A partial exponential lumped parameter model to evaluate groundwater age distributions and nitrate trends in long-screened wells

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SUMMARY

A partial exponential lumped parameter model (PEM) was derived to determine age distributions and nitrate trends in long-screened production wells. The PEM can simulate age distributions for wells screened over any finite interval of an aquifer that has an exponential distribution of age with depth. The PEM has 3 parameters – the ratio of saturated thickness to the top and bottom of the screen and mean age, but these can be reduced to 1 parameter (mean age) by using well construction information and estimates of the saturated thickness. The PEM was tested with data from 30 production wells in a heterogeneous alluvial fan aquifer in California, USA. Well construction data were used to guide parameterization of a PEM for each well and mean age was calibrated to measured environmental tracer data (3H, 3He, CFC-113, and 14C). Results were compared to age distributions generated for individual wells using advective particle tracking models (PTMs). Age distributions from PTMs were more complex than PEM distributions, but PEMs provided better fits to tracer data, partly because the PTMs did not simulate 14C accurately in wells that captured varying amounts of old groundwater recharged at lower rates prior to groundwater development and irrigation. Nitrate trends were simulated independently of the calibration process and the PEM provided good fits for at least 11 of 24 wells. This work shows that the PEM, and lumped parameter models (LPMs) in general, can often identify critical features of the age distributions in wells that are needed to explain observed tracer data and nonpoint source contaminant trends, even in systems where aquifer heterogeneity and water-use complicate distributions of age. While accurate PTMs are preferable for understanding and predicting aquifer-scale responses to water use and contaminant transport, LPMs can be sensitive to local conditions near individual wells that may be inaccurately represented or missing in an aquifer-scale flow model.

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1. Introduction

The susceptibility of a well to contamination depends on the distribution of groundwater age captured by the well. The age distribution reflects the combined effects of velocity, dispersion, and travel distance on parcels of water that recharged the aquifer and traveled to a well. Calibration of lumped parameter models (LPMs) to environmental tracer data has been the most common method for estimating groundwater age distributions at wells (Maloszewski and Zuber, 1982; Turnadge and Smerdon, 2014). Recent work has focused on the inclusion of mixed tracers of young and old groundwater in the calibration process (Corcho Alvarado et al., 2007; Solomon et al., 2010; Jurgens et al., 2012, 2014; Visser et al., 2013) and ways to improve the estimation of age distributions given uncertainty in tracer concentrations and their history in recharge, model complexity, transient distributions of age, or by using shape-free or general distributions such as the gamma or log-normal distribution (Long and Putnam, 2006; Massoudieh et al., 2012, 2013, 2014; Massoudieh, 2013; Green et al., 2014).

As work in this area progresses, there is still a need for the development and testing of simple, physically based age distribution models. The calibration of LPMs to tracer data can often be limited to a single tracer at a well and so it may not be possible to obtain an estimate of the age distribution using a complex LPM (2 or more model parameters) without estimating values of the other parameters. Even when the collection effort includes
several tracers, the data may not yield multiple tracer concentrations that can be used in the calibration process because of the absence of measurable concentrations, or because degradation, contamination, or sampling issues lead to unreliable results.

The purpose of this study was to (1) develop a partial exponential model (PEM) for groundwater age distributions and (2) test the model in an aquifer where hydrogeology and groundwater age was previously studied (Burrow et al., 2008; Green et al., 2010, 2014), where multiple environmental tracer data were available, and where nonpoint-source nitrate contamination trends have been documented (Landon et al., 2011). In this paper, we present the equations for a partial exponential model (PEM) that can be parameterized using well construction information and saturated thickness. The PEM was calibrated to environmental tracer data for 30 long-screened production wells (mostly public-supply) in the central eastside of the San Joaquin Valley, California. In this aquifer, heterogeneity of the sediments is expected to give rise to complex distributions of age that would not be expected to mimic the simpler distributions predicted by an exponential distribution of age with depth in the aquifer. For comparison with the PEMs, age distributions for each well also were generated using advective particle tracking models (PTMs) within a numerical groundwater flow model of the regional aquifer. Each age distribution was used to evaluate the histories of tracer concentrations in recharge for travel time delays through the unsaturated zone (UZ) and for dilution or enrichment of tracer concentrations from the application of surfacewater and groundwater for irrigation. Mean ages, recharge rates, and age distributions from the PTMs and PEMs were compared in order to understand the limitations of the different approaches, given the complexity of hydrogeology and land use in this system. Finally, current and historic nitrate concentrations were simulated for the calibrated PTMs and PEMs. These predictions can provide an independent evaluation of model performance, information about the stability of groundwater age in wells over time and factors affecting nitrate transport in the aquifer.

2. Description of study area

The study area is located within the Central Valley of California (Fig. 1). The Central Valley is a large, northwest-trending, asymmetric structural trough filled with marine and continental sediments up to 10 km thick (Page, 1986). The southern two-thirds of the Central Valley is the San Joaquin Valley (SJV), which is more than 400 km long and 30–90 km wide. East of the Central Valley, the Sierra Nevada rise to an altitude of more than 2500 m; west of the Valley, the Coast Ranges form a series of parallel ridges up to 1500 m high (Gronberg et al., 1998). Streams in the northern part of the SJV drain northward through the San Joaquin River to the San Francisco Bay; the southern part of the SJV is a hydrologically closed basin.

The study area is about 2700 km² and is bounded on the west by the San Joaquin River, on the north near the Stanislaus River, on the south near the Merced River, and on the east by the Sierra Nevada foothills (Fig. 1). These boundaries correspond to those used for the numerical groundwater flow model used in this paper (Phillips et al., 2007a,b).

Land-surface elevation in the study area rises from near sea level along the axial trough in the center of the SJV to more than 100 m at the top of dissected older alluvium near the valley margins. The climate is arid-to-semiarid, characterized by cool, wet winters and hot, dry summers. Precipitation averaged 315 mm annually from 1931 to 1997 (National Oceanic and Atmospheric Administration, 2005).

The aquifer system can be generally described as an unconfined to semi-confined aquifer underlain by a confined aquifer, where separated by a regional lacustrine clay unit commonly referred to as the Corcoran Clay (Williamson et al., 1989; Bertoldi et al., 1991). Aquifer materials are dominated by eastern and western alluvial fan deposits interspersed with fine-grained basin and floodplain deposits, and coarser-grained fluvial deposits.

Since 1850, diversion of surface water from streams and intensive groundwater pumping associated with agricultural irrigation and urban growth has substantially altered the natural flow system (Davis et al., 1959; Page and Balding, 1973; Londquist, 1981; Williamson et al., 1989). Development of the groundwater resource accelerated after about 1930 due to improvements to the turbine pump, which allowed farmers to pump groundwater from greater depths at greater rates (Williamson et al., 1989). At the time of this study, percolating irrigation water was the primary form of groundwater recharge, and pumping was the primary form of groundwater discharge (Faunt, 2009).

The widespread use of groundwater has caused water-level declines in many parts of the SJV and has greatly reduced the extent of artesian conditions. Depth-to-water varies east-to-west and north-to-south. In the study area (Fig. 1), depth-to-water can be more than 35 m near the SJV margins in the east and less than 3 m near the axial trough in the center of the basin. In urban areas, focused groundwater pumping and relatively low recharge rates have caused water-level depressions within Modesto and Turlock (Burrow et al., 2004; Phillips et al., 2007b).

Agriculture is the primary land use in the area and increased annual application of nitrogen fertilizers over the last 50 years resulted in concentrations of nitrate in recharge that were significantly higher than background levels (approx. 2 mg/L as N). Recently, the Priority Basin Project of the California Groundwater Ambient Monitoring and Assessment (GAMA-PBP) program found nitrate concentrations were either high (above USEPA MCL of 10 mg/L as N) or moderately high (above ½ the USEPA MCL) in 16.7% of the aquifer used for public-supply in the central eastside San Joaquin Valley (Landon et al., 2010).

