

Multi-tracer approach to constraining groundwater age structure

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To assess trends in water quality, four wells near Fresno, California, were sampled multiple times between 2013 and 2019 for a suite of dissolved noble gases, isotopes, organic and inorganic constituents. The noble-gas chronometers krypton-85 (⁸⁵Kr), krypton-81 (⁸¹Kr), argon-39 (³⁹Ar), and helium-4 (⁴He), as well as tritium (³H), sulfur hexafluoride (SF₆), and carbon-14 (¹⁴C) were measured from two long-screened supply wells, one shallow and one deep, and two short-screened monitoring wells, one shallow and one deep, to better constrain groundwater age structure and flow velocities. While ⁸⁵Kr, ³H, and SF₆ are frequently measured to constrain water recharged after 1950, the combination of ⁸¹Kr, ¹⁴C, and ³⁹Ar were used to identify more complex mixtures of groundwater recharged before 1950. These tracers also provide information on how fluids and gases move through the shallow crust.

Initial measurements of ¹⁴C and ³H indicated the age of groundwater in the shallow and deep supply wells was about 3,300 and 6,500 years, respectively. Subsequent measurements of ⁸¹Kr and ³⁹Ar showed that water from the deep supply well had about 25% modern argon, and 100% modern ⁸¹Kr, while the deep monitoring well had ~99% modern ⁸¹Kr. Lumped parameter modeling showed that ¹⁴C concentrations were not consistent with a single mixture of groundwater older than 100 years and that geochemical corrections of ¹⁴C from dead-carbon sources alone could not explain the difference in measured ¹⁴C, and ⁸¹Kr and ³⁹Ar. Consequently, the distribution of groundwater age from the supply wells clearly indicates a binary mixture of water less than 1,000 years and water up to 10,000 years. ⁸⁵Kr, SF₆, and ³H-³He ages for the shallow monitoring and supply wells generally agreed, with ages between ~20 and 60 years. Iterations of models using these age-tracer data provide a means of evaluating the stability of apparent groundwater ages and which tracers are most appropriate to monitor groundwater quality change over seasonal, annual, and decadal timescales.