1 **DISTRIBUTION OF TRITIUM IN PRECIPITATION AND SURFACE WATER** 2 **IN CALIFORNIA**

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10 **ABSTRACT**

11 The tritium concentration in the surface hydrosphere throughout California was
12 characterized to examine the reasons for spatial variability and to enhance the
13 applicability of tritium in hydrological investigations. Eighteen precipitation samples
14 were analyzed and 148 samples were collected from surface waters across California in
15 the summer and fall of 2013, with repeat samples from some locations collected in winter
16 and spring of 2014 to examine seasonal variation. The concentration of tritium in present
17 day precipitation varied from 4.0 pCi/L near the California coast to 17.8 pCi/L in the
18 Sierra Nevada Mountains. Concentrations in precipitation increase in spring due to the
19 ‘Spring Leak’ phenomenon. The average coastal concentration (6.3 ± 1.2 pCi/L) in
20 precipitation matches estimated pre-nuclear levels. Surface water samples show a trend of
21 increasing tritium with inland distance. Superimposed on that trend, elevated tritium
22 concentrations are found in the San Francisco Bay area compared to other coastal areas,
23 resulting from municipal water imported from inland mountain sources and local

24 anthropogenic sources. Tritium concentrations in most surface waters decreased between
25 Summer/Fall 2013 and Winter/Spring 2014 likely due to an increased groundwater signal
26 as a result of drought conditions in 2014. A relationship between tritium and electrical
27 conductivity in surface water was found to be indicative of water provenance and
28 anthropogenic influences such as agricultural runoff. Despite low initial concentrations in
29 precipitation, tritium continues to be a valuable tracer in a post nuclear bomb pulse world.

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31 **KEYWORDS:**

32 Tritium

33 Precipitation

34 Surface water

35 Residence time

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44 1. INTRODUCTION

45 Tritium, a radioactive isotope of hydrogen ($t_{1/2} = 12.32 \pm 0.02$ years) (Lucas and
46 Unterweger, 2000), has been applied widely to study the residence times of water in the
47 hydrological cycle . In particular, residence times of groundwater and surface water have
48 been derived by matching observed concentration time series to outflow concentrations
49 of a mixing model with the historical concentrations of tritium in precipitation as input
50 (Blavoux et al., 2013; Eastoe et al., 2011; Izbicki et al., 2000; Kluge et al., 2010; Michel,
51 1992; Plummer et al., 2001; Robert, 2004; Rose, 2007; Stewart et al., 2010).

52 Historically, studies have focused on anthropogenic tritium released into the upper
53 atmosphere during nuclear testing (Michel et al., 2015). Between 1953 and 1963, over 600
54 kg of tritium was added to the atmosphere, mainly above the tropopause, by atmospheric
55 nuclear weapons testing, dramatically increasing the tritium concentration in precipitation
56 globally. At the peak in 1963 tritium concentrations in precipitation reached several
57 thousand TU, from an estimated 2-8 TU in precipitation the United States prior to
58 weapons testing (Michel, 2005). (One tritium unit (TU) is equivalent to one tritium atom
59 per 10^{18} hydrogen atoms, corresponding to 3.24 pCi/L (120 mBq/L) for water at standard
60 temperature and pressure. For reference, the Maximum Contaminant Level for tritium in
61 drinking water is 20,000 pCi/L (EPA, 2002)). The natural background mass of tritium in
62 the atmosphere from cosmic ray spallation is estimated at 4 kilograms (Michel et al.,
63 2015).

64 Tritium in precipitation has been monitored extensively in the past and data are available
 65 through the Global Network of Isotopes in Precipitation (GNIP), created by the
 66 International Atomic Energy Agency (IAEA) in partnership with the World
 67 Meteorological Organization (WMO) in 1958. Water isotope data (including ^3H , $^2\text{H}/^1\text{H}$
 68 and $^{18}\text{O}/^{16}\text{O}$) are collected and submitted on a voluntary basis by various institutes,
 69 companies, and private citizens. Monthly precipitation samples were collected from over
 70 1,000 stations in more than 125 countries in the past. The database currently has data for
 71 over 115,000 samples (International Atomic Energy Agency, 2015). The Ottawa station
 72 in Canada has the earliest and longest tritium record, with data from 1953 to present.

