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Distribution of tritium in precipitation and surface water in California

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SUMMARY

The tritium concentration in the surface hydrosphere throughout California was characterized to examine the reasons for spatial variability and to enhance the applicability of tritium in hydrological investigations. Eighteen precipitation samples were analyzed and 148 samples were collected from surface waters across California in the Summer and Fall of 2013, with repeat samples from some locations collected in Winter and Spring of 2014 to examine seasonal variation. The concentration of tritium in present day precipitation varied from 4.0 pCi/L near the California coast to 17.8 pCi/L in the Sierra Nevada Mountains. Concentrations in precipitation increase in spring due to the 'Spring Leak' phenomenon. The average coastal concentration (6.3 ± 1.2 pCi/L) in precipitation matches estimated pre-nuclear levels. Surface water samples show a trend of increasing tritium with inland distance. Superimposed on that trend, elevated tritium concentrations are found in the San Francisco Bay area compared to other coastal areas, resulting from municipal water imported from inland mountain sources and local anthropogenic sources. Tritium concentrations in most surface waters decreased between Summer/Fall 2013 and Winter/Spring 2014 likely due to an increased groundwater signal as a result of drought conditions in 2014. A relationship between tritium and electrical conductivity in surface water was found to be indicative of water provenance and anthropogenic influences such as agricultural runoff. Despite low initial concentrations in precipitation, tritium continues to be a valuable tracer in a post nuclear bomb pulse world.

1. Introduction

Tritium, a radioactive isotope of hydrogen ($t_{½} = 12.32 \pm 0.02$ years) (Lucas and Unterweger, 2000), has been applied widely to study the residence times of water in the hydrological cycle. In particular, residence times of groundwater and surface water have been derived by matching observed concentration time series to outflow concentrations of a mixing model with the historical concentrations of tritium in precipitation as input (Blavoux et al., 2013; Eastoe et al., 2011; Izbicki et al., 2000; Kluge et al., 2010; Michel, 1992; Plummer et al., 2001; Robert, 2004; Rose, 2007; Stewart et al., 2010).

Historically, studies have focused on anthropogenic tritium released into the upper atmosphere during nuclear testing (Michel et al., 2015). Between 1953 and 1963, over 600 kg of tritium was added to the atmosphere, mainly above the tropopause, by atmospheric nuclear weapons testing, dramatically increasing the tritium concentration in precipitation globally. At the peak in 1963 tritium concentrations in precipitation reached several thousand TU, from an estimated 2–8 TU in precipitation the United States prior to weapons testing (Michel, 2005). (One tritium unit (TU) is equivalent to one tritium atom per 10^{18} hydrogen atoms, corresponding to 3.24 pCi/L (120 mBq/L) for water at standard temperature and pressure. For reference, the Maximum Contaminant Level for tritium in drinking water is 20,000 pCi/L (EPA, 2002)). The natural background mass of tritium in the atmosphere from cosmic ray spallation is estimated at 4 kg (Michel et al., 2015).

Tritium in precipitation has been monitored extensively in the past and data are available through the Global Network of Isotopes in Precipitation (GNIP), created by the International Atomic Energy Agency (IAEA) in partnership with the World Meteorological Organization (WMO) in 1958. Water isotope data (including ^{3}H, $^{2}H/^{1}H$ and $^{18}O/^{16}O$) are collected and submitted on a voluntary basis by various institutes, companies, and private citizens. Monthly precipitation samples were collected from over 1000 stations in more than 125 countries in the past. The database currently has data for over 115,000 samples (International Atomic Energy Agency, 2015). The Ottawa station in Canada has the earliest and longest tritium record, with data from 1953 to present.

Several methods have been applied for predicting historical tritium concentrations in precipitation. A nearby GNIP station may be

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chosen, with missing data interpolated using a correlation with long running stations like Ottawa or Vienna:

$$C_i = a \times C_{Ott} + b \quad (1)$$

where C_i and C_{Ott} are the unknown tritium concentration and the concentration at the Ottawa station at the time of interest, respectively, and a and b are determined from station data. For locations not near GNIP stations, a tritium curve may be reconstructed by triangulation or inverse distance weighting of the correlation parameters of nearby stations.

Doney et al. (1992) used tritium data obtained from the IAEA database to model the global distribution of tritium. The global model of tritium in precipitation (GMTP), based on an equation relating tritium at a set time and location to a reference curve and spatial function (Weiss and Roether, 1980), showed a poleward increase in tritium from a minimum around 0°–20°S (related to the latitudinal dependence of cosmogenic production rates) and approximately 10-fold higher tritium values in the northern compared to the southern hemisphere (due to the preponderance of nuclear tests carried out in the northern hemisphere).

Zhang et al. (2011) modified the GMTP using updated GNIP data from 2005, adjusted the model to better fit the new data, and included a model of seasonal tritium cycling developed using a cosine function. This model has been criticized mainly for the large (50%) under-prediction of tritium concentrations during the 1960s peak concentration and for some negative number predictions (Newman et al., 2013; Wu, 2013). A detailed study of tritium in precipitation over Australia was recently published by Tadros et al. (2014).

