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A Combined Radio- and Stable-Isotopic Study of a California Coastal Aquifer System

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Received: 15 February 2013; in revised form: 3 April 2013 / Accepted: 3 April 2013 / Published: 19 April 2013

Abstract: Stable and radioactive tracers were utilized in concert to characterize geochemical processes in a complex coastal groundwater system and to provide constraints on the kinetics of rock/water interactions. Groundwater samples from wells within the Dominguez Gap region of Los Angeles County, California were analyzed for a suite of major cations (Na⁺, K⁺, Mg²⁺, Ca²⁺) and anions (Cl⁻, SO₄²⁻), silica, alkalinity, select trace elements (Ba, B, Sr), dissolved oxygen, stable isotopes of hydrogen (δD), oxygen ($\delta^{18}O$), dissolved inorganic carbon ($\delta^{13}C_{DIC}$), and radioactive isotopes (³H, ²²²Rn and ^{223,224,226,228}Ra). In the study area, groundwater may consist of a complex mixture of native groundwater, intruded seawater, non-native injected water, and oil-field brine water. In some wells, Cl⁻ concentrations attained seawater-like values and in conjunction with isotopically heavier δ^{18} O values, these tracers provide information on the extent of seawater intrusion and/or mixing with oil-field brines. Groundwater ³H above 1 tritium unit (TU) was observed only in a few select wells close to the Dominguez Gap area and most other well groundwater was aged pre-1952. Based on an initial ¹⁴C value for the study site of 90 percent modern carbon (pmc), groundwater age estimates likely extend beyond 20 kyr before present and confirm deep circulation of some native groundwater through multiple aquifers. Enriched values of groundwater $\delta^{13}C_{DIC}$ in the absence of SO₄²⁻ imply enhanced anaerobic microbial methanogenesis. While secular equilibrium was observed for $^{234}U/^{238}U$ (activity ratios ~1)

in host matrices, strong isotopic fractionation in these groundwater samples can be used to obtain information of adsorption/desorption kinetics. Calculated Ra residence times are short, and the associated desorption rate constant is about three orders of magnitude slower than that of the adsorption rate constant. Combined stable- and radio-isotopic results provide unique insights into aquifer characteristics, such as geochemical cycling, rock/water interactions, and subsurface transport and mixing.

Keywords: radium; radon; groundwater; coastal aquifer; stable isotopes; residence times; desorption rate constant

1. Introduction

Widespread demands on the groundwater resources of Los Angeles County, California during the early 20th century have resulted in substantial groundwater-level declines, as well as associated coastal seawater intrusion and deteriorating water quality [1,2]. In an effort to stave off saltwater intrusion in the 1950s to the early 1970s, three series of injection wells were installed along the coast where injected water could create artificial hydraulic barriers, named West Coast Basin, Dominguez Gap, and Alamitos Gap barrier projects [3,4]. Over the past decade, ~26 to 37 million m³ of water are annually injected into these three barriers and while seawater intrusion has been generally reduced, at Dominguez Gap saltwater intrusion is still occurring [4]. This inefficiency in halting the seawater intrusion is due in part to an incomplete characterization of the stratigraphic architecture that partially controls the groundwater flow in this region. In an effort to better understand the geochemical character of this regional groundwater and to better predict future groundwater quality change, a study incorporating stable isotopes was initiated [4–6] and complemented with select U/Th radionuclide work.

Geochemical and isotopic tracers have been widely used to investigate rock/water interactions, recharge rates of meteoric water, evaporation effects, and groundwater transport phenomena [7,8]. For example, stoichiometric ratios of various cations and anions may provide insight into the chemical weathering rates of source minerals [9]. Oxygen isotopes in groundwater have been used to identify source water and to assess evaporation kinetics [10,11]. Furthermore, a fingerprint of historic fluctuations in water vapor and air mass trajectories can be preserved in the isotopic composition of meteoric groundwater [12,13]. The presence of ³H, with a half-life of 12.3 years, in groundwater can provide information on recharge rates and vertical flow velocities [14]. Stable isotopic composition of carbon in the dissolved inorganic matter in groundwater may yield information on the carbonate equilibrium, infiltration of atmospheric CO₂, as well as the microbial degradation of organic matter. In principal, the ¹⁴C concentration in groundwater can yield information on age data from a few thousand years to 45,000 years that can be used to help constrain groundwater flow velocities and direction, recharge rates, hydraulic conductivities, and effective porosity.

Select U/Th series radionuclides have been utilized to characterize an aquifer's physicochemical properties, such as adsorption-desorption rate constants and aquifer retardation factors [15–21]. Because the geochemical behavior of many contaminants of interest is quite similar to the geochemistry of select members of the U- and Th-series radionuclides, these nuclides can provide

unique information on the rates of some of these subsurface processes [22]. The movement of a dissolved species in groundwater can be retarded by several processes, such as ion exchange, adsorption, diffusion into blind pores, chemical precipitation, and membrane filtration [15,23,24]. The retardation of these species depends on particular aquifer characteristics (e.g., lithology, water chemistry, residence time), but parameters that control the retardation factor and absorption-desorption rate constants are not fully understood [17–20,25]. In particular, the dependence of these parameters on aquifer characteristics that are complexly mixed with diverse source waters, warrants further study.

To apply our combined radio- and stable-isotope approach, a suite of groundwater samples from the Dominguez Gap region of the southwest Los Angeles Basin, California were collected and analyzed for major and minor ions, select trace elements (Ba, B, and Sr) and stable isotopes ($\delta^{18}O$, δD , $\delta^{13}C_{DIC}$), tritium (³H) and a suite of U- and Th-series radionuclides (²²³Ra, ²²⁴Ra, ²²⁶Ra, ²²⁸Ra, and ²²²Rn). The study area is tectonically active [26–29], and as a result, uplift and erosion have winnowed many of the fine-grained confining units that serve to protect the underlying aquifers from seawater intrusion. As a consequence, there exists the potential for enhanced vertical and horizontal migration of seawater into the producing aquifers and subsequent landward migration of intruded waters beneath the Dominguez Gap Barrier Project [4,30,31]. The interaction between seawater and the aquifer system makes the sorption characteristics study of this aquifer of interest due to its relevance to other tectonically-active or structurally complex coastal areas.