73 Several methods have been applied for predicting historical tritium concentrations in
 74 precipitation. A nearby GNIP station may be chosen, with missing data interpolated using
 75 a correlation with long running stations like Ottawa or Vienna:

$$76 \quad C_i = a \times C_{Ott} + b \quad [\text{Eq 1}]$$

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

82 (Doney et al., 1992) used tritium data obtained from the IAEA database to model the
 83 global distribution of tritium. The global model of tritium in precipitation (GMTP), based

84 on an equation relating tritium at a set time and location to a reference curve and spatial
85 function (Weiss and Roether, 1980), showed a poleward increase in tritium from a
86 minimum around 0°-20°S (related to the latitudinal dependence of cosmogenic production
87 rates) and approximately 10-fold higher tritium values in the northern compared to the
88 southern hemisphere (due to the preponderance of nuclear tests carried out in the northern
89 hemisphere).

90 (Zhang et al., 2011) modified the GMTP using updated GNIP data from 2005, adjusted
91 the model to better fit the new data, and included a model of seasonal tritium cycling
92 developed using a cosine function. This model has been criticized mainly for the large
93 (50%) under-prediction of tritium concentrations during the 1960s peak concentration
94 and for some negative number predictions (Newman et al., 2013; Wu, 2013). A detailed
95 study of tritium in precipitation over Australia was recently published by Tadros et al.
96 (2014).

97 In addition to global efforts to reconstruct the historical concentration of tritium in
98 precipitation, *Stewart and Farnsworth* (1968), the first study of tritium in US
99 precipitation in which tritium data from samples collected at 15 sites across the US on a
100 bi-weekly basis from 1963 to 1965 was compiled, found that the tritium content in
101 precipitation generally increased with latitude and was higher at inland than coastal sites.
102 Within California, tritium was shown to generally increase inland, especially to the
103 northeast, which was explained by continuous mixing of low-tritium, marine-sourced
104 moisture with higher-tritium, land-sourced moisture, as clouds move inland. In contrast,

105 Michel (1989) found a strong latitudinal gradient in California, with tritium increasing to
106 the north in a follow-up study including data collected between 1953 and 1983 from a 14
107 point sample network. Recently, Eastoe (2011) found tritium in precipitation in New
108 Mexico to be constant over the past few decades, but increasing with latitude and
109 possibly inland.

110 Since the cessation of above ground testing, tritium in precipitation has been decreasing
111 towards natural, cosmogenic-production levels. When annual, precipitation-weighted,
112 mean concentrations are constant, water residence times can be derived directly, for
113 piston flow and homogeneous media (Cartwright and Morgenstern, 2012; Michel et al.,
114 2015; Morgenstern and Daughney, 2012; Morgenstern et al., 2010).

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

126 arctic), and strong climate variability leading to extended periods of drought (Mao et al.,
127 2015).

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

134 **2. METHODS**

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

143

145 Figure 1: Map of California with surface water (black dots) and precipitation (red dots)
146 sampling locations.

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148 Samples were collected from surface waters across California in the summer/fall of 2013
149 to capture base flow conditions. Repeat samples were collected at a subset of the
150 sampling locations during the winter and spring of 2014, in an attempt to capture runoff
151 conditions. However, the precipitation and runoff during the winter/spring of 2013-14
152 was below average due to severe drought conditions in California (Mao et al., 2015).

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

160 Sample locations were grouped according to California groundwater provinces
161 established by the U. S. Geological Survey for the California Groundwater Ambient
162 Monitoring and Assessment program (<http://ca.water.usgs.gov/gama/>), which are based
163 on California Department of Water Resources-defined groundwater basins. The following
164 provinces are included in this study: Northern Coast Ranges (Northern Coast), Southern

165 Coast Ranges (Southern Coast), Klamath Mountains (Klamath), Central Valley, Sierra
166 Nevada and Transverse Ranges and Selected Peninsular Ranges (Transverse).
167 Additionally, an Ocean group was added to include ocean and heavily tidally-influenced
168 samples.