3. Conceptual model of groundwater age

The age structure of groundwater in the Central Valley Aquifer has been radically altered over the last 150 years (Fig. 2). Prior to development, recharge to the aquifer was low (<10 mm/yr) and was mainly fed by streams draining the Sierra Nevada. Although the aquifer has sediments up to several km thick, increased clay content and consolidated material below 150 m may limit the connection to deeper parts of the aquifer (Burrow et al., 2004). Consequently, the groundwater age structure of the predevelopment system likely resembled an exponential distribution with some component of piston flow away from the streams and having a mean residence time greater than 10,000 years (blue line in Fig. 2).

Currently, irrigation with groundwater and imported surface water is the primary source of recharge and recharge rates can be 100 times higher than pre-development rates. The application of irrigation water and pumping from deep parts of the groundwater system have increased the downward movement of shallow groundwater and stratified both the chemistry and age of water in the aquifer (Fig. 2) (Landon et al., 2010, 2011). The groundwater age structure in the shallower part of the aquifer system reflects the rapid, post-development recharge rates and could resemble the age structure of an exponential model (black line in Fig. 2) if allowed to evolve through the entire saturated thickness. In contrast, the deeper part of the system reflects the low recharge rates of the pre-development system (blue lines in Fig. 2). The interface between groundwater recharged in pre- and post-development times (50 and 70 m below the water table in Fig. 2) is not uniform across the valley and may be deeper or shallower.
depending on local heterogeneities of aquifer properties and recharge rates. The combined age structure of the pre- and post-development systems is conceptualized in Fig. 2 and provides a simplistic view of groundwater age in the aquifer that may not be valid in places where heterogeneity causes substantial disturbances to the exponential age–depth profile. The first lower panel in Fig. 2 shows the hypothetical age–depth relationship that would be expected from a uniform recharge rate (0.4 m/yr) (black line) and from a binary model of recharge rates that are dramatically different, one representing a post-development part that lies above a predevelopment part with an interface between 50 and 70 m below the water table.

Wells that are screened across this interface can have \(^{14}C\) and \(^{3}H\) values that are inconsistent with an age model assuming a uniform recharge rate and produce bimodal age distributions that resemble truncated forms of the exponential model which are equivalent to the PEM. The middle panel of Fig. 2 shows that several wells in this study have \(^{14}C\) values that reflect mixing of pre-development and post-1950s groundwater or have values that entirely reflect the predevelopment or the post-development system.

4. Material and methods

Groundwater was collected from 30 production wells in the central-eastside of the San Joaquin Valley between March and June of 2006 as part of the California GAMA – PBP (Landon and Belitz, 2008; Landon et al., 2010). A description of sample collection methods and calculations of recharge temperature and environmental tracer concentrations are provided in the Supplemental Material. Tables of analytical concentrations of noble gases and chlorofluorocarbons, and results of recharge temperature analysis are given in Tables S1 and S2 in the Supplemental Material. Tritium was analyzed at all 30 wells and dissolved noble gases and isotopes of helium were analyzed at 29 wells; \(^{14}C\) was analyzed at 13 wells; and chlorofluorocarbons (CFCs) were analyzed at 10 wells. Tritogenic helium-3 (\(^{3}{}\)He\(_{\text{trig}}\)) was quantifiable (>1 TU) at 23 of the 30 wells (Table 1). Of the 10 wells where CFCs were analyzed, only 7 had at least one CFC compound that could be used for dating groundwater. In this study, only CFC-113 was used to date groundwater because of evidence for widespread contamination of CFCs by urban sources and partial degradation of CFC-11 in the area. A previous study by Jurgens et al. (2008) found that \(^{14}C\) concentra-
tions in this system were largely unaffected by dilution from 14C-free sources of carbonate or organic carbon and do not require adjustment for geochemical reactions within the saturated or unsaturated zone. Measurable amounts of radiogenic helium (4He rad) – the helium generated from the decay of uranium and thorium in aquifer material – were found in 22 of 29 samples that had noble gas measurements.

4.1. Atmospheric tracer input histories

Local histories of atmospheric tracer and nitrate concentrations in recharge were reported in the documentation of the program TracerLPM (Jurgens et al., 2012). Tritium concentrations in precipitation from 1953 to 2002 for the central eastside San Joaquin Valley area were estimated from updated monthly tritium data from Michel (1989; written communication, 2011). Tritium concentrations in precipitation prior to nuclear weapons testing were assumed to be about 3 TU based on the reconstructed tritium curve. Northern Hemisphere atmospheric mixing ratios of CFC-113 were obtained from the U.S. Geological Survey Chlorofluorocarbon Laboratory (2009).

The common co-occurrence of 3H greater than 0.2 TU and 14C less than 100 pMC indicated mixtures of old groundwater with low 14C originating from decay of naturally fluctuating paleo-atmospheric 14C levels since the late Pleistocene and young groundwater with elevated 14C concentrations that came from above-ground nuclear bomb testing since the early 1950s. To develop models of tracer concentrations for binary mixtures of old 14C and bomb-derived 14C, TracerLPM (Jurgens et al., 2012) provides a comprehensive 14C input curve that combines the 2009 international radiocarbon calibration curve (IntCal09; Reimer et al., 2009) with modern historical tropospheric 14C data for the northern hemisphere (zone 2; Hua and Barbetti, 2004). The combined curve allows consistency between lumped parameter model calculations of age and calibrated radiocarbon ages.

Radiogenic helium concentrations were calculated using a helium production rate of 6.08 \times 10^{-12} cubic centimeters at standard temperature and pressure per gram of water (cc/g) of water per year, which was based on average uranium and thorium sediment concentrations of 2.65 and 8.3 ppm, respectively (Phillips et al., 1993), with a porosity of 0.2 and bulk density of 2.2 (Jurgens et al., 2008). The simulated concentrations do not include a deep crustal flux or enhanced mineral weathering.

4.2. Age classification

To provide context for modeled and measured tracer concentrations on figures and tables, samples were categorized as Modern,
Table 1

Well construction and concentrations of environmental age tracers for long-screened wells in the central eastside San Joaquin Valley, California.