2. Geographic Setting

Natural and artificial recharge to the Los Angeles Basin occurs through local precipitation and infiltration, seawater intrusion along the coast, injection of non-native water into the barrier wells, and regional groundwater flow from adjacent basins. Each water-mass end member is geochemically distinct and has been identified with a suite of isotopes and geochemical parameters [6]. Groundwater samples for this study were collected from the Dominguez Gap region of the southwest Los Angeles Basin, located along the coastal plain of Los Angeles County adjacent to San Pedro Bay (Figure 1). The Dominguez Gap denotes a hydrologic "gap" that occurs just south of the Dominguez Hills, where the Los Angeles River transverses the Newport-Inglewood Uplift. In general, exposed Late Pleistocene alluvial deposits cover large parts of the coastal plain except close to the Los Angeles River, where as much as ~ 10 m of Holocene-aged fluvial and marine sediment has filled in parts of the paleo-river channel of the Los Angeles River during a lower sea level stand. The hydrogeology of the Dominguez Gap region has been well studied [26,27,32] and is summarized in a shore-perpendicular cross-section (Figure 2). Injection of fresh water in the West Coast Basin and Dominguez Gap Barrier Projects is a significant source of recharge to the West Coast Groundwater Basin [6]. Ponti et al. [30] developed a sequence stratigraphic model of the Dominguez Gap area that further refined these water-bearing depositional systems relative to sediment supply, sea level, and accommodation space. Their work also identified the Pacific Coast Highway (PCH) Fault, which may play an important role in the mixing of seawater into deep aquifers.

Figure 1. Base map of the well sites and the prominent geologic and hydrologic features of the study area, Los Angeles County, California. The Huntington Park monitoring well site is located in the adjacent Central Basin, 6.5 km south of downtown Los Angeles, and in an area known as the Los Angeles forebay. The forebay is an area of groundwater recharge for some of the water contained in the West Coast Basin. Note the following abbreviations: LWEB = Webster; LBCH = Cabrillo; LBPC = Pier C; LBPF = Pier F are used throughout the text, figures, and tables.



Figure 2. An idealized hydrogeologic cross-section of the Dominguez Gap area, also showing the sequence boundaries as defined by Ponti *et al.* [30]. Geographic location of the **A**–**A**' transect is shown in Figure 1.



3. Groundwater Radionuclide Transport

The fate of U/Th series radionuclides in groundwater continues to be an active area of research primarily to better understand and predict subsurface contaminant actinide transport [21]. Many of the early advances in modeling naturally-occurring radionuclides in groundwater were pioneered by Rama and Moore [25] and Krishnaswami *et al.* [15] and later summarized by Ku *et al.* [20] and Porcelli and Swarzenski [21]. The following model stems largely from the original Krishnaswami *et al.* [15] formulations. The dominant processes that can control the fate of U/Th series radionuclides in groundwater include both *input* terms, such as, (1) recoil mechanisms, (2) congruent dissolution within an aquifer solid, (3) desorption reactions from solid surfaces, and (4) *in-situ* radioactive decay of a dissolved parent nuclide, as well as *removal* terms, such as (1) chemical precipitation, (2) radioactive decay, and (3) reversible sorption onto particle surfaces. If we assume the kinetics of adsorption and desorption to be first order [20,21], then the steady-state mass balance reactions for a radionuclide in an aquifer can be reduced to the following equations [15]:

Dissolved phase:
$$P + k_2 N_s = \lambda N_d + k_1 N_d$$
 (1)

Solid phase:
$$k_1 N_d = \lambda N_s + k_2 N_s$$
 (2)

Here *P* (atoms per second per volume of water) defines the production rate of a nuclide in solution by such processes as chemical dissolution (*i.e.*, weathering), *in-situ* production and recoil, λ is the decay constant (0.693/ $t_{1/2}$) of a radionuclide, k_1 and k_2 are first-order adsorption and desorption rate constants, respectively, and N_d and N_s describe the respective concentration of a nuclide in water (atoms per volume of water) and adsorbed onto an aquifer matrix. The recoil term is the dominant supply term for short-lived radionuclides (*i.e.*, ²²⁴Ra, ²²³Ra, ²²⁸Ra, with a mean-life < 10 years), although there could be some contribution from congruent weathering for ²²⁶Ra (mean-life = 2309 years). The ratio (Ω) of the activity of a nuclide (= λN_d) to its production (*P*) in solution can be calculated from Equations (1) and (2), as follows:

$$\Omega = \lambda N_{\rm d} / P = (k_2 + \lambda) / (k_1 + k_2 + \lambda)$$
(3)

Assuming negligible isotopic fractionation [21], the adsorption (k_1) and desorption (k_2) rate constants are expected to be the same for two isotopes of the same element. If we assume "*i*" and "*j*" to describe two isotopes of one element, then the mass balance equations of each of these nuclides can be combined and solved for k_1 and k_2 [15] as follows:

$$k_1 = \left[\left(\lambda_i - \lambda_j \right) \left(1 - \Omega_i \right) \left(1 - \Omega_j \right) \right] / \left(\Omega_i - \Omega_j \right)$$
(4)

and

$$k_2 = [\Omega_i \Omega_j (\lambda_j - \lambda_i) + \lambda_i \Omega_j - \lambda_j \Omega_i)]/(\Omega_i - \Omega_j)$$
(5)

From the measured groundwater 222 Rn, 224 Ra, and 228 Ra activities and their radiogenic parents, 230 Th, 228 Th, and 232 Th activities, in the solid phase, we can determine k_1 and k_2 using Equations (4) and (5).

4. Materials and Methods

Most samples for this effort were collected as part of a larger U.S. Geological Survey (USGS) project on the groundwater quality and geochemical character underlying Los Angeles County and thus more complete sampling protocols and analytical methods are described in detail therein [4–6]. Briefly, each well was sufficiently purged and then sampled using "clean" procedures to avoid contamination as per standard USGS water quality sampling protocols. Chemically unstable constituents, such as alkalinity and ²²²Rn, were processed and/or preserved in the field. Water quality data including stable and radiogenic isotopes were determined at the USGS Water Quality Laboratory in Denver, CO [5,6]. Stable isotopes were determined using isotope mass spectrometry with a gas-source stable isotope mass spectrometer, as per methods described in Epstein and Mayeda [33] and Coplen *et al.* [34]. The 2-sigma uncertainty of oxygen and hydrogen isotopic results is 0.2‰ and 2‰, respectively.