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

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

178 **3. RESULTS**

179 **3.1. STATISTICAL DISTRIBUTION**

180 The mean tritium concentration of 164 surface water and precipitation samples within
181 California was 9.4 ± 3.6 pCi/L. The lowest value, 1.3 pCi/L, was collected from the
182 Pacific Ocean at Salmon Creek Beach in Marin County. The highest tritium value, 23.7
183 pCi/L, was measured in a sample collected from San Benito River above the confluence
184 with the Pajaro River in July, 2013. The tritium distribution is represented on a histogram

185 with 1 pCi/L intervals between 0 and >18 pCi/L (Figure 2) and can be approximated by a
 186 Gaussian distribution with a mean of 9.4 and a standard deviation of 3.6. The absence of
 187 samples with less than 1.0 pCi/L indicates that all samples have a component of modern
 188 (post-1950) precipitation.

189
 190 Figure 2: Sample distribution in 1.0 pCi/L intervals (blue histogram) approximated by a
 191 Gaussian distribution (red line).

192 The range, median, and mean of tritium values in each of the seven groups is displayed in
 193 Figure 3. The mean concentration (4.4 ± 2.1 pCi/L) of samples in the Ocean group, with
 194 samples collected from the Pacific Ocean and estuaries, is less than half the statewide
 195 mean (9.4 pCi/L). Tritium concentrations in the other coastal study units (Southern Coast
 196 (8.0 ± 3.5 pCi/L), Northern Coast (6.4 ± 1.3 pCi/L), and Transverse Ranges (5.7 ± 1.6

197 pCi/L)) are below the statewide mean, reflecting the low tritium signal in precipitation
 198 derived from the ocean. The Klamath (7.8 ± 1.7 pCi/L) and Central Valley (9.4 ± 1.6 pCi/L)
 199 study unit means are similar to the population mean. Samples from the Sierra Nevada
 200 group have a higher mean (11.7 ± 2.9 pCi/L), reflecting the higher concentrations of
 201 precipitation at higher elevations and inland locations. The two highest tritium values,
 202 observed in samples from San Benito Creek and Atascadero Lake in the Southern Coast
 203 group, are explained in more detail below and were excluded from further statistical
 204 analyses as these samples were considered outliers, and not representative of regional
 205 tritium values. The standard deviation within each group is typically less than 2 pCi/L,
 206 with the exception of the Sierra Nevada and Southern Coast groups. Southern Coast
 207 samples may have been impacted by urbanization as discussed below. The variation
 208 within the Sierra Nevada group can be explained by the large latitudinal and
 209 topographical extent of the sample locations.

211 Figure 3: Tritium statistics for each spatial group. Count represents the number of
212 samples per group.

213 **3.2. SPATIAL TRENDS**

214 Tritium results were mapped and interpolated to explore spatial relationships (Figure 4).
215 Interpolation was performed by Empirical Bayesian kriging within ESRI ArcGIS 10.2.2.
216 Tritium values and spatial locations were the only parameters considered in the
217 calculation; outliers were not excluded.

218 The resulting interpolation highlights the expected trend of increasing tritium with inland
219 distance. Samples collected from coastal rivers contain lower levels of tritium, in the
220 range of approximately 4-6 pCi/L while samples collected in the Sierra Nevada contain
221 higher levels of tritium, often greater than 11 pCi/L. Central Valley surface water
222 samples contained tritium levels slightly lower than in the mountain source areas. This is
223 likely due to mixing between water draining the Sierra Nevada with groundwater and/or
224 local (lower elevation) runoff. Of the two main rivers that drain the Central Valley, the
225 southern San Joaquin River (10.8 pCi/L) has an average tritium concentration that is 3.1
226 pCi/L higher tritium than the northern Sacramento River (7.7 pCi/L). While the peaks of
227 Mt Shasta (4322m), which drains to the Sacramento River, and Mt Whitney (4421m)
228 reach similar elevation, the expansive mountain range of the Southern Sierra Nevada that
229 drains to the San Joaquin River results in stronger mixing with the upper atmosphere and
230 higher concentrations of tritium in precipitation. In addition, the contributing sources of
231 Sacramento River water are more distributed, and include lower elevation tributaries.