In addition to global efforts to reconstruct the historical concentration of tritium in precipitation, Stewart and Farnsworth (1968), the first study of tritium in US precipitation in which tritium data from samples collected at 15 sites across the US on a bi-weekly basis from 1963 to 1965 was compiled, found that the tritium content in precipitation generally increased with latitude and was higher at inland than coastal sites. Within California, tritium was shown to generally increase inland, especially to the northeast, which was explained by continuous mixing of low-tritium, marine-sourced moisture with higher-tritium, land-sourced moisture, as clouds move inland. In contrast, Michel (1989) found a strong latitudinal gradient in California, with tritium increasing to the north in a follow-up study including data collected between 1953 and 1983 from a 14 point sample network. Recently, Eastoe et al. (2011) found tritium in precipitation in New Mexico to be constant over the past few decades, but increasing with latitude and possibly inland.

Since the cessation of above ground testing, tritium in precipitation has been decreasing toward natural, cosmogenic-production levels. When annual, precipitation-weighted, mean concentrations are constant, water residence times can be derived directly, for piston flow and homogeneous media (Cartwright and Morgenstern, 2012; Michel et al., 2015; Morgenstern and Daughney, 2012; Morgenstern et al., 2010).

For tritium to be useful in future hydrological research, natural, cosmogenic production rates and activities in precipitation need to be established. Unfortunately, interest in establishing the levels of tritium in precipitation have dwindled since the 1980s and many stations have been abandoned. In addition, the correlation structure between GNIP stations has been changing due to the shift from legacy anthropogenic tritium toward natural, cosmogenic tritium and due to the stronger importance of recycling of anthropogenic tritium over continents resulting from decreasing concentrations in atmospheric water vapor. Several additional challenges are specific to California: large latitudinal, longitudinal and elevation gradients and a Mediterranean climate with distinct sources of moisture in precipitation (referred to as low-tritium Pineapple express storms from the equatorial Pacific and high tritium Pinecone express storms from the continental arctic), and strong climate variability leading to extended periods of drought (Mao et al., 2015).

The purpose of this study is to characterize the tritium concentration in the surface hydrosphere throughout California to address the following outstanding questions: (1) What is the concentration of tritium in present-day precipitation, how does it vary spatially and seasonally across California, and how does it compare to natural, pre-bomb, cosmogenic tritium production levels?, and (2) How do tritium concentrations in California surface water vary spatially, seasonally and along river reaches?

2. Methods

Surface water sampling locations (Fig. 1) were selected to provide coverage over the state's main rivers, focusing on locations where stream gage data were available. Dammed rivers were sampled above and below the dam when feasible to investigate the effect of the reservoir residence time on tritium concentration. Samples were also collected above and below the confluence of major river tributaries to investigate mixing ratios. Several samples were collected from coastal locations (including an estuary, a slough, and the Pacific Ocean) to investigate ocean-river mixing. Sample location data are provided in Supplementary Information Table 1.

Samples were collected from surface waters across California in the Summer/Fall of 2013 to capture base flow conditions. Repeat samples were collected at a subset of the sampling locations during the Winter and Spring of 2014, in an attempt to capture runoff conditions. However, the precipitation and runoff during the Winter/Spring of 2013–14 was below average due to severe drought conditions in California (Mao et al., 2015).

Our study includes 164 samples, 147 of which were collected between June 2013 and April 2014; 113 samples were collected during Summer/Fall 2013 and 34 samples were collected during Winter/Spring 2014. The remaining 17 samples were collected in conjunction with a previous study, between January 2012 and April 2013, from Martis Valley in the Sierra Nevada Mountains (Segal et al., 2014). Nine precipitation samples were collected during the 2013–2014 sample collection phase of this project. Nine additional snow samples were collected previously in Martis Valley in 2012.

Sample locations were grouped according to California groundwater provinces established by the U.S. Geological Survey for the California Groundwater Ambient Monitoring and Assessment program (http://ca.water.usgs.gov/gama/), which are based on California Department of Water Resources-defined groundwater basins. The following provinces are included in this study: Northern Coast Ranges (Northern Coast), Southern Coast Ranges (Southern Coast), Klamath Mountains (Klamath), Central Valley, Sierra Nevada and Transverse Ranges and Selected Peninsular Ranges (Transverse). Additionally, an Ocean group was added to include ocean and heavily tidally-influenced samples.

Water quality parameters, including pH, temperature, electrical conductivity (EC), dissolved oxygen, and oxidation–reduction potential were collected in the field with a YSI 556 MPS multimeter for 72 of the 164 samples. When a multi-meter was unavailable or not operational during a sampling trip, temperature was recorded in the field with a mercury or digital thermometer and electrical conductivity was recorded in the laboratory with a multi-meter at a later time.

Samples were collected in 1L Pyrex glass bottles and analyzed for tritium by helium-3 accumulation and noble gas mass spectrometry following (Surano et al., 1992). Measurement uncertainty is less than 1 pCi/L (0.6 pCi/L average).