Radon-222 activities were measured in the field using a commercially available Rn-in-air monitor (RAD7—DURRIDGE, Inc., Billerica, MA, USA) coupled to a RAD-H2O discrete water sampling kit [35–38]. Radium-223 and ²²⁴Ra activities were quantified using delayed-coincidence alpha counting techniques [37–39]. Briefly, Ra was quantitatively removed from large groundwater samples (50–100 L) using MnO₂ fiber cartridges. The partially dried fiber was subsequently placed into a closed, recirculating loop and a RaDeCC detector. The ²²³Ra and ²²⁴Ra isotopes were recounted after ~20 days to correct for supported ²²⁴Ra activities (from ²²⁸Th), and subsequently decay-corrected to the mid-point sampling time. Propagated errors for the delayed coincidence counters are typically <10%. After the counting for short-lived Ra isotopes was completed, the fiber was leached with a 6M HCl-H₂O₂-hydroxylamine hydrochloride mixture to quantitatively remove Ra from the Mn fiber. The Ra was co-precipitated with BaSO₄ using Ba(NO₃)₂-H₂SO₄ [40] and the BaSO₄ precipitate was counted after 20 days (allowing for the in-growth of ²²²Rn daughters) in a high-purity Ge well detector coupled to an InSpector gamma spectrometry software package. The ²²⁶Ra and ²²⁸Ra activities were quantified using gamma energies of 352 and 609 keV for ²²⁶Ra and 338 and 911 keV for ²²⁸Ra.

Seven soil samples from well cuttings that represented a spectrum of geologic material from the well sites were also analyzed for ²³⁸U, ²³⁴U, and ²³⁰Th using an inductively coupled plasma mass spectrometer (ICP-MS). Briefly, ~200 mg of dried, pulverized sample was brought into solution using HF and concentrated HNO₃. Blanks and reference standards for radionuclides in sediment, IAEA 385 (Irish Sea sediment) were prepared and analyzed as quality control measures. The concentrations of ²³⁸U, ²³⁴U and ²³⁰Th were measured by ICP-MS in the single-collector mode.

5. Results and Discussion

5.1. Major Ion Composition

In addition to two well parameters (approximate horizontal flow path distance, x, and depth to the top of the screened interval, z), concentrations of the major cations (Na⁺, K⁺, Ca²⁺ and Mg²⁺) and anions (Cl⁻, alkalinity (as CaCO₃), and SO₄^{2^-}), dissolved oxygen (DO), as well as Ba, B, and Sr are presented in Table 1. The DO concentration, which can be a useful proxy for oxidation effects during sampling of reduced groundwater, ranged between <0.1 to 2.6 mg L⁻¹. Of the 30 samples that were measured for DO, only one sample (LWEB-4) was slightly above a "hypoxic" condition. While most chloride concentrations of native groundwater did not exceed 35 mg L^{-1} in the Lower aquifer systems, some wells close to the coast had historic Cl⁻ values as high as 90 mg L⁻¹. Table 2 lists summary parameters and descriptions of well waters. Water levels of many of these near-shore wells increased in response to sustained freshwater injection, yet a concomitant decrease in Cl⁻ values is not always observed [41]. For example, elevated Cl⁻ concentrations have been measured in several Upper and Lower aquifer system wells east of the Dominguez Gap Barrier Project; Long Beach 3 and Long Beach 4. In water from the wells, the Na⁺ concentration varied between 39 (Huntington Park #1) and 10,800 mg L^{-1} , while the Cl⁻ concentration ranged from 18.5 to 19,900 mg L^{-1} (seawater-like value observed at LBPF-2). Excluding LBPF-2 as groundwater here consist mostly of seawater, a plot of Cl⁻ as a function of Na⁺ (Figure 3A) illustrates that many of the wells are variably influenced by elevated Cl⁻ concentrations. There is an expected [41] strong positive correlation ($R^2 = 0.88$) between SO₄²⁻ and Ca^{2+} concentrations (Figure 3B). Extensive SO_4^{2-} reduction and cation exchange reactions result in most native groundwater within the study area having a characteristic Ca/Na-bicarbonate to Na-bicarbonate composition with very low Cl⁻ concentrations, <65 mg L⁻¹ [6.42]. Non-native water typically exhibits a dominant Ca/Na-sulfate composition, while wells intruded by seawater or mixed with oil-field brines have a Na-Cl composition [6]. As many Tertiary brine fluids are also defined by a high Na-Cl composition, it is not easy to separate these from seawater-intruded waters (e.g., Wilmington-2 #2). See Table 2 for a summary of characteristic geochemical parameters that define these well waters as well as recent trends in water quality.

Table 1. Select well characteristics and water quality data for wells sampled. Well location for all but Huntington Park sites shown in Figure 1. The Huntington Park site is located in a recharge area of the adjacent Central Basin, near downtown Los Angeles [6].