232 Samples collected from sources in the east and south San Francisco Bay Area have
233 tritium concentrations between 10.2 pCi/L and 17.4 pCi/L, comparable to those found in
234 the Sierra Nevada group and well above the concentrations found in samples along the
235 rest of the coast (3.9 pCi/L to 9.5 pCi/L). The effects of urbanization are apparent in these
236 areas. Two factors related to dense urbanization are likely contributing to increased
237 tritium concentration in surface waters: 1) municipal wastewater, which is supplied in
238 part from high-elevation inland mountain sources and 2) anthropogenic sources, such as
239 tritium-laden wastewater, or in the case of Alameda Creek, authorized releases from
240 Lawrence Livermore National Laboratory (LLNL). According to the Agency for Toxic
241 Substances & Disease Registry (ATSDR), tritium is released from LLNL primarily as
242 water vapor from several holding tanks (Agency for Toxic Substances & Disease
243 Registry, 2009). Ambient air, surface water, groundwater, and waste water are
244 periodically monitored for tritium concentration. In 1999, tritium in storm water
245 originating from LLNL was measured at a maximum concentration of 1,000 pCi/L. This
246 was the latest measurement date in the report, however, measurements over the previous
247 ten years showed a steady decline in released tritium concentration. Similarly, surface
248 water bodies in Orange County, CA, used for managed aquifer recharge, exhibit
249 relatively high levels of tritium (14 to 24 pCi/L), which is attributed to water imported
250 from the Sierra Nevada and Colorado River and a significant component of treated
251 wastewater (Clark et al., 2004; Davisson et al., 2004). In contrast, surface water samples
252 from the less populated areas to the north of the bay exhibit consistently low tritium
253 concentration. The hotspot along the coast to the south was a sample collected from

254 Atascadero Lake, in the city of Atascadero. The anomalously high tritium found in this
255 lake is most likely the result of tritium-releasing waste (wristwatches, exit signs or other
256 devices using tritium for illumination) than a representation of regional background
257 concentration. The other samples in this region contained low levels of tritium, consistent
258 with the coastal trend.

259 Some anomalous features of the interpolated map appear to be an artifact of the kriging
260 calculation. An area in Lassen County, in northeastern California, is mapped as higher
261 tritium than the surrounding area. This is not supported by empirical data; no samples
262 were collected in this area. Additionally, the trends in the area approximately south of
263 37°N and east of 119°W are also not supported by empirical data and should be ignored.

264 Compared to the previous models of tritium deposition in the United States, this high-
265 resolution model supports the findings of Stewart and Farnsworth (1968), showing a
266 longitudinal (East-West; coastal-to-inland) trend in California. Both models indicate that
267 tritium concentration increases toward the Sierra Nevada Mountains. A predominantly
268 latitudinal trend in California (Michel, 1989) was not observed in this study. This may be
269 attributed to a bias in sample locations during this study. Sample population density was
270 greatest in the northern portion of the Southern Coast group and the Sierra Nevada group,
271 creating a possible bias toward a longitudinal trend. More samples would need to be
272 collected in the northern and southern portions of the state to determine if a latitudinal
273 trend is also present. However, results for samples from e.g., the Klamath and Shasta
274 rivers, which drain high watersheds in far northern California, do not show increased

tritium concentrations. In addition, there is no observable trend in coastal rivers, although
 a North-South distance of more than 850 km is covered.

278 Figure 4: Discrete sample locations with interpolated tritium concentration mapped over
279 hydrologic features in California.

280 3.3. PRECIPITATION

281 The eighteen precipitation samples are compared to a reconstruction of historical tritium
282 concentrations in precipitation comprising a combination of records from Ottawa, Canada
283 (1953-1960) Menlo Park, California (1961-1974), and Portland, Oregon (1975-2002)
284 from the IAEA Global Network of Isotopes in Precipitation (GNIP) database
285 (IAEA/WMO, 2006) (Figure 5). Data for this reconstruction were obtained from the
286 GNIP Water Isotope System for Data Analysis, Visualization and Electronic Retrieval
287 (WISER) database on February 15, 2011 (<http://nds121.iaea.org/wiser/index.php>). Time-
288 series from Ottawa (Canada), Portland (OR), and Menlo Park (CA) were combined, by
289 cross-correlation of overlapping time periods and exponential fitting to extrapolate to
290 2010. Figure 5a shows monthly data for all three stations combined with the
291 precipitation-weighted annual average concentrations. Ottawa ($^3\text{H}_\text{O}$) is the only station
292 where data was acquired prior to 1961, and while it does provide a complete series from
293 1953 to 2007, the closer Portland station ($^3\text{H}_\text{P}$) provides a more reliable estimate of
294 tritium concentrations in California precipitation. For the period 1961 to 1975, the Menlo
295 Park station ($^3\text{H}_\text{MP}$) offers a reliable time series for coastal California. Samples collected
296 after 1975 showed anomalies attributed to local sources and the data from Menlo Park
297 was considered not representative of regional precipitation. For the period prior to 1961,
298 a linear regression with the Ottawa time series was derived as $^3\text{H}_\text{MP} = 0.20 * ^3\text{H}_\text{O}$, based

