 6 months to allow degradation of contaminants (10). The contribution of dissolved  $\text{O}_2$  in excess air plays a critical role in the redox chemistry of groundwater and therefore the fate of many organic pollutants (11). The proportion of dissolved  $\text{O}_2$  added by excess air relative to equilibrium solubility,  $\Delta\text{O}_2$ , is less than  $\Delta\text{Ne}$  ( $\Delta\text{O}_2/\Delta\text{Ne}$  is  $\sim 0.3$  for unfractionated air, but can exceed 0.5 for fractionated conditions). Therefore artificially

recharged groundwater could have a dissolved O<sub>2</sub> concentration up to twice that of equilibrium solubility.

Improved understanding of excess air generation is key for both managing the physical process of artificial recharge and predicting water quality changes related to artificial recharge. Few studies have addressed the issue of gas dissolution during artificial recharge (43, 45). Long-term field studies in well characterized media would be particularly helpful in assessing the impact of dissolved gases on artificially recharged groundwater.

Three main noble gas models exist to interpret dissolved gas concentrations. Parameters deduced from model output (recharge temperatures or <sup>3</sup>H–<sup>3</sup>He ages) systematically differ among models because of the different physical processes upon which the models are based. As demonstrated in this study, all three models may adequately fit measured data. This suggests that goodness-of-fit is not a robust indicator for model appropriateness and caution is necessary when interpreting results from noble gas modeling. Furthermore, gas concentration ratios suggest that diffusive degassing may have occurred. Further research aimed at understanding the physical processes controlling gas dissolution during groundwater recharge is warranted. For example, analyses of dissolved gas isotopic ratios would provide information on the possible occurrence of diffusive degassing at artificial recharge sites.

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## Supporting Information Available

Details of noble gas models and their application using NOBLE90, tabulation and statistical summary of dissolved gas concentrations and calculated quantities, and figures showing sample locations, modeled versus measured gas concentrations, differences between calculated recharge temperatures, and calculated <sup>3</sup>H–<sup>3</sup>He ages for each of three models. This information is available free of charge via the Internet at <http://pubs.acs.org>.

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