	x^{1}	z^2	DO ³	Ca ²⁺	Mg ²⁺	\mathbf{K}^{+}	Na ⁺	Alk. ⁴	Cl	SO ₄ ²⁻	Ba	В	Sr
well ID	km	m	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$mg L^{-1}$	$\mu g \ L^{-1}$	$\mu g \; L^{-1}$	$\mu g \ L^{-1}$
Huntington Park #1 (4/9/1997)	0.0	271	0.2	59	14	3	39	168	21	80	58	132	451
Huntington Park #2 (4/10/1997)	0.0	210	0.5	59	14	3	40	178	22	82	70	133	470
Carson-1 #1 (1/6/1998)	16.7	279	< 0.1	19	4	3	51	141	20	< 0.1	12	96	185
Carson-1 #2 (1/5/1998)	16.7	238	0.2	32	7	2	42	169	21	< 0.1	39	102	369
Carson-1 #3 (1/6/1998)	16.7	168	0.2	44	12	3	47	164	23	62	58	105	398
Carson-1 #4 (1/6/1998)	16.7	69	0.2	86	21	4	74	204	112	112	199	117	835
Wilmington-1 #1 (4/24/1999)	20.8	279	0.1	50	16	7	106	134	213	< 0.1	12	123	371
Wilmington-1 #2 (4/25/1999)	20.8	238	0.2	124	27	6	130	135	337	59	11	175	1,153
Wilmington-1 #3 (4/25/1999)	20.8	168	< 0.2	214	47	9	346	173	907	50	27	240	2,129
Wilmington-1 #4 (4/25/1999)	20.8	69	0.1	282	96	13	457	142	1,209	288	121	221	3,688
Wilmington-1 #5 (4/24/1999)	20.8	37	< 0.2	85	31	7	145	197	233	140	103	203	1,089
Wilmington-2 #1 (4/21/1999)	23.0	290	< 0.1	3	2	5	195	377	56	< 0.1	7	653	39
Wilmington-2 #2 (2/18/1999)	23.0	230	< 0.1	35	24	13	499	450	513	< 0.1	57	1,578	407
Wilmington-2 #3 (2/21/1999)	23.0	165	< 0.1	20	7	4	102	180	72	< 0.1	23	266	177
Wilmington-2 #4 (4/21/1999)	23.0	119	< 0.1	143	67	16	492	308	1,012	29	117	557	1,266
Wilmington-2 #5 (2/18/1999)	23.0	37	< 0.1	761	363	31	2,604	202	5,232	595	162	732	6,905
LWEB-1 (3/29/2001)	19.0	411	0.1	11	3.47	3.8	156	392	18.5	1	8.7	372	120
LWEB-2 (3/29/2001)	19.0	304	0.2	15.9	2.73	2.5	61.5	144	18.8	25.3	10	138	191
LWEB-3 (3/28/2001)	19.0	204	0.4	17.9	3.24	2.7	55.8	159	24.8	0.2	13	132	226
LWEB-4 (3/27/2001)	19.0	162	2.6	88.8	24	6.2	72.9	139	213	57.9	31	109	962
LWEB-5 (3/26/2001)	19.0	125	0.2	238	57.3	7.8	98.6	148	619	62.7	109	110	2,530
LBCH-1 (8/27/2003)	21.4	360	< 0.1	6.2	3.03	4.8	206	503	22.9	3	6.3	785	77.2
LBCH-2 (8/26/2003)	21.4	198	0.1	13.5	4.08	3.5	107	181	74.4	1.2	4.6	238	171
LBCH-3 (8/26/2003)	21.4	143	< 0.1	12.8	4.43	3.2	97.1	177	67.6	4	3.5	223	185
LBCH-4 (8/25/2003)	21.4	110	0.2	463	174	21	615	145	2,100	278	113	419	4,860
370-AJ (6/08/2005)	21.0	66	-	295	109	12	438	129	1,420	184	78	198	2,770
370-AH (6/08/2005)	21.0	20	-	454	335	34	1,440	200	3,810	391	167	361	4,650
LBPC-1 (4/03/2001)	24.2	366	< 0.1	9.57	4.63	5.8	259	492	21.4	3.6	15	1,100	134
LBPC-2 (4/04/2001)	24.2	244	< 0.1	6.55	7.18	11	422	614	337	1.4	17	1,150	97.5
LBPF-1 (4/24/2002)	27.0	332	0.1	17.8	30.5	26	1,500	1,230	1,650	-	127	8,400	734
LBPF-2 (4/24/2002)	27.0	102	0.1	519	1,220	272	10,800	289	19,900	2,640	82	4,130	8,500

Notes: ¹ Approximate distance along flow path [6]; ² Depth to top of perforation; ³ Dissolved oxygen, mg L^{-1} ; ⁴ As CaCO₃; ⁵ LWEB = Webster; LBCH = Cabrillo; LBPC = Pier C; LBPF = Pier F.

Wilmington-2 #4

Upper Wilmington

Na-Cl

mixing

Well ID	Stratigraphic unit ¹	Chemical composition ²	Change in chemical composition (1998–2011) ³	Chloride range ⁴	Stable isotope ⁵	Relative age of water ⁶	Comment
Huntington Park #1	Bent Spring	Ca-HCO ₃	unchanged	low	N	old	Native water of good quality; end member for flow system
Huntington Park #2	Harbor	Ca-HCO ₃	unchanged	low	Ν	old	Native water of good quality; end member for flow system
Carson-1 #1	Upper Wilmington	Na-HCO ₃	unchanged	low	Ν	old	Native water of good quality; source of recharge similar to Huntington Park
Carson-1 #2	Upper Wilmington	Na/Ca-HCO ₃	unchanged	low	Ν	old	Native water of good quality; source of recharge similar to Huntington Park
Carson-1 #3	Harbor	Ca/Na-HCO ₃	unchanged	low	Ν	old	Native water of good quality; source of recharge similar to Huntington Park
Carson-1 #4	Pacific	Ca/Na-HCO ₃	mixing	low	Ν	old	Gradual decrease in TDS since initial sampling; [Cl] from 210 to \sim 40 mg L ⁻¹
Wilmington-1 #1	Upper Wilmington	Na-Cl	unchanged	low	Ν	old	Possible enhanced lateral movement due to intense nearby pumping
Wilmington-1 #2	Upper Wilmington	Ca/Na-Cl	mixing	medium	Ν	old	Possible enhanced lateral movement due to intense nearby pumping
Wilmington-1 #3	Upper Wilmington	Na/Ca-Cl	mixing	medium	I-S-N	recent	Inland from Dominguez Gap Seawater Barrier Project; contains mixture of native water, seawater, and imported water from overlying unit
Wilmington-1 #4	Harbor	Na-Cl	variable	medium	Ι	recent	Likely mixture of imported and seawater
Wilmington-1 #5	Pacific	Ca/Na-Cl	variable	low	Ι	recent	Likely mixture of imported and seawater
Wilmington-2 #1	Pliocene B	Na-HCO ₃	variable	low	Ν	old	Isotopically light water recharged during Pleistocene
							Principally isotopic light water (similar to Wilm2 #1);
Wilmington-2 #2	Pliocene A	Na-Cl	mixing	medium	S	old	localized saline unit attributed to partial mixing with an oil-field brine
Wilmington-2 #3	Lower Wilmington	Na-Cl/HCO ₃	variable	low	Ν	old	Native, fresh, sodium-bicarbonate water

I-S-N

recent

medium

Table 2. Summary parameters and description of well water for this study.

Significant improvement in TDS likely a result of more

effective injection; [Cl] decreased from ~1000 to 290 mg L^{-1}

Table 2. Cont.