on the overlapping period. For the period between 1975 and 2002, a linear regression with the Portland time series was derived as ${}^3\text{H}_{\text{MP}} = 0.67 * {}^3\text{H}_{\text{P}}$, based on the period 1968 to 1974. Prior measurements (near the peak of tritium concentrations) caused the regression to deviate from the more relevant recent period and were excluded. The most recent period (2003 to 2010) was based on an exponential regression model fitted through the Portland data since 1970 (Eq. 2).

$${}^3\text{H}_{\text{MP}} = a + b \times e^{(c \times y)} \quad [\text{Eq 2}]$$

where y is the number of years since 1970 and fitted parameters $a=8.1$ pCi/L, $b=170$ pCi/L and $c=-0.186 \text{ y}^{-1}$.

The recent precipitation samples range in concentration between 4.0 pCi/L and 17.8 pCi/L and are in general agreement with the reconstructed values (Figure 5d). The lower values are consistent with pre-bomb background levels. The projected value for 2013 and 2014 of 8.0 pCi/L is close to the mean sample value of 6.3 ± 1.2 pCi/L for coastal samples. The estimated pre-bomb pulse value is 6 pCi/L, indicating that the average tritium in present day precipitation is still greater than pre-bomb pulse background concentrations.

315

316 Figure 5: Measured tritium concentrations in Ottawa, Vienna, Portland and Menlo Park

317 (a), correlation between Menlo Park and Ottawa (b (log scale), e (linear scale)) and

318 Portland (c (log scale), f (linear scale)) and the reconstructed tritium curve for Menlo

319 Park (d) with measured precipitation samples from Coastal (black) and Sierra Nevada

320 (grey) locations.

321 The precipitation data suggest a trend of increasing tritium with increasing elevation and

322 inland distance (Figure 6). The coastal low-elevation samples collected in Oakland and

323 Los Angeles have less tritium, by more than 10 pCi/L in some cases, than the inland high

324 elevation samples collected from the Tahoe Basin. These findings are consistent with

325 previous studies of tritium in precipitation (Eastoe et al., 2011; Izbicki et al., 2000). Two

326 data points were found in reverse of the trend. The sample collected from Fremont (14.75

327 pCi/L) has almost 10 pCi/L greater tritium concentration than samples collected in
328 Oakland, probably due to an (unidentified) anthropogenic source. A rain sample collected
329 near Lake Tahoe (5.00 pCi/L) is also in contrast to the overall trend, but was collected
330 during a warm, marine 'Pineapple Express'-type storm in February, 2012.

331 Previous models of tritium in precipitation across the United States have predicted a
332 positive gradient from the coast to the mountains in California, based on low spatial
333 resolution empirical data. The tritium data from recent precipitation samples generally
334 support this trend.

335

a

Figure 6: Tritium measurements from precipitation samples grouped by sample location. (a) Tritium concentration as a function of inland distance measured as longitudinal distance from the coast to sample location; (b) time series of Martis Valley snow samples collected between January and May 2012.

Time series of precipitation data from a Sierra basin show seasonal variability. Nine Martis Valley snow samples collected in 2012 and show a steady increase in tritium concentration between January and May (Figure 6b). The lowest concentration sample of 8.7 pCi/L was collected in January; the highest concentration of 17.8 pCi/L was collected in May. The precipitation weighted mean concentration is 13.7 pCi/L. This seasonal variation may be attributed to the Spring Leak phenomenon, which describes the mixing in the upper atmosphere and release of tritium from the stratosphere into the troposphere due to heating of the continents in spring (Zahn et al., 1998).

349

350 3.4. SEASONAL TRENDS IN SURFACE WATER

351 Repeat samples were collected from select locations in order to analyze seasonal
 352 trends in tritium. Seventeen locations were sampled twice with a spacing of
 353 approximately nine months. The seasonal difference in tritium values between sample
 354 pairs was examined in order to assess whether a significant change in tritium due to
 355 runoff or storage could be observed (Figure 7). Ten of the sample pairs showed a
 356 negative seasonal difference, indicating a decrease in tritium between seasons. Six of the
 357 sample pairs showed a positive seasonal difference. The anomalous Pajaro River sample
 358 collected in 2013 was considered an outlier (23.71 pCi/L) and not included in this
 359 analysis.