| Well ID | Sample date | Sample | CFC-113 atmos. mixing ratio | CFC-113 atmos. mixing ratio error | 14C helium, cc STP/g of H2O | 14C helium error | Radiogenic helium error, cc STP/g of H2O | Age class | Pumpage, m^3/day | Altitude, m (NAVD 88) | Simulated depth to water, m | Depth to top of screen, m | Depth to bottom of screen, m | Well depth, m |
|---------|-------------|--------|-----------------------------|-----------------------------------|-----------------------------|----------------|---------------------------------|----------|----------------|-----------------|----------------|-----------------|-----------------|----------------|----------------|
| CE-QPC-01 | 3/20/2006 10.8 | 0.6 | 57.8 | 1.3 | cont. | na | 111.9 | 11.2 | Modern | 2128 | 69.36 | 34.39 | 54.88 | wd | 85.37 |
| CE-QPC-02 | 3/22/2006 2.8 | 0.1 | 52.0 | 9.2 | Modern | 743 | 53.17 | 15.98 | 37.80 | wd | 91.46 |
| CE-QPC-03 | 3/28/2006 8.5 | 0.4 | 43.8 | 1.0 | Modern | 1250 | 70.63 | 26.32 | 3.05 | wd | 86.89 |
| CE-QPC-FP01 | 5/3/2006 1.7 | 0.1 | Modern | 287 | 70.73 | 36.15 | 96.04 | 184.76 | 186.28 |
| MER-02 | 3/29/2006 5.2 | 0.4 | 50.4 | 9.1 | 48.1 | 5.2 | 83.4 | 8.3 | 2.12E-07 | 1.17E-08 | Mixed | 727 | 42.68 | 17.18 | 91.46 | wd | 156.10 |
| MER-04 | 3/30/2006 3.7 | 0.2 | 3.1 | 0.3 | Modern | 250 | 51.61 | 4.99 | 7.62 | wd | 22.87 |
| MER-15 | 4/18/2006 8.5 | 0.3 | 26.0 | 0.7 | Modern | 250 | 69.21 | 35.40 | 44.21 | wd | 56.40 |
| MOD-01 | 3/13/2006 5.6 | 0.4 | 26.1 | 7.8 | 65.5 | 5.6 | 93.3 | 9.3 | 1.82E-07 | 9.93E-09 | Modern | 329 | 22.07 | 5.79 | 24.70 | wd | 36.89 |
| MOD-02 | 3/14/2006 4.0 | 0.4 | 34.6 | 3.6 | cont. | na | 98.7 | 9.9 | 7.90E-08 | 5.96E-09 | Modern | 13,381 | 27.86 | 10.04 | 27.74 | 111.59 | 120.43 |
| MOD-03 | 3/20/2006 4.1 | 0.2 | <1 | na | Modern | 755 | 25.69 | 8.34 | 54.88 | wd | 77.74 |
| MOD-04 | 3/20/2006 1.6 | 0.1 | 11.2 | 0.9 | 9.6 | 0.8 | 32.7 | 3.2 | 1.28E-08 | 3.90E-09 | Modern | 1392 | 22.34 | 7.14 | 50.00 | 84.15 | 92.68 |
| MOD-05 | 3/20/2006 4.8 | 0.2 | 32.3 | 2.8 | Modern | 870 | 29.93 | 7.49 | 43.28 | 82.62 | 89.02 |
| MOD-06 | 3/21/2006 2.4 | 0.1 | 38.1 | 10.6 | Modern | 730 | 27.87 | 9.71 | 39.02 | 58.54 | 65.85 |
| MOD-07 | 3/21/2006 4.6 | 0.3 | nq | na | Modern | 723 | 29.09 | 11.19 | 47.26 | 68.60 | 70.43 |
| MOD-08 | 3/21/2006 5.3 | 0.2 | 65.3 | 5.6 | Modern | 491 | 50.76 | 15.28 | 60.98 | wd | 90.24 |
| MOD-09 | 3/21/2006 1.0 | 0.3 | 7.0 | 0.3 | 1.7 | 1.0 | 0.3 | 95.2 | 9.5 | Modern | 250 | 61.89 | 26.34 | 93.60 | wd | 103.05 |
| MODFP-04 | 3/30/2006 10.9 | 0.6 | 70.7 | 1.6 | Modern | 239 | 40.99 | 14.17 | 35.37 | wd | 83.84 |
| TRLK-01 | 3/15/2006 0.1 | 0.2 | nq | na | 2.0 | 0.0 | 14.2 | 1.4 | 1.11E-06 | 4.65E-08 | Modern | 53 | 31.71 | 7.35 | 85.37 | wd | 106.10 |
| TRLK-02 | 3/16/2006 1.7 | 0.2 | 22.2 | 7.4 | 5.1 | 1.7 | 56.5 | 5.7 | 1.74E-07 | 9.32E-09 | Mixed | 765 | 32.62 | 7.62 | 54.88 | 76.83 | 82.93 |
| TRLK-03 | 3/21/2006 0.1 | 0.2 | nq | na | cont. | na | 19.2 | 1.9 | 3.71E-07 | 1.74E-08 | Modern | 1018 | 38.72 | 12.01 | 70.12 | 140.24 | 151.52 |
| TRLK-04 | 3/22/2006 8.0 | 0.3 | 43.7 | 4.6 | Modern | 251 | 53.17 | 18.36 | 31.71 | wd | 101.22 |
| TRLK-05 | 3/22/2006 0.4 | 0.2 | 30.4 | 18.0 | Modern | 7717 | 32.62 | 9.32 | 62.20 | 139.33 | 143.90 |
| TRLK-06 | 3/22/2006 9.2 | 0.4 | 50.5 | 4.8 | Modern | 1862 | 22.99 | 3.53 | 32.01 | 64.94 | 67.38 |
| TRLK-08 | 3/23/2006 4.5 | 0.3 | 10.8 | 0.8 | Modern | 250 | 37.01 | 16.00 | 21.95 | wd | 39.02 |
| TRLK-11 | 3/28/2006 0.5 | 0.2 | 10.6 | 5.3 | Modern | 1374 | 36.89 | 15.92 | 64.02 | 121.95 | 125.00 |
| TRLK-12 | 4/3/2006 6.1 | 0.6 | 62.3 | 1.8 | Modern | 250 | 20.61 | 4.27 | 35.98 | wd | 48.17 |
| TRLK-14 | 4/4/2006 1.6 | 0.7 | nq | na | Modern | 273 | 29.57 | 5.58 | 48.78 | 108.23 | 109.76 |
| TRLK-15 | 4/4/2006 0.5 | 0.1 | nq | na | Modern | 273 | 31.10 | 6.69 | 100.61 | 118.90 | 121.95 |
| TRLPF-01 | 4/5/2006 4.6 | 0.4 | 1.9 | 0.2 | Modern | 2510 | 18.90 | 5.42 | 12.20 | wd | 24.39 |
| TRLPFP-02 | 4/5/2006 3.8 | 0.3 | 7.7 | 0.8 | Modern | 3023 | 29.88 | 6.29 | 28.35 | 52.44 | 52.44 |

1H, tritium; 3He-trit: tritogenic helium-3; atmos., atmospheric; 14C, carbon-14; nq, not quantifiable; na, not applicable; TU, tritium units; CFC, chlorofluorocarbon; pptv, parts per trillion by volume; cont., contaminated; pmC, percent modern Carbon; cc STP/g of H2O, cubic centimeters at standard temperature and pressure per gram of water; m^3/day, cubic meters, NAVD 88, North American Vertical Datum 1988; wd, well depth.
Premodern, or Mixed based on \(^3\)H and \(^{14}\)C concentrations. Modern groundwater is defined as having recharged since about 1955 and Premodern groundwater is defined as having recharged prior to about 1955. Samples with substantial fractions of both Modern and Premodern components were designated as Mixed. In reality, Premodern groundwater could contain very small fractions (<5%) of Modern water and Modern groundwater could contain very small fractions of Premodern water.

Modern groundwater was identified by \(^3\)H and \(^{14}\)C concentrations greater than 0.2 TU and 99 pmC, which were average concentrations (decay corrected to 2006) of the input records between 1950 and 1955. Premodern groundwater had \(^3\)H and \(^{14}\)C concentrations less than 0.2 TU, and 99 pmC while Mixed groundwater had \(^3\)H above 0.2 TU and \(^{14}\)C below 99 pmC. Samples without \(^{14}\)C data were classified on the basis of the percentage of terrigenic \(^4\)He (\(\text{He}_{\text{terr}}\); total helium minus helium from solubility equilibrium and excess air) in samples using the relationship between \(^{14}\)C and \(\text{He}_{\text{terr}}\) for classified samples having both measured \(^3\)H and \(^{14}\)C. The percentage of \(\text{He}_{\text{terr}}\) was as high as 47% in Modern samples and as low as 27% in Premodern samples. Based on this analysis, samples with \(^3\)H greater than 0.2 TU and \(\text{He}_{\text{terr}}\) greater than 47% were classified as Modern. There were no samples with \(^{14}\)C below 0.2 and \(\text{He}_{\text{terr}}\) greater than 47%, which would be classified as PrerModern.