Well ID	Stratigraphic unit ¹	Chemical composition ²	Change in chemical composition (1998–2011) ³	Chloride range ⁴	Stable isotope ⁵	Relative age of water ⁶	Comment
Wilmington-2 #5	Harbor	Na-Cl	mixing	high	S-I	recent	Some imported water is present, though masked by seawater intrusion. Significant improvement in TDS likely a result of more effective injection; [CI] decreased from \sim 5200 to 2600 mg L ⁻¹
LWEB-1	Pliocene A	Na-HCO ₃	unchanged	low	Ν	old	Isotopically light water recharged during Pleistocene
LWEB-2	Upper Wilmington	Na-HCO ₃	mixing	low	Ν	old	Geochemistry suggests subtle reactions or long-term pumping effects
LWEB-3	Upper Wilmington	Na-HCO ₃	variable	low	Ν	old	Native, fresh, sodium-bicarbonate water
LWEB-4	Bent Spring	Ca-Cl	variable	low	Ν	old	Native, fresh, sodium-bicarbonate water
LWEB-5	Harbor	Ca-Cl	variable	low	Ν	old	Native, fresh, sodium-bicarbonate water
LBCH-1	Lower Wilmington	Na-HCO ₃	unknown	low	Ν	old	Isotopically light water recharged during Pleistocene
LBCH-2	Upper Wilmington	Na-HCO ₃	unknown	low	Ν	old	Isotopically light water recharged during Pleistocene
LBCH-3	Upper Wilmington	Na-HCO ₃	unknown	low	Ν	old	Isotopically light water recharged during Pleistocene
LBCH-4	Bent Spring	Na/Ca-Cl	unknown	low	N-S	recent	
370-AJ	Harbor	Na/Ca-Cl	unknown	medium	N-S	recent	
370-AH	Dominguez	Na-Cl	unknown	high	N-S	recent	
LBPC-1	Pliocene B	Na-HCO ₃	unknown	low	Ν	old	Isotopically light water recharged during Pleistocene
LBPC-2	Pliocene A	Na-HCO ₃ /Cl	unknown	medium	Ν	old	Isotopically light water recharged during Pleistocene
LBPF-1	Pliocene A	Na-Cl/HCO ₃	unknown	medium	Ν	old	Old seawater, distinct major ion composition and trace element ratios
LBPF-2	Bent Spring	Na-Cl	unknown	high	S	old	Groundwater consisting mostly of seawater

Notes: ¹ Nomenclature consistent with most recent model layer assignments [43]; as well as in Ponti *et al.* [30] and Figure 2; ^{2,3} Change in chemical composition: where period of record is available, a general description of water quality over time is given; ⁴ Chloride range: low = <250 mg L⁻¹, medium = 250–2500 mg L⁻¹, and high = >2500 mg L⁻¹; ⁵ N, native water; S, seawater; I, imported water; ⁶ Relative age: see Section on Tritium; about 1 tritium unit (TU) used for recent/old categorization.

5.2. Tritium

The tritium data provide insight as to the relative age or "old" *versus* "new" groundwater in our study. Tritium (³H; $t_{1/2} = 12.4$ years) is the only radioactive isotope of hydrogen and while it is naturally present only in minute (<<1%) quantities, it is also produced as a fission product in nuclear weapons tests and nuclear power reactors. The convention for reporting ³H concentrations is the tritium unit (TU), which equals 3.2 pCi L⁻¹ (7.104 dpm L⁻¹). As tritium is naturally incorporated into the water molecule and its abundance is only affected by radioactive decay, ³H serves as a useful tracer for identifying recently recharged water. A pre-fallout (pre-1952) background ³H abundance in southern California coastal precipitation was ~2 TU [44]. Beginning in 1952, ³H was released into the atmosphere, reaching a maximum in 1963 [45]. A reconstructed Los Angeles County precipitation tritium concentration curve [6] identifies a narrow 1963 peak at ~700 TU that rapidly decreased to <100 TU by 1970. As a consequence, without consideration for complex mixing scenarios, groundwater with a ³H value less than <1 TU may be considered "older" water that was recharged prior to 1952. Conversely, groundwater with a tritium content >1 TU can be interpreted as "recent" water being wholly or partially recharged post-1952. Along the coast, such interpretation may be more complicated as recent seawater may provide another source of tritium.





Of the 31 groundwater samples analyzed for tritium (average ³H value = 4.3 TU), seven samples had a ³H concentration >1 TU and of these, three had ³H >10 TU (Table 3); each of these wells perforated the Pacific and Harbor sequences. The large number of low or less than measureable (0.1 TU) tritium values indicates that most sampled groundwater in the Dominguez Gap region appears to be older water (pre-1952). Notable exceptions include wells close to the coast (Wilmington-1 #4, Wilmington-1 #5, and Wilmington-2 #5) that are directly influenced by recent seawater intrusion and the seawater barrier injection wells that may introduce additional, substantial ³H as a result of complex mixing scenarios (Table 2; Figure 2).

	δ ¹⁸ Ο	δD	³ H	$\delta^{13}C_{DIC}$	¹⁴ C
Well ID	(‰)	(‰)	(TU)	(‰)	(pmc)
Huntington Park #1	-7.32	-47.5	< 0.1	-13.6	83.7
Huntington Park #2	-7.23	-47.3	< 0.1	-13.5	83.5
Carson-1 #1	-7.33	-48.4	0.1	-12.4	27.6
Carson-1 #2	-7.27	-46.6	< 0.1	-12.3	43.6
Carson-1 #3	-7.30	-47.3	< 0.1	-14.2	56.1
Carson-1 #4	-7.12	-47.0	0.1	-	-
Wilmington-1 #1	-7.29	-46.8	< 0.1	-15.8	29.6
Wilmington-1 #2	-7.13	-46.0	< 0.1	-18.4	44.5
Wilmington-1 #3	-7.34	-49.4	1.6	-	-
Wilmington-1 #4	-9.77	-77.5	19	-	-
Wilmington-1 #5	-9.58	-73.3	11.9	-	-
Wilmington-2 #1	-8.73	-59.7	< 0.1	-0.3	2.5
Wilmington-2 #2	-8.63	-55.8	< 0.1	-0.3	5.2
Wilmington-2 #3	-7.84	-50.6	< 0.1	-15.0	14.4
Wilmington-2 #4	-7.96	-51.3	1.5	-	-
Wilmington-2 #5	-7.57	-57.7	16.9	-	-
LWEB-1	-9.17	-62.7	< 0.1	6.3	1.8
LWEB-2	-7.72	-51.1	0.1	-15.8	24.1
LWEB-3	-8.07	-53.2	< 0.1	-18.9	14.1
LWEB-4	-7.32	-48.4	< 0.1	-14.3	42.8
LWEB-5	-7.10	-47.4	< 0.1	-13.9	55.1
LBCH-1	-9.39	-64.0	< 0.1	4.7	3.5
LBCH-2	-8.37	-55.1	0.1	-10.6	8.8
LBCH-3	-8.15	-53.6	< 0.1	-16.0	9.8
LBCH-4	-6.86	-45.9	1.8	-16.0	61.4
370-AJ	-7.12	-49.9	1.1	-	-
370-AH	-6.76	-47.3	0.9	-	-
LBPC-1	-9.23	-61.1	0.2	3.1	2.5
LBPC-2	-7.54	-49.2	<0.1	-12.7	4.3
LBPF-1	-7.47	-47.1	<0.1	-6.4	0.8
LBPF-2	-0.42	-3.65	< 0.1	-12.3	48.5

Table 3. Select stable and radiogenic isotope data for wells sampled in the study site. Note: pmc = percent modern carbon.