360

361 Figure 7: Seasonal difference in tritium between pairs of repeat samples collected in
362 Summer/Fall of 2013 and in Winter/Spring of 2013-2014. Bar color indicates spatial
363 group: Sierra Nevada (green), Central Valley (orange), Klamath (purple), and Southern
364 Coast (red). Negative differences indicate a decrease in tritium between sample dates.
365 Black lines indicate propagated uncertainty.

366 Surface water in the Sierra Nevada and Central Valley groups showed large to moderate
367 differences in tritium between seasons. The most significant negative seasonal difference
368 was observed in the South Fork of the American River, above Folsom Lake. Tritium
369 concentration decreased from Summer/Fall to Winter/Spring in the majority of the Sierra
370 Nevada and Central Valley locations. This decrease is likely due to a greater proportion
371 of low-tritium groundwater contribution to surface waters in 2013-2014 Winter/Spring
372 samples collected under drought conditions.

373 **3.5. ELECTRICAL CONDUCTIVITY AND TRITIUM**

374 Electrical conductivity (EC) measurements were collected when possible from the sample
375 location or from the sample in the laboratory in order to assess whether a relationship
376 exists between EC and tritium. Results for tritium surface water and precipitation samples
377 with an EC measurement were plotted on a semi-logarithmic graph (Figure 8) on which
378 groupings can be identified by shared geographic and hydrologic characteristics. Five
379 groups were identified according to the primary influence on EC: Precipitation, Spatial,
380 Agriculture, Oceanic, and Anthropogenic/Anomalous. Seven of the eight precipitation
381 samples included in this analysis plotted on the lower left side of the graph in the

Precipitation group, with low EC and moderate to low tritium. The tritium and EC values for precipitation ranged from 4.0 to 8.0 pCi/L and from 11 to 21 $\mu\text{S}/\text{cm}$. Other precipitation samples were not included in this analysis because EC was not available. It should be noted that samples were collected from roof top drip points, rather than dedicated precipitation collectors, and contamination by dissolved solids from the roof tiles may be the cause of some of the variability in EC.

Figure 8: Tritium and electrical conductivity plotted semi-logarithmically to emphasize group distributions.

Pacific Ocean samples and tidally-influenced river samples plot on the lower right side of the graph in the Ocean group, characterized by high EC and moderate to low tritium. The EC and tritium values in this group ranged from 15,190 $\mu\text{S}/\text{cm}$ and 1.3 pCi/L to 50970

394 $\mu\text{S}/\text{cm}$ and 6.7 pCi/L, respectively. Tritium is expected to be low in ocean samples
395 because of mixing of bomb pulse and cosmogenic tritium with old marine water due to
396 size and age of the ocean reservoir.

397 The Spatial group is composed of three sub-groups that represent samples of mountain,
398 inland or mixed, and coastal origin. Samples within this group trend along a line with an
399 R^2 value of 0.66. Samples collected in the Sierra Nevada Mountains above major
400 reservoirs and those collected in the Central Valley and below the reservoirs are
401 intermingled, showing a similar distribution. The samples collected from the northern
402 coastal range are spread midway down to the higher EC/lower tritium section of the trend
403 line between 121-543 $\mu\text{S}/\text{cm}$ and 4.4-8.9 pCi/L. The samples collected from the Bay
404 Area and Central Coast represent the lowest group on the trend line, between 201-773
405 $\mu\text{S}/\text{cm}$ and 3.6-8.2 pCi/L. This correlation is caused by the physiography of California.
406 The granites of the Sierra Nevada Mountains are relatively resistant to erosion and the
407 steep topographic slope reduces time for water-rock interaction. Electrical conductivity is
408 higher in the Central Valley and along the coast due to mixing with groundwater and
409 saline ocean vapor.

410 A dispersed group of samples that deviate from the Spatial group by increasing EC are
411 identified as possibly influenced by agricultural runoff or return flow. Samples in the
412 Agriculture group are largely collected from rivers that flow through agricultural areas.
413 The increased EC is therefore likely a product of increased salinity from agricultural
414 runoff (California CVRWQCB, 2006). This group includes samples with EC as high as

415 3008 $\mu\text{S}/\text{cm}$. These high TDS samples are distinct from the ocean and tidally influenced
416 samples by an approximately one order of magnitude higher tritium concentrations.