5. Calculations

5.1. Particle tracking models

Only a brief description of the regional groundwater flow model is provided below. A more thorough description can be found in Phillips et al. (2007a,b). Steady-state, three-dimensional groundwater flow was simulated using MODFLOW-2000 (Harbaugh et al., 2000). The model grid was made up of 16 layers with each layer having 153 rows and 137 columns of cells that were 400 by 400 m. Large-scale heterogeneity of aquifer sediments was incorporated into the permeability field of the model using lithologic descriptions from over 3500 well logs (Burow et al., 2004; Phillips et al., 2007b). The lithology was discretized into 0.3068 m increments and assigned a numeric value of 1 for coarse material (gravel or sand) or 0 for fine material (clay and silt). Three-dimensional kriging was used to interpolate between boreholes and the fraction of coarse material was calculated for each cell in the model. This effort reproduced general patterns of major geologic features of the aquifer such as river channels and floodplain deposits (Burow et al., 2004; Phillips et al., 2007b). A water budget was computed to estimate recharge and pumpage (irrigation and municipal supply) by dividing the model into 47 subareas for which surface water and groundwater deliveries could be obtained or estimated for water year 2000. The groundwater flow model was calibrated to water levels and gradient information collected between 2000 and 2005 (Phillips et al., 2007b). Thus, the numerical model simulates the steady-state post-development Modern groundwater flow system.

For the current study, age distributions and delineation of the contributing recharge areas were computed for 30 production wells from the groundwater flow model using MODPATH (Pollock, 1994). For each cell where a well was located, a finer grid-mesh groundwater flow model was constructed for each model layer to make the well become a strong sink for flow entering the cell. Approximately 2000 particles were uniformly distributed along the screened interval of each well. Particles were distributed over all cell faces where water entered a cell representing the well in the finer grid-mesh flow model and the flow associated with each particle was computed by dividing inflow at the cell face by the number of particles started at the face. The fraction of recharge associated with each particle was calculated by dividing the flow of each particle by the total flow contributed by all the particles. Particles were tracked backwards to recharge locations and the travel times were recorded. The particles were binned into half-year age increments by summing the total fraction of recharge spanning each half-year age bin so that the fractions correspond to time points in the tracer input history in recharge.

The ensemble of PTMs was initially calibrated to environmental tracer data by varying porosity and subsequently each PTM was individually calibrated further by adjusting for travel time delays through the unsaturated zone, and dilution or enrichment of tracers from application of tracer-free or tracer-enriched groundwater for irrigation. Calibration was done by minimizing the differences between measured and modeled environmental tracer concentrations. Modeled tracer concentrations were calculated by convolution of the tracer input history in recharge and the simulated age distribution for each well:

\[
C_{\text{out}} = \int_{-\infty}^{t} g(t - \tau)C_{\text{in}}(\tau)e^{-\lambda(t-\tau)}
\]  

where \(C_{\text{out}}(t)\) is outlet tracer concentration, \(C_{\text{in}}(\tau)\) is concentration of tracer at inlet at time \(\tau\), \(g(t - \tau)\) is the fraction of recharge associated with a parcel of water for an age interval, \(t\) is sample date, \(\tau\) is date at which a water parcel entered the system, \(\lambda\) is decay constant, fractional loss per unit of time, and \(t - \tau\) is age of water parcel.

Porosity was assigned uniformly to the entire model domain. The total error between modeled and measured tracer concentrations for all 30 wells was calculated for a range of porosity values from 0.2 to 0.4. The porosity value with the lowest total error was 0.3.

Goodness-Of-Fit (GOF) between measured and modeled tracer concentrations was evaluated using the chi-square test statistic:

\[
\chi^2 = \sum_{i=1}^{k} \left( \frac{O_i - M_i}{\sigma_i^2} \right)^2
\]

where \(k\) is number of modeled tracers, \(O_i\) is the observed concentration of the i-th tracer, \(M_i\) is the modeled concentration of the i-th tracer, \(\sigma_i\) is the standard error of the i-th tracer concentration.

The probability of model acceptance was calculated using the chi-square distribution and the degrees of freedom (number of observations minus the number of fitted parameters). Models with a probability of greater than 1% were considered acceptable. The probability was only calculated for models having a degree of freedom greater than 0.

Transport between the land surface and water table in some parts of the study area can typically occur within the irrigated growing season (summer); however, travel times through the unsaturated zone may be greater at locations with relatively thick unsaturated zones. In addition, routing of surface water and storage behind reservoirs may also delay recharge of precipitation derived tracers. Travel time delays can cause differences between concentrations derived from precipitation records and the concentrations that enter the saturated zone and mainly affect the short-lived tracers such as \(^3\)H and its decay product \(^{3}\)He\(_{\text{terr}}\). Consequently, \(^3\)H and \(^{3}\)He\(_{\text{terr}}\) were used to assess travel time delays of tracers to the water table. For wells having measurable \(^3\)H and \(^{3}\)He\(_{\text{terr}}\), a travel time delay was used to offset and decay the input of \(^3\)H at the water table, which subsequently causes lower accumulation of \(^{3}\)He\(_{\text{terr}}\) and alteration of the ratio of \(^3\)H to initial \(^3\)H in the saturated zone. If travel time delays improved the PTM fit to measured tracer data – as measured by the chi-square probability (see above) – then the delay was accepted, otherwise the delay was assumed to be zero. Travel time delays of CFCs were not considered because...
the gas tracers commonly move more rapidly through the UZ and equilibrate with recharge at the water-table. Carbon-14 concentrations in recharge are largely determined by equilibration with soil CO₂(g) in the soil zone and were not expected to be useful for determining travel time delays.

A scaling factor for ³H and ¹⁴C input histories also was used to improve PTM fits to measured tracer data. Irrigation with old groundwater can cause dilution of the tracers and use of Mixed or Modern groundwater can cause dilution or enrichment of tracer concentrations in recharge. Only cases where the chi-square probability increased significantly were accepted as final results.

5.2. Partial exponential model

The PEM is a derivative of the exponential model (EM) described by Vogel (1967). The PEM can be used to describe tracer concentrations for long-screened wells that partially penetrate unconfined aquifers receiving uniform recharge (Jurgens et al., 2012). The exponential model assumes age in the aquifer increases logarithmically from zero at the water table to infinity at the base of the aquifer (Vogel, 1967). The EM, as typically used in past research, applies to wells that are screened over the entire saturated thickness of aquifer; however, in practice this requirement is not frequently met. Public-supply wells or production wells typically have long-screens, but often are not screened up to the water table or down to the bottom of the aquifer. Domestic wells can be screened near the water table but typically do not extend to the bottom of the aquifer and can have relatively short screens. Monitoring wells often have short screens (less than 10 m) and can be screened at various depths in an aquifer. Therefore, tracer concentrations from these wells might not be expected to follow outlet tracer concentrations from the traditional EM, but they could follow a partial exponential model that accounts for the portion of aquifer that is sampled by the well (Fig. 3A). Because the PEM can be parameterized in part from well construction and water level information, it can provide a more conceptually accurate depiction of the ages captured by the well than the EM, potentially without additional fit parameters. Previous studies addressing similar problems include Böhlke (2002), Jurgens et al. (2012), Böhlke et al. (2014), and Baillieux et al. (2015).