5.3. Isotopic Composition of Oxygen ($\delta^{18}O$) and Hydrogen (δD)

The behavior of stable oxygen (δ^{18} O) and hydrogen (δ D) isotopes in groundwater can provide insight into the geochemical character, origin, and transport phenomena of groundwater [8]. Reporting convention for both isotopes is expressed in terms of relative difference, per mill (‰), from the Vienna Standard Mean Ocean Water (VSMOW) value. In general, the predominant source of precipitation is from evaporation of seawater, and as a result, the observed global composition of δ^{18} O and δ D in rainwater is linearly expressed as the global meteoric water line (GMWL; δ D = $8\delta^{18}$ O + 10‰; [46,47]).

In the 31 groundwater samples, the δ^{18} O composition ranged from -0.42% (LBPF-2) to -9.77% (Wilmington-1#4), while the δ D composition varied between -3.65% (LBPF-2) to -77.5% (Wilmington-1#4) (Table 3). A plot of δ D *versus* δ^{18} O (Figure 4) indicates a strong linear relationship ($R^2 = 0.93$), with a slope of 7.2—close to that of the global meteoric water line (GMWL; slope = 8). Notable exceptions of groundwater (*i.e.*, Wilmington-1#4; Wilmington-2 #5) that influence such a shift below the GMWL include isotopically heavier water that likely consists of a recent mixture of saline (e.g., seawater) and imported fresh water [4]. Lighter δ D values (<-50‰), observed in some groundwater samples (e.g., LBPF-1,2, Wilmington-1#1-3, Huntington Park 1,2, Carson-1#1-4, 370-AJ, 370-AH, LWEB-4,5) may identify older groundwater with a isotopically unique signature.

Figure 4. δD *versus* $\delta^{18}O$ in selected groundwater samples from the study area. The global meteoric water line is per Craig (1961). Regression results include all groundwater data. Water recharged from Los Angeles and Montebello Forebays has a $\delta^{18}O$ signature of -7.5% to -6.7% and -9.5% to -8.0%, respectively, and is isotopically distinct from non-native, seawater, and oil-field brine values.



The composition of δD and $\delta^{18}O$ in precipitation may also be influenced by local air mass and vapor trajectories, changes in evaporation, and isotope exchange processes below the cloud base [10,47]. Thus, climatic variations may be recorded in the composition of $\delta^{18}O$ and δD in groundwater [12]. In LBPF-2, where the Cl⁻ concentration approaches a seawater-like value (Figure 4), both $\delta^{18}O$ and δD isotopic compositions are highly enriched (heavy) (-0.42% for $\delta^{18}O$ and δD for -3.65%) compared to other well waters (-6.76 to -9.77% for $\delta^{18}O$ and -45.9 to -77.5% for δD). The isotopic composition of the well waters, coupled with the major ion chemistry, implies variable mixing with recent seawater. In addition, isotopically lighter water with low Cl⁻ content has also been attributed to Colorado River water [6] that is used as a source of injection water at the barrier wells [48]. Observed high Cl⁻ concentrations along with enriched $\delta^{18}O$ reveal non-native inputs from seawater and/or oil-field brines (Table 2).

5.4. Isotopic Composition of $\delta^{13}C$ in Dissolved Organic Carbon (DIC)

Dissolved inorganic carbon (DIC = $[CO_{2aq}] + [HCO_3^-] + [CO_3^{2^-}]$) is generally produced in groundwater by the dissolution of CO₂ during plant (*i.e.*, C₃ and/or C₄) respiration, the microbial decomposition of organic matter, and the direct dissolution of carbonate minerals [49]. The composition of δ^{13} C, expressed as per mill (‰) relative to the VPDB (Vienna PeeDee Belemnite) standard, provides a useful tracer to assess the relative contribution of C from these various sources. Under an open CO₂ system, the groundwater δ^{13} C_{DIC} should approach ~9‰ by simple hydrolysis reactions of soil CO₂ alone [7]. Conversely, if the groundwater is closed to soil CO₂, then the δ^{13} C_{DIC} should approach values of about -13‰. In groundwater that is strongly reducing and sulfate-poor [50], the composition of δ^{13} C_{DIC} can increase to values in excess of 30‰ as a result of methanogenesis [51]. Observed saturation calculations for portions of the study area, and elsewhere in the basin, indicate that calcite should precipitate.

In this study, the groundwater δ^{13} C in dissolved inorganic carbon ranged from -18.9 (LWEB-3) to 6.3‰ (LWEB-1) (Table 3), which reflects the contribution of different DIC sources and/or the evolution from an open to a closed system. Wells sampled for this study, with the exception of 370-AH and possibly Wilmington-1#5 appear to respond within a confined system. Three deep samples (LWEB-1, LBCH-1, LBPC-1) contain $\delta^{13}C_{DIC}$ values >0‰ and very little SO₄²⁻, which would suggest a unique carbon source, such as from an incomplete bacterially-mediated methanogenic pathway [52]. There have been a number of studies indicating a linear relationship between $\delta^{13}C_{DIC}$ and 1/dissolved inorganic carbon (DIC) [49,52–55]. In lieu of direct dissolved inorganic carbon measurements alkalinity (expressed as CaCO₃) can serve as a proxy for DIC, under the condition that CO₂ remains constant [56]. If one excludes values from wells closest to the coast and down-gradient from the PCH Fault (e.g., LBPC-2, LBPF-1,2) there is a good correlation ($R^2 = 0.88$) between $\delta^{13}C_{DIC}$ and 1/alkalinity (Figure 5). Such a trend, which implies more than simple carbonate mineral dissolution, is expected in a complexly mixed coastal aquifer undergoing chemical evolution [11,13,57].



Figure 5. $\delta^{13}C_{DIC}$ versus 1/alkalinity (excluding wells closest to the coast; LBPC-2, LBPF1,2).

5.5. Carbon-14 (¹⁴C)

To assess the relative age of select groundwater samples, ¹⁴C ($t_{\frac{1}{2}} = 5730$ years) was also determined. Natural ¹⁴C is mainly produced in the atmosphere by interaction of cosmic ray derived secondary neutrons with ¹⁴N. Carbon-14 derived age results are often expressed as percent modern carbon ¹⁴C (pmc) by comparing the ¹⁴C activity of a sample to the known activity of an oxalic acid standard. Carbon-14 age data are generally interpreted within the context of a geochemical reactions/evolution model that can account for the various sources and sinks of carbon [58].