417 A final trend can be identified beginning at approximately 500 $\mu\text{S}/\text{cm}$ and 12 pCi/L and
418 increasing in tritium and EC. This trend, labeled Anomalous/Anthropogenic, is
419 characterized by EC in the agriculturally-influenced range along with the highest tritium
420 concentrations. Tritium in this trend is between 11-24 pCi/L. The Coyote Creek and
421 Guadalupe River samples are the lowest in tritium along this trend. Coyote Creek is
422 influenced by agriculture from the area to the south, and so may be mixed with older
423 groundwater used for irrigation. Guadalupe River runs through urban San Jose, so the
424 increased tritium may be attributed to an anthropogenic source such as recycled
425 municipal wastewater. Elevated tritium in Alameda Creek is also likely anthropogenic.
426 The creek is fed in part by tritiated runoff or groundwater that originated from LLNL.
427 The cause of elevated tritium in Atascadero Lake is unknown. This man-made lake is
428 situated in a residential area and may be impacted by waste streams with enhanced
429 tritium-, such as hospital or industrial waste, wristwatches and other tritium-illuminated
430 products. This is likely significantly exacerbated by recent reductions in lake water
431 elevations, increasing concentrations of tritium from an anthropogenic source. Similarly,
432 elevated tritium in a sample collected from the San Benito River above the confluence
433 with the Pajaro River may be attributed to tritiated waste sources in a low-volume stream.
434 However, this high level of tritium (23.71 pCi/L) was only observed in the first sample
435 collected at this location. In a subsequent sample, collected nine months later, the tritium
436 concentration of 9.02 pCi/L was consistent with those found in the Pajaro River above

437 and below the confluence. The higher tritium sample is greater than three standard
438 deviations from the mean (9.42 pCi/L), whereas the second San Benito and Pajaro River
439 samples are within one standard deviation. This is likely the result of a spike in tritium
440 from a temporary source, such as contaminated runoff. Further sampling would be
441 required to confirm this.

442 **3.6. DOWNSTREAM TRENDS AND RESERVOIR RESIDENCE TIMES**

443 To examine downstream trends and the effect of reservoirs on surface water tritium,
444 samples were collected at multiple locations along the same stream when feasible, with
445 emphasis on collection above and below large reservoirs in order to analyze downstream
446 trends and reservoir residence times. Seventeen groups of samples were collected at
447 different locations of the same stream on the same day; five of these were collected
448 upstream and downstream of dams below large reservoirs. The downstream change
449 in tritium was found by calculating the difference between tritium values of upstream
450 and downstream sample pairs. The tritium difference was then compared to the
451 distance between sample points (Figure 9). For groups with more than two sample
452 points, the tritium difference and sample distance were found between each
453 consecutive pair and between the pair with the greatest distance between them (i.e.,
454 the first and last sample points on the same stream), resulting in 30 total pairs.

455 It was expected that a negative correlation would emerge between tritium difference
456 and sample point distance. Increased distance allows for more input from
457 groundwater and for input from lower elevation runoff, diluting the higher tritium

458 concentrations from the upper part of the catchment with shorter flow paths
459 (Morgenstern et al., 2010). It was also hypothesized that tritium concentration would
460 be lower below dammed reservoirs based on reservoir size, turnover times, and
461 possible groundwater input. Conceptually, waters released from reservoirs might be
462 expected to have lower tritium concentration than waters flowing into reservoirs because
463 of radioactive decay of tritium in the reservoir and because of input of groundwater into
464 the reservoir.

465 As can be seen in Figure 9, the data do not show the correlation that was expected.
466 Of the 30 sample pairs, 12 showed a positive tritium difference, indicating that the
467 downstream signal was higher than the upstream signal. Only three of the five
468 reservoirs showed a negative difference between the upstream and downstream
469 tritium signal. In view of the seasonal variability in surface water tritium, a single
470 upstream sample may not be representative of the average tritium concentration of
471 waters flowing into the reservoir. As explained above, a decrease in tritium was
472 observed between Summer/Fall and Winter/Spring in Sierra Nevada surface waters.
473 Most of the sample pairs were collected in fall, when the background tritium input
474 was lower than during peak snowmelt. This may be contributing to a lesser
475 difference between upstream and downstream samples.