A homogeneous aquifer with constant thickness (H), and porosity (φ), and uniform recharge rate (r) has the following depth-dependent age relation (Vogel, 1967):

$$T(z) = -\frac{H\phi}{r} \ln \left(\frac{H - z}{H}\right)$$  

(3)

where z is the depth below the top of the saturated interval or water table. This equation can be used to determine the mean age of groundwater in the aquifer (τₚ) or any continuous portion of the aquifer spanning a depth of z₁ to z₂ (τₛ) by calculating the first moment (Fig. 3A):

$$τₛ = -\frac{1}{(z₂ - z₁)} \int_{z₁}^{z₂} \frac{H\phi}{r} \ln \left(\frac{H - z}{H}\right) dz$$  

(4)

The general solution to 4 follows:

$$τₛ = \left(\frac{H}{z₂ - z₁}\right) \left[\frac{H\phi}{r} \ln \left(\frac{H - z₂}{H}\right) - \frac{H - z₁}{H}\right] - \left(\frac{H - z₁}{H}\right) \ln \left(\frac{H - z₁}{H}\right) + \left(\frac{H - z₁}{H}\right)$$  

(5)

From this equation, the mean age of groundwater in the aquifer is found when z₁ = 0 and z₂ = H:

$$τₛ = τₚ = \left(\frac{H\phi}{r}\right)$$

Then, substitution of $n₁ = \frac{H}{z₁}$ and $n₂ = \frac{H}{z₂}$, and $τₚ = \frac{H\phi}{r}$ yields

![Fig. 3.](image-url)
The relation between the mean age of groundwater in any sampled portion of the aquifer, $\tau_s$, and the mean age of groundwater in the aquifer, $\tau_{aq}$, allows the direct calculation of outlet tracer concentrations at a well by computing the convolution over the sampled portion. The exit-age frequency distribution function of the PEM, $g(t)$, is the same as the EM, but the PEM convolution is calculated over the sub-domain of ages after normalizing the fractions of ages to the proportion of flow captured by the well screen:

$$g(t)_{\text{PEM}} = \left(\frac{1}{\tau_{aq}}\right)^n \left(\frac{1}{\tau_{aq}}\right) e^{-\frac{t}{\tau_{aq}}}; \text{ for } t_1 \leq t \leq t_2; 0$$

where $t_1 = \tau_{aq} \ln(n_1)$, and $t_2 = \tau_{aq} \ln(n_2)$.

Eq. (7) is the general solution to the partial exponential mixing model or PEM (Jurgens et al., 2012). The model as defined above has three parameters: mean age of the sampled portion ($\tau_t$), $n_1$, and $n_2$. However, this model can be reduced to a single parameter model if $n_1$ and $n_2$ can be defined in terms of depth-to-water level ($W$), depth-to-top of screen ($T$), depth-to-bottom of screen and the saturated thickness of the aquifer ($H$). In applying the model, the parameters $n_1$ and $n_2$ were reformulated in terms of PEM ratios:

$$PEM_{upper} = n_1 - 1 = \frac{z_1}{z_2 - z_1}$$

$$PEM_{lower} = n_2 - 1 = \frac{z_2}{z_2 - z_1}$$

$$z_1 = T - W,$$ and

$$z_2 = B - W.$$
with a median mean age of 76.3 years (Table 2). Six of the 30 wells had age distributions that were entirely younger than 50 years while 8 wells had at least 95% of their age distributions older than 50 years. Eight wells had age distributions with significant fractions (>20%) that were younger than 50 years and older than 100 years indicating the distributions were bimodal or multimodal.

The majority of wells (19) had chi-square probabilities greater than 1% and computed tracer concentrations that were somewhat similar to observed concentrations. Probabilities calculated from chi-square errors ranged from 0% to 99%. Computed tracer concentrations for 11 wells had probabilities of less than 1% and 10 of those wells had chi-square values greater than 1000, which suggested the numerical groundwater flow model did not fully characterize the age distributions for those wells. Those wells tended to have age distributions dominated by water older than 50 years and so computed concentrations of $^3$H and $^{3}$He$_{trit}$ were most often lower than measured values.

Analysis of travel time delays indicated that unsaturated-zone residence times of $^3$H or other dissolved tracers was minimal in most places in the study area. Travel time delays affecting $^3$H and $^{3}$He$_{trit}$ concentrations in recharge ranged from 0 to 33.2 years, but most wells had travel time delays of 0 years suggesting that $^3$H may not deviate substantially from precipitation values. Eleven wells had travel time delays greater than 0, and ranged from 2.7 to 33.2 years with a median of 6.7 years. Four wells had travel time delays between 18 and 33 years; three of those wells were in areas where depth-to-water was <7 m and two wells had travel time delays longer than the mean age of the age distribution. In addition, the model fit for the well with the longest travel time delay had a very low probability. These observations suggest the groundwater flow model did not accurately estimate the age distributions for these wells or that tracer concentrations in recharge were altered in ways not simulated, or perhaps that other processes such as diffusion into and out of fine-grained layers have caused differences between the transport of water and tracer in the aquifer.

Dilution and enrichment of tracer concentrations in recharge were evaluated for all wells. All but one well had an optimal solution using the original, precipitation-derived tracer concentrations in recharge with no dilution or enrichment. For one well, a better fit was obtained by using tracer input histories at 1.6 times higher than the original, precipitation-derived tracer concentrations. This

Fig. 4. Simulated concentrations of environmental age tracers and nitrate from partial exponential model and particle tracking model results. Colors correspond to the age classification determined from the measured tracer concentrations of tritium, carbon-14, and helium-4. Errors associated with tracer data are shown; except for radiogenic helium-4 and nitrate were too small to be distinguished.
well, MODFP-04 had the highest concentration of $^3$H, $^3$He$_{cut}$, and $^{14}$C of all the wells in this study. Because the PTM age distribution for this well was a significant fraction of water older than 50 years, the high scaling factor was needed to offset the contribution of tracer-free water contributed by the old fraction. The fact that none of the other wells required enrichment factors suggests the particle tracking model did not accurately reflect the actual age distribution sampled by the well MODFP-04.

Most of the deviation between modeled and measured tracer concentrations was from $^3$H concentrations, while modeled $^3$He$_{cut}$, $^{14}$C, and CFC-113 concentrations fit measured concentrations better for many wells (Fig. 4). In general, simulated $^3$H concentrations were lower than measured concentrations for wells classified as Modern, whereas simulated $^3$H in Mixed wells were generally higher than measured concentrations.

The groundwater flow model simulated the modern, perturbed groundwater flow system and did not account for the low recharge that occurred prior to development of the groundwater system (before the 1900s). Consequently, the PTM concentrations were generally higher for $^{14}$C and substantially lower for $^4$He than measured concentrations because the PTMs underestimated the age and (or) contribution of old groundwater entering the well (Fig. 4). In this aquifer, $^{14}$C concentrations generally did not require geochemical corrections that would be caused by dilution from reactions with $^{14}$C-free sources of carbon within the saturated zone (Jurgens et al., 2008). In addition, differences between modeled and measured values were too large to be caused by geochemical dilution alone for samples with measured values of $^{14}$C less than about 40 pmC and support a binary model of age for deeper wells (Fig. 2).

The contrast between older mean ages for younger groundwater and younger mean ages for older groundwater may be partly caused by the calibration of the PTMs to all the measured tracer data. Ideally, the calibration of the PTM should be restricted to only those wells with tracer concentrations that largely represent the modern system of recharge. This likely would yield better tracer fits to wells with modern groundwater but exacerbate the difference in measured and modeled $^{14}$C concentration for wells that largely capture premodern groundwater.

6.2. PEM results

PEM results indicated production wells in the study area captured a wide range of groundwater ages (Table 3). Mean ages ranged from 6.2 to 19,138 years, with a median mean age of 57.3 years. Chi-square test statistics ranged from nearly zero to 9.3 with a median of 2.4. Many of the samples had Chi-square fits less than 1 which can be an indication of overfitting caused by too few constraints for the number of estimated parameters. Many of these cases occurred when only $^3$H or $^{14}$C was used to calibrate the model.