In the Los Angeles County groundwater samples, the percent modern carbon (pmc) exhibited a wide range from 0.8 pmc (LBPF-1) to 83.7 pmc (Huntington Park #1) (Table 3) with an average value of ~30 pmc. Assuming an initial ¹⁴C value of 90 pmc [4], the corresponding groundwater age estimates may extend from recent to beyond 20 kyr before present and suggest that some well water undergoes deep circulation of native water through multiple aquifer systems. Age estimates, however, are not corrected for potential exchange reactions of carbon within the aquifer, and thus may not reflect the true age of the groundwater. The observed variations in the percentage of modern ¹⁴C indicate that the groundwater system is comprised of complex mixtures of diverse waters. A plot of $\delta^{13}C_{DIC}$ versus ¹⁴C (Figure 6) indicates that in samples with <10 pmc, $\delta^{13}C_{DIC}$ values fluctuated from -16‰ to +6‰, while in samples with >10 pmc, the $\delta^{13}C_{DIC}$ values ranged from -12‰ to -18‰. Select groundwaters (e.g., Wilmington 2-1, LWEB1,2, LBCH1-3, and LBPC1,2) that likely were recharged during Pleistocene, are also isotopically light. Nonetheless, ¹⁴C data confirm complex water mixing and transport scenarios involving multiple aquifer systems that reside within a tectonically active geologic framework.





5.6. U- and Th-Series Radionuclides

The isotopic systematics of many of the naturally occurring radionuclides in the U- and Th-series decay series are invaluable in investigating aquifer behavior. Specifically, U, Th, Ra, and Rn are all ubiquitous in groundwater and are represented by multiple isotopes with very different half-lives such that groundwater processes can be studied over a large range in time-scales. Within aquifer host minerals, these radionuclides are generally expected to be in secular equilibrium. However, these same radionuclides may exhibit strong fractionations with the surrounding groundwaters. Such disequilibria can be used, for example, to obtain information of radionuclide release from aquifer host rocks, groundwater flow rates, or age dates.

5.6.1. Specific Activities of ²³⁸U, ²³⁰Th and ²³²Th in Well Cuttings

The specific activity of ²³⁸U ($t_{1/2} = 4.47$ Gyr) from select well cuttings varied between 0.46 and 0.73 dpm g⁻¹ (2.22 dpm = 1 pCi), while the ²³⁴U/²³⁸U activity ratios varied between 0.99 and 1.02 (Table 4). Within one sigma, ²³⁴U ($t_{1/2} = 2.5$ Gyr) and ²³⁸U are in secular equilibrium with one another, which indicates that the alpha recoil loss [59] of ²³⁴U is generally negligible in these samples. In contrast, the activity of ²³⁰Th ($t_{1/2} = 73$ kyr) was considerably greater than that of ²³⁸U in host rock, thus recoil and/or long-term weathering reactions can provide an additional source of ²³⁰Th (21,60]. The ²³²Th/²³⁸U activity ratios varied between 1.30 and 2.25, a range considerably higher than the average crustal value [61].

	²³⁸ U ^a	²³⁰ Th	²³² Th	²³⁴ U/ ²³⁸ U	
Well ID	$(dpm g^{-1})$	$(dpm g^{-1})$	$(dpm g^{-1})$	AR	
LWEB, Harbor	0.47	0.72 ± 0.06	0.84 ± 0.06	1.01 ± 0.01	
LWEB, Bent Spring	0.49	0.66 ± 0.06	0.84 ± 0.06	1.00 ± 0.01	
LWEB, Upper Wilmington	0.46	0.60 ± 0.06	0.60 ± 0.06	0.99 ± 0.02	
LWEB, Upper Wilmington	0.42	0.60 ± 0.06	0.90 ± 0.06	1.02 ± 0.01	
LBPC, Pliocene A	0.56	0.72 ± 0.06	1.26 ± 0.09	0.99 ± 0.01	
LWEB, Pliocene A	0.73	1.02 ± 0.06	1.44 ± 0.09	1.02 ± 0.01	
LBPC, Pliocene B	0.6	0.90 ± 0.06	0.90 ± 0.06	1.01 ± 0.01	

Table 4. Solid-phase activities of ²³⁸U, ²³⁰Th, ²³²Th, and ²³⁴U/²³⁸U activity ratios (AR).

Note: ^a Analytical error < 3%.

5.7. Concentrations and Activity Ratios of ²²²Rn and Ra Isotopes

Ra isotopes can provide unique information regarding the production of U/Th series radionuclides in groundwater and reveal where significant transformations in adsorption or parent element distribution can occur along a groundwater flow path [62,63]. Values for Ra partitioning coefficients and retardation factors can also be obtained from the Ra isotopes but only by assuming that ²²²Rn provides a reasonable proxy for the recoil production rates of radium.

The concentrations of ²²²Rn ($t_{\frac{1}{2}} = 3.825$ days) ranged from 142,000 dpm m⁻³ (LWEB-2) to 442,000 dpm m⁻³ (370-AJ) (average ²²²Rn = 260,000 dpm m⁻³), which are expectedly the highest values observed as compared to other members of U- and Th-series radionuclides reported here (Table 5). The large ²²²Rn concentrations are the result of radon's inert character as a noble gas and its resulting inability to participate in any scavenging reactions. The concentration of ²²⁶Ra ($t_{\frac{1}{2}} = 1600$ years) varied between 29 dpm m⁻³ (Wilmington-2#3) and 1632 dpm m⁻³ (Wilmington-2#5) (average ²²⁶Ra = 257 dpm m⁻³), which is ~2–4 orders of magnitude lower than the ²²²Rn activities. Rn-222 is a direct measure of ²²⁶Ra (direct radiogenic parent of ²²²Rn) in the host rocks as well as a measure of the relative emanation efficiency from the host rock [64]. A plot of ²²⁶Ra activity as a function of Cl⁻ concentration is shown in Figure 7. Elevated Ra follows an increase in Cl⁻ and is attributed to solubilization of chloride complexes and/or through displacement from clays by ion exchange and desorption reactions.





Table 5. Activities (dpm m^{-3}) of dissolved ²²²Rn and four Ra isotopes in select wells from within the study area.