476

Figure 9: The difference in tritium between upstream/downstream sample pairs and the distance between these points.

Considering that 40% of the tritium differences are negative, both overall and of the reservoir subset, estimating the residence time from the tritium differences is no longer a valid method for obtaining even a basic residence time without considering additional sources of tritium.

4. DISCUSSION

The post-bomb era has many advantages for the application of tritium in hydrological studies. Once the bomb-pulse has decayed to a concentration equal to the natural background levels in precipitation and has been flushed out of the hydrological system, the precipitation-weighted concentration of tritium in precipitation can be considered constant and mean apparent ages of water samples can be derived directly from the tritium concentration (Morgenstern et al., 2010). The accuracy of this calculation depends

on the variability of the tritium in precipitation and the analytical uncertainty of the tritium measurement (Eq. 3).

$$\sigma_{\tau} = \lambda^{-1} \sqrt{(\sigma_C/C)^2 + (\sigma_{C0}/C_0)^2} \quad [\text{Eq. 3}]$$

where σ_{τ} is the uncertainty of the apparent age, λ is the decay constant, and σ_C and σ_{C0} are the uncertainties of the measured (C) and initial (C_0) tritium concentrations respectively.]

In California, if one assumes a precipitation concentration C_0 of 6 ± 1 pCi/L and a measurement uncertainty σ_C of 0.3 pCi/L (typically achieved at LLNL), then the uncertainty of the mean apparent age increases from 1 year at zero age, to less than 5 years at 30 years, to less than 10 years for a sample with a mean apparent age of 40 years. Hydrologic research faced a similar time horizon between 1990-2000, 30-40 years after the first nuclear tests, but with the added complexity that 1960s recharge could overwhelm and bias a sample of mixed age. In parts of the world with higher concentrations of tritium in precipitation (e.g. 30 pCi/L at present in Vienna, Austria), tritium ages of 70 ± 9 years can be achieved, and the time horizon for tritium dating will be extended compared to what it is today. Low initial concentrations of tritium in precipitation will cause larger uncertainty of $^3\text{H}/^3\text{He}$ groundwater dating because differentiating the smaller tritiogenic helium-3 component from atmospheric and terrigenous components will be more difficult. The error in age includes just the analytical error and the estimate of the initial concentration, but not the complexity of the stream

511 water travel time distribution. In addition, variable anthropogenic tritium input in
512 urbanized areas and close to nuclear power plants complicate direct age determination.

513

514 **5. CONCLUSION**

515 The concentration of tritium in present day precipitation in California varies between 4.0
516 pCi/L near the coast and 17.8 pCi/L in the Sierra Nevada Mountains. Concentrations
517 increase in spring due to the Spring Leak phenomenon. The average coastal concentration
518 (6.3 ± 1.2 pCi/L) is nearly back to estimated pre-nuclear levels.

519 Tritium concentrations in California surface water decreased between Summer/Fall 2013
520 and Winter/Spring 2014 in most streams in the Sierra Nevada and Central Valley, most
521 likely due to an increased groundwater signal with lower concentrations compared to
522 recent snowmelt as a result of drought conditions in 2014. Surface waters in the Klamath
523 and Southern Coast groups showed increases, possibly due to mixing with groundwater,
524 agricultural and urban runoff, or waste water in areas with intense human activity.

525 No correlation was found between tritium concentrations and distances downstream,
526 or above and below surface water reservoirs. Forty percent of the samples showed a
527 higher concentration in the reservoir outflow sample. Sampled surface water
528 concentrations feeding the reservoirs could be lower due to higher groundwater
529 contributions to streams than before the onset of the drought. Therefore, the storage

530 time of surface water reservoirs could not be derived from tritium decay and the
531 differences between upstream and downstream sample locations.

532 The relationship between tritium and electrical conductivity in surface water and
533 precipitation are indicative of water provenance and anthropogenic influences such as
534 agricultural runoff.

535 Tritium continues to be a valuable tracer in a post nuclear bomb pulse world. Despite low
536 concentrations in precipitation, the absence of the tritium transient allows for direct
537 assessment of residence times by comparing precipitation and river water tritium
538 concentrations.

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