Computed travel time delays between atmospheric concentration records and those assumed in recharge, for example travel through the unsaturated zone, ranged from 0 to 10 years, and most wells (24) had a travel time delay of 0 years. These results are generally consistent with PTM results, indicating the history of tracers in recharge may largely be unaffected by processes that could cause a delay between recorded concentrations in the atmosphere or precipitation and concentrations in recharge. However, travel time delays greater than 0 were required to fit tracer data for six wells; four of those six samples also had PTM travel time delays and another 4 of the 6 samples had depth-to-water greater than 14 m which suggests that some parts of the study area may have tracer histories in recharge that were affected by travel time delays through the unsaturated zone.

Seven of the 13 wells with $^{14}$C data had concentrations of $^{14}$C that could not be explained by a single PEM. These wells were identified as binary age mixtures of groundwater derived from two very different recharge conditions as described earlier. It is
Table 3
Partial exponential model results for production wells in the central eastside San Joaquin Valley, California.

<table>
<thead>
<tr>
<th>Well ID</th>
<th>LPM</th>
<th>Travel time delay, years</th>
<th>Mean age, years</th>
<th>Mean age error, years</th>
<th>PEM upper ratio</th>
<th>PEM lower ratio</th>
<th>Mixing fraction - 1st comp.</th>
<th>Mixing fraction error</th>
<th>2nd Mean age, years</th>
<th>$\chi^2$</th>
<th>$\chi^2$-PR, %</th>
<th>Tracers in calibration</th>
<th>Recharge rate, meters per year</th>
<th>Aquifer residence time, years</th>
<th>Pre-modern. recharge rate, meters per year</th>
<th>Pre-modern. aquifer residence time, years</th>
<th>Prop. of 50-year water</th>
<th>Depth to 50-year water, m</th>
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<td>0.51</td>
<td>1.61</td>
<td>2.78</td>
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<td>0.00</td>
<td>na</td>
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<td>0.05</td>
<td>0.14</td>
<td>9.26</td>
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PEM, partial exponential model; BMM, binary mixing model; $^3$H, tritium; $^3$He(trit), tritiogenic helium-3; $^{14}$C, carbon-14; CFC-113, chlorofluorocarbon-113. Fit parameters for single PEMs was mean age and for binary PEMs were mean age and fraction of young water.

*Fitted value.

b PEM ratios were calculated with a saturated thickness of 183 m.
possible that additional wells lacking \(^{14}\)C data could have a significant component of water derived from predevelopment conditions.

All PEMs predicted lower \(^{4}\)He\(_{\text{rad}}\) concentrations than measured. \(^{4}\)He\(_{\text{rad}}\) was simulated but not included in the calibration of the PEMs because there are other sources of \(^{4}\)He that make it difficult to use \(^{4}\)He\(_{\text{rad}}\) as a tracer of age in the study area. Potential sources could include a crustal flux of \(^{4}\)He\(_{\text{rad}}\) or enhanced mineral weathering. A complete investigation into the generation of \(^{4}\)He\(_{\text{rad}}\) was beyond the scope of this paper. However, simulated \(^{4}\)He\(_{\text{rad}}\) for binary PEMs of Mixed samples and single PEMs of PreModern samples provided better fits to measured \(^{4}\)He\(_{\text{rad}}\) than PTM results, which may indicate that the PEMs provided more realistic estimates of the age of old groundwater in the samples (Fig. 4). Several Mixed samples had substantial \(^{4}\)He\(_{\text{rad}}\) concentrations, indicting a component of old groundwater was likely present, but because \(^{14}\)C was not measured, the sample was treated as a single mixture. Further study of the sources of \(^{4}\)He in the study area and the relation of \(^{4}\)He\(_{\text{rad}}\) to \(^{14}\)C might demonstrate that \(^{4}\)He\(_{\text{rad}}\) could be used to develop mixing models between young and old components when \(^{14}\)C is absent.

6.3. Model comparison

Overall, PTM mean ages were generally older than PEM mean ages when PEM mean ages were less than 100 years, whereas PTM mean ages were significantly younger than PEM mean ages when PEM mean ages were greater than 100 years (Fig. 5). Differences between PTM mean ages and PEM mean ages were mainly related to (1) All PTMs were calibrated to hydraulic and tracer data by assuming a steady-state flow system corresponding to modern conditions, whereas some PEMs included a predevelopment component; (2) Sub-aquifer-scale estimates of permeability and recharge in the groundwater flow model used for the PTMs may not accurately represent local conditions around individual wells; and (3) calibration of a single PEM at wells lacking \(^{14}\)C measured data may misrepresent samples that appear to be binary mixtures based on other data.

All PTM mean ages for PreModern and Mixed samples with significant fractions of old groundwater were much younger than the PEM mean ages (Fig. 5). The median of PTM mean ages was 215 years as compared to more than 10,000 years for PEM mean ages for Premodern samples. Although PTM results included bimodal age distributions and substantial tailing of old groundwater caused by long flow paths in low-permeability units, they commonly appeared to underestimate the age of the Premodern groundwater because the numerical groundwater flow model simulated velocities for the entire system assuming post-development recharge rates and large groundwater withdrawals that cause groundwater to move vertically and horizontally at much higher rates than under predevelopment conditions.

In contrast to the PTMs, the PEMs were configured in some cases to account for the change in recharge by including a secondary PEM for the predevelopment recharge condition and calibrating to multiple tracers that span the age range captured by the well. These binary PEMs therefore provided better fits to the data and possibly more accurate descriptions of age distributions for wells with large fractions of PreModern groundwater in this system.

For five wells, only \(^{3}\)H was available to calibrate a single PEM but PTM results and \(^{4}\)He concentrations indicated that a sizable fraction of very old groundwater was present along with a fraction of young water (Table 1). At least 4 of these wells would have been calibrated using a binary PEM if \(^{14}\)C data were available. Calibration of wells to \(^{3}\)H alone caused the mean age to appear younger because the fraction and age of old groundwater was not well defined by the model. In addition, the age distribution of the young fraction was not well defined because the distribution was shifted older to account for the influence of old groundwater on the \(^{3}\)H concentration. These results highlight the importance of collecting \(^{14}\)C data for wells in systems where there has been a dramatic shift in recharge.

The PTM underestimated \(^{3}\)H concentrations in many Modern wells (Fig. 4) because it underestimated the fraction and (or) age of young groundwater in those wells. Such discrepancies may be due to poor representations of permeability or recharge around the well in the PTM. That is, a numerical groundwater flow model may provide a good representation of an aquifer-scale flow system but may not adequately capture local conditions around some wells. In these situations, LPMs can sometimes provide better estimates of age distributions at individual wells.

It is emphasized that the PTMs and PEMs were constrained in different ways. Each well in the PTM had a flow field defined by coarsely gridded estimates of hydraulic conductivity and recharge for large parts of the model area. These conditions imposed a constraint on the distribution of age at the well that may not accurately capture the travel time of water to the well locally. The PEM was constrained only by the well construction data so that the mean age of groundwater was free to adjust locally to average recharge rates and travel times that best explain the measured environmental tracer data at the well. But the averaging employed by the PEM, and lumped parameter modeling in general, lacks detailed, spatial information about the contributing areas, the distribution of recharge at the water table, and flow paths of water to the well. Consequently, an accurate PTM would be preferable to a PEM for understanding and predicting aquifer-scale responses to water use and contaminant transport, but a calibrated PEM can identify missing features in a PTM and it may provide local information about individual wells affected by small-scale heterogeneity or water use characteristics that might be difficult to predict with an aquifer-scale PTM.

6.3.1. Age distributions

Age distributions calculated using the PEM provide a unimodal, truncated form of the exponential mixing model (Fig. 6A and B) or a bimodal distribution of two truncated exponential age distributions. The PTM age distributions generally had broad age spans that displayed non-uniform, bi-modal to multi-modal characteristics (Fig. 6C and D). The character of many of the PTM age distributions reflect the complex distribution of hydraulic conductivity in
the model while the PEMs provide smoother distributions based on local, well-specific assumptions of homogeneity and uniform recharge. The heterogeneity of the aquifer might suggest that the PEM would not be an ideal model for representing groundwater ages in this system but the PEM could provide important information about age distributions in public-supply wells where the PTM did not perform well.

For example, the steady-state contributing area defined by the regional PTM for well MOD-02 indicates that groundwater can travel long distances along diverse flow paths caused by large-scale geomorphic features in the subsurface (buried river channels; Fig. 7). The contributing area was based on flow paths for the current, steady-state groundwater flow system and may provide a reasonable estimate of where recharge occurred for water less than 100 years. Water older than 100 years was likely recharged along streams or rivers (Page, 1986; Williamson et al., 1989).

For comparison to the regional PTM and PEM age distributions for well MOD-02, a local-scale PTM was previously computed from a detailed, small-area numerical groundwater flow model using the same methods in this study (Burow et al., 2008; McMahon et al., 2008b) and is presented in Fig. 8. The local PTM and regional PTM for MOD-02 both indicated the age distribution at MOD-02 was bimodal or perhaps multi-modal. Although the local PTM had more detailed vertical discretization of permeability and finer resolution of the distribution of recharge at the land surface (Burow et al., 2008), the regional and local PTMs gave age distributions that were similarly complex and non-uniform. The PTMs indicated most of the well water (~75%) originated from the upper part of the screen and had ages spanning from about 10 years to about 150–200 years. A smaller fraction of water (~25%) came from the lower part of the screen and had ages between 700 and 1100 years (Fig. 8). Both PTMs underestimated the age of the old groundwater component and therefore, overestimated the $^{14}$C concentration at MOD-02 because the change in recharge rates between Premodern and Modern flow conditions was not simulated.

In contrast, the binary PEM for MOD-02 (Table 3; Fig. 8) provided a better fit to the $^{14}$C data, yielding a larger mean age for the old component and implying a lower recharge rate. The PEM results indicated the well screen at MOD-02 (and some other wells in this study) intersected the boundary between groundwater recharged in Modern and Premodern conditions (Fig. 2).

For the young fraction, the binary PEM for MOD-02 yielded similar fractions and age spans as the PTMs but the shape of the distribution was markedly different. The binary PEM follows a truncated form of the exponential distribution with the youngest and oldest ages removed because the well screen starts below the water table and ends above the bottom of the aquifer (about 152 mbls; Tables 1 and 3). In contrast to the PTM age distributions, the peak or mode of the PEM distribution is always the first age entering the well, which in this case was about 10 years.

Although the PTM and PEM results were not completely dissimilar, differences between the peaks and modes of the age distributions may indicate that the PEM may not characterize the shape or parts of the age distribution accurately when heterogeneity complicates the distribution of flow and age across the well screen. For comparison, a binary dispersion model was fit to $^3$H, $^3$He$_{int}$, and $^{14}$C concentrations; this model is capable of replicating many of the features of the PTM age distribution for this particular well (Fig. 8). The binary dispersion model yielded a mean age of the...
young fraction of 62.3 years (±24.9 years), a dispersion parameter of 0.29 (±0.11) and a fraction of young groundwater of 76% (±6%). The dispersion model had an additional fit parameter compared to the parameterized PEM presented here. The DM therefore requires additional tracer data for proper calibration which can limit its application at wells lacking sufficient tracer data. Although the PEM was simple, it predicted a similar span and fraction of ages for the young fraction as the PTMs, indicating it is capable of capturing important parts of the age distribution that are most responsible for observed tracer concentrations (see also Eberts et al., 2012). In addition, the PEM results could be used to improve future PTMs because they revealed some features that were necessary to give more accurate estimates of groundwater age in the flow model.

6.3.2. Recharge rates
Recharge rates were computed using the PEM results for all 30 wells by rearranging Eq. (6). Porosity was set to 0.30 based on the environmental tracer calibration of the PTM to facilitate comparison of the models. Recharge rates were segregated into two groups according to the timescale the LPM results represent: values derived predominantly from the Modern, post-development system, and those derived for the PreModern or predevelopment system. For binary PEMS, the screen length was divided into Modern and PreModern portions based on the fraction of the Modern component in Table 3 and the screen interval of each fraction was used to derive a recharge rate for the Modern and PreModern components.

Twenty-eight PEM recharge rates were calculated for the Modern groundwater system and ranged from 0.19 to 1.9 m/yr with a median of 0.40 m/yr and average of 0.54 m/yr (Table 3; Fig. 9). PEM recharge rates for the Modern flow system were similar to recharge rates used to construct the regional groundwater flow model in this paper (Burow et al., 2004). For the regional groundwater flow model, areal recharge rates were computed from water budget estimates for 47 subareas and ranged from 0.23 to 0.76 m/yr and had an average value of 0.54 m/yr, which compares well with the distribution and average of PEM recharge rates. Thus, the PEM gave independent support to regional recharge estimates derived from a water budget analysis under modern conditions.

Predevelopment recharge rates were calculated from 9 samples and ranged from 0.001 to 0.025 m/yr with a median of 0.003 m/yr. The predevelopment recharge rates were about 100 times lower.
than recharge rates estimated for the Modern system and about 10 times lower than a regional value from Williamson et al. (1989), who estimated the predevelopment recharge rate at about 0.05 m/yr for the entire Central Valley.

6.4. Simulated nitrate

Nitrate concentrations were measured in 24 wells and ranged from 0.45 to 49.9 mg/L as nitrogen (N), with a median concentration of 3.42 mg/L as N. Two wells had concentrations greater than the US EPA maximum contaminant level (MCL) of 10 mg/L as N, but those wells were not used for public supply.

To simulate nitrate concentrations in wells, nitrate in recharge since about 1955 was computed from nitrogen fertilizer application rates in Stanislaus County (Ruddy et al., 2006). The nitrate input history used in this study was modified slightly from the one developed by Burow et al. (2008). The history of nitrate concentrations in recharge was based on the assumption that 50% of the applied nitrogen at the land surface reached the water table using the calibrated best-fit PTM porosity of 0.3 and median PEM recharge rate of 0.4 m/yr. Because nitrate application rates generally leveled off beginning in the 1980s, nitrate in recharge was set to 15 mg/L (as nitrogen) for dates after the year 2000 (Fig. S1). Before 1955 nitrate concentrations in recharge were...
assumed to reflect an estimated background concentration of 2 mg/L as nitrogen. Landon et al. (2011) found that concentrations of excess nitrogen gas produced by denitrification generally were low across the study area, but higher rates of denitrification can occur locally (McMahon et al., 2008a; Green et al., 2008, 2010, 2014). For the current analysis, an average nitrate decay constant of 0.01/yr (half-life of 693 yrs) was used in the simulations (McMahon et al., 2008a).

Simulated concentrations of current (2006) nitrate using the PEM age distributions were found to be more consistent with measured nitrate in wells than were nitrate concentrations determined from PTM age distributions (Table S3; Figs. 4 and S2). Although root mean squared errors (RMSE) of the PEM and PTM nitrate concentrations were similar (8.50 and 9.13, respectively), the median squared error for PEM nitrate (2.23) was significantly lower than for PTM nitrate (13.88). This indicates that, overall, PEM nitrate concentrations were consistently more similar to measured concentrations than were PTM nitrate concentrations.

Most of the error between simulated and measured nitrate concentrations was from 5 wells that had poor simulated nitrate concentrations for both PEM and PTM age distributions (Fig. S2). Two of the 5 wells (TRLKFP-01 and TRLKFP-02) were surrounded by agricultural land and had nitrate concentrations that were higher than the input of nitrate in recharge indicating the history of nitrate in recharge was not spatially uniform and could be higher or lower depending on local application rates and leaching fractions. Nitrate was modeled assuming all recharge was predominately from agricultural areas; however two of the five wells (TRLK-04 and MOD-05) with high errors were located in predominately urban areas and may not receive all their water from agricultural land. Most of the error could be removed for these two wells by scaling the nitrate input history in recharge by the percentage of agricultural land in a 500 m radius (Table S3) and assuming background levels of nitrate in recharge for urban areas.

Age distributions computed from the two methods produced a steady-state picture of age at the time of sampling in the case of the PEMs or water budget conditions for year 2000 in the case of the PTMs. But these depictions did not account for transient variations in the distribution of age over time. If the hydrogeologic system could be approximated by a steady state description of groundwater flow, then the age distributions might reproduce nitrate trends in wells if the nitrate history in recharge was spatially uniform and could be adequately characterized and if denitrification was minimal or could be quantified.

To test this possibility, nitrate trends were calculated for 24 production wells having at least 2 nitrate measurements since 1985 (Table S3). Both PEM and PTM age distributions were used to calculate nitrate trends and the RMSE was used to quantify the goodness of fit between measured and simulated concentrations. The two best and two worst RMSEs are shown in Fig. 10.

Overall, the PEMs tended to reproduce nitrate trends for more wells than the PTM results. The PEM had a median RMSE of 2.2 compared to 3.4 for the PTM age distributions. However, both the PEM and PTM had 4 wells with good fits (RMSE below 1) indicating that both models reproduced nitrate trends accurately for some wells. Eleven wells had PEM nitrate trends with RMSE less than 2 and these were considered satisfactory fits to the nitrate trends and seven of the 11 wells had PEM nitrate trends with RMSE less than 1.5. Wells with RMSEs between 1.5 and 3 tended to have larger fluctuations in measured nitrate concentrations through time, presumably caused by transient changes in age distributions that may be caused by seasonal changes in hydraulic stresses, short-circuiting, or well operation (Bexfield and Jurgens, 2014).

Even where nitrate concentrations were variable through time, the PEM was often able to follow the general trend of the data.

There were 7 PEMs with a RMSE greater than 3 whereas 13 PTMs had a PTM RMSE greater than 3. RMSEs greater than 3 fit the data very poorly and other factors such as redox, source of recharge (agricultural versus urban), and spatial variations of nitrate concentrations in recharge affect the results. The nitrate simulations performed in this work were meant to illustrate the usefulness of the PEM but the issues raised here would be important topics to investigate further in order to better simulate nitrate concentrations for wells in the Central Valley. For example, McMahon et al. (2008b) explored the combined effects of changing...
agricultural practices and spatial patterns of land use change on nitrate trends in a water-supply well in this area using a PTM.

6.5. Aquifer characteristics derived from PEMs

Results from the PEM can be used to infer additional information about the groundwater system besides mean ages and recharge rates. For example, by rearranging Eq. (3), the PEM can be used to estimate the mean residence time of the aquifer, proportion of water aged 50 years or less and the approximate depth at which 50-year old water is likely to occur. The 50-year cutoff was chosen to identify the approximate depth of groundwater that predates the 1950s, thus predating major effects of nuclear bombs and artificial fertilizer production. These aquifer characteristics can provide important information about anthropogenic effects on the resource as a whole; although the values should be interpreted with caution given the complexity of age in this system and the simple conceptual model used to estimate the values at individual wells.

The mean residence time of the aquifer calculated for each well ranged from 24 to 237 years, with a median of 114 years (Table 3; Fig. 11). These residence times reflect the mean age of the Modern, developed aquifer system and differ vastly from the estimated residence time of the predevelopment system which ranged from 1840 years to about 32,000 years, with a median of 17,200 years.

The estimated proportion of aquifer aged 50-years or older ranged from 20% to 87%, with a median of about 36%, assuming an aquifer thickness of 152 m. Estimated depth to 50-year old groundwater ranged from 36 to 134 mbls, with a median of 61 mbls. The median depth in this study is the same as the depth used to demarcate the depth below which tracers of Modern groundwater was not likely to occur (Landon et al., 2010). PEM results also predict that in 10 years (about 2016), the median proportion of aquifer having groundwater aged 50 years or less will increase to about 41% and the median depth of 50-year old groundwater will be about 69 mbls. These values were based on the assumption that old groundwater is now moving as if it were part of the Modern flow system while preserving its Premodern recharge characteristics.

7. Conclusions

This paper presented a 3-parameter partial exponential lumped parameter model (PEM) that was calibrated to tracers of groundwater age for 30 production wells in a heterogeneous alluvial fan aquifer in the central eastside San Joaquin Valley, CA. A PEM for each well was partially parameterized from well construction information and estimates of saturated thickness and then calibrated to groundwater age tracers. This procedure allowed the PEM to be reduced to a single fit parameter – mean age – when travel through the unsaturated zone was negligible. In principle, the PEM could be calibrated to a single tracer when the sample is comprised of water that is entirely Modern (recharged since about 1955) or entirely Premodern (free of modern tracers); although tracers with histories of peak concentrations followed by falling concentrations such as tritium and post 1950s 14C can produce two or more solutions that need to be evaluated.

A regional numerical groundwater flow model was used to generate a particle tracking model (PTM) for each well for comparison with PEM results and to evaluate unsaturated zone travel times and tracer histories in recharge. Both PTM and PEM results show that wells in the study area capture groundwater with a broad range of ages spanning decades to millennia. Although the history of tracers in recharge can deviate from their history in precipitation in some aquifer systems, the PTM and PEM results suggest the precipitation records are reasonable estimates in this system but the input of tracers at the water table can be delayed in some parts of the valley where depth-to-water exceeds 15 m.

The PEMs generally provided good fits to tracer data spanning the full range of time scales, and in particular for wells having age mixtures derived from the pre- and post-development groundwater systems. Samples from more than half the wells (7 of 13) where 14C was measured were found to be mixtures of pre- and post-development groundwater. PTM results and 4He concentrations in wells lacking 14C data indicate some additional wells may also be binary mixtures but could not be correctly identified by the PEM without 14C data. The PTMs did not fit 14C concentrations for wells with large fractions of predevelopment groundwater because the numerical model did not simulate the lower rate of recharge that occurred prior to development of the groundwater system for irrigation and other water uses (about 1900). As a result, velocities calculated in the model were much higher than would be expected for water older than 100 years. Consequently, the age of old groundwater was significantly underestimated and led to higher than expected 14C concentrations. These results indicate that particle-tracking models based on flow simulations with modern hydraulic data that do not account for the age mass of the predevelopment system can be less successful at reproducing multiple age tracer data.

The PEM is based on a simplistic representation of age distributions within the aquifer and while it predicted similar age spans for Modern groundwater as did the PTM, the PEM did not reproduce the complex, asymmetric shapes of the age distributions commonly indicated by the PTM in this system. Despite the lack of agreement in detail, the PEMs simulated current nitrate concentrations reasonably well for many wells and gave acceptable nitrate trends (RMSE < 2) for at least 11 out of 24 wells where nitrate was measured. Consequently, these results show that the PEM can provide meaningful predictions of age distributions and concentration trends for long-screened wells, even in systems where heterogeneity can complicate the distribution of age. This study highlights the potential usefulness of PEMs and other lumped-parameter models calibrated with environmental tracer data for identifying larger scale processes that should be incorporated into more complex aquifer-scale models. In addition, it is possible that age distributions derived from lumped-parameter models are more sensitive to local conditions near individual wells where aquifer-scale flow models lack detailed, or rely on uncertain, representations of local hydraulic features.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jhydrol.2016.05.011.

References


14C data for carbon cycle


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