Wall ID	²²² Rn	²²³ Ra	²²⁴ Ra	²²⁸ Ra	²²⁶ Ra	
wen ID	$(dpm m^{-3})$	$(dpm m^{-3})$	$(dpm m^{-3})$	$(dpm m^{-3})$	$(dpm m^{-3})$	
Huntington Park #1	-	147.4	2,138.8	457 ± 25	421 ± 9	
Huntington Park #2	-	44.1	1,720.4	306 ± 24	159 ± 7	
Carson-1 #1	-	26.2	844.6	172 ± 15	76 ± 4	
Carson-1 #2	-	35.6	2,270.7	311 ± 19	128 ± 5	
Carson-1 #3	-	56.5	1,976.2	353 ± 23	154 ± 6.7	
Carson-1 #4	-	109.8	3,310.2	694 ± 32	296 ± 8	
Wilmington-1 #1	-	3.8	111.9	199 ± 16	76 ± 4	
Wilmington-1 #2	-	11	296.6	511 ± 26	183 ± 6	
Wilmington-1 #3	-	9.1	284.4	452 ± 19	166 ± 5	
Wilmington-1 #4	-	73.4	1,392.2	825 ± 35	455 ± 9	
Wilmington-1 #5	-	16	466.9	654 ± 30	479 ± 10	
Wilmington-2 #1	-	14.7	792.2	173 ± 17	66 ± 4	
Wilmington-2 #2	-	23.4	2,903.1	177 ± 17	145 ± 6	
Wilmington-2 #3	-	4.9	1,813.5	378 ± 18	29 ± 1	
Wilmington-2 #4	-	4.3	2,254.6	553 ± 27	225 ± 7	
Wilmington-2 #5	-	204.5	3,918.8	$2,716 \pm 85$	$1,632 \pm 18$	
LWEB-1	$244,000 \pm 39,000$	3.4	170	84 ± 9	51.6 ± 5.0	
LWEB-2	$142,000 \pm 47,000$	4.1	115	-	-	
LWEB-3	$242,\!000\pm47,\!000$	13.5	277	83 ± 10	36.7 ± 4.4	
LWEB-4	$202,000 \pm 23,000$	60.6	1,285	581 ± 17	275 ± 7	
LWEB-5	$195,000 \pm 36,000$	55.9	1,301	826 ± 21	282 ± 7	
LBCH-1	$217,000 \pm 11,000$	2.9	95	53.6 ± 9.1	31.1 ± 4.2	
LBCH-2	$418,\!000 \pm 27,\!000$	9.5	152	55.2 ± 8.6	29.2 ± 4.0	
LBCH-3	$336,000 \pm 75,000$	18	690	-	-	
LBCH-4	$388,000 \pm 39,000$	151.4	11,351	-	-	
370-AJ	$442,000 \pm 39,000$	52.9	765	$1,269 \pm 24$	522 ± 9	
370-AH	$347,000 \pm 58,000$	49.2	2,976	$2,944 \pm 58$	515 ± 10	
LBPC-1	$160,000 \pm 24,000$	22.2	294	826 ± 21	282 ± 7	
LBPC-2	$223,\!000\pm 46,\!000$	10	138	86 ± 12	38 ± 4.6	
LBPF-1	$172,000 \pm 20,000$	24.5	1,022	631 ± 23	192 ± 6.5	
LBPF-2	$173,000 \pm 11,000$	54.5	4,489	-	-	

The concentration of ²²³Ra ($t_{1/2} = 11.4$ days) varied between 2.9 dpm m⁻³ (LBCH-1) and 204.5 dpm m⁻³ (Wilmington 2#5) (mean ²²³Ra = 42 dpm m⁻³), while the concentrations of ²²⁴Ra ($t_{1/2} = 3.66$ days) and ²²⁸Ra ($t_{1/2} = 5.75$ years) varied between 95 dpm m⁻³ (LBCH-1) and 11,351 dpm m⁻³ (LBCH-4) (mean ²²⁴Ra = 1665) dpm m⁻³ and 54 dpm m⁻³ (LBCH-1) and 2944 dpm m⁻³ (370-AH) (mean ²²⁸Ra = 606 dpm m⁻³), respectively. The ²²³Ra/²²⁶Ra activity ratio (AR) varied between 0.02 and 0.37 (Table 6), with a mean value of 0.18, a value substantially higher than the expected value of 0.046. Because ²²³Ra and ²²⁶Ra are both generated after three α decays, groundwater should have a ²²³Ra/²²⁶Ra activity ratio is similar to the host rock (²³⁵U/²³⁸U) activity ratio of 0.046. Higher ²²³Ra/²²⁶Ra activity ratio may be observed in groundwater after a recharge or precipitation event, as ²²⁶Ra, due to its longer half-life, will not yet have reached a steady state concentration [16,65,66].

Wall ID	²²⁸ Ra/ ²²⁶ Ra	²²⁴ Ra/ ²²⁸ Ra	²²⁴ Ra/ ²²³ Ra	²²⁴ Ra/ ²²² Rn	²²³ Ra/ ²²⁶ Ra	Ω_{224}	Ω_{228}	k_1	$k_2 (\min^{-1})$	R_{f}
weii ID	AR	AR	AR	$AR(\times 10^{-4})$	AR	(× 10 ⁻⁴)	(× 10 ⁻⁴)	(min ⁻¹)	(× 10 ⁻⁴)	(× 10 ³)
LWEB-1	1.61 ± 0.23	2.04 ± 0.23	50.7 ± 5.7	7.0 ± 1.2	0.065 ± 0.009	4.9	2.4	0.53	1.3	4.1
LWEB-2			28.1 ± 3.1	8.1 ± 2.7	-	5.4	-	-	-	
LWEB-3	2.25 ± 0.38	3.34 ± 0.43	20.5 ± 2.3	11.4 ± 2.3	0.367 ± 0.058	8.8	2.6	0.21	0.56	3.8
LWEB-4	2.11 ± 0.08	2.21 ± 0.13	21.2 ± 2.4	63.8 ± 8.1	0.220 ± 0.023	50	23	0.05	1.1	0.5
LWEB-5	2.93 ± 0.10	1.57 ± 0.09	23.3 ± 2.6	66.7 ± 12.8	0.198419	57	36	0.06	2.3	0.3
LBCH-1	1.72 ± 0.38	1.78 ± 0.32	32.5 ± 3.6	4.4 ± 0.3	0.094 ± 0.016	2.9	1.7	1	1.7	5.9
LBCH-2	1.89 ± 0.39	2.76 ± 0.45	16.0 ± 1.8	3.7 ± 0.3	0.325 ± 0.055	2.4	0.88	0.85	0.74	11.5
LBCH-3	-	-	38.2 ± 4.3	20.5 ± 4.7	-	-	-	-	-	
LBCH-4	-	-	74.9 ± 8.4	293 ± 33	-	-	-	-	-	
370-AJ	2.43 ± 0.06	0.60 ± 0.03	14.5 ± 1.6	17.3 ± 1.7	0.101 ± 0.010	15	25	-	-	
370-AH	5.72 ± 0.16	1.01 ± 0.05	60.5 ± 6.8	86 ± 15	0.096 ± 0.010	73	72	1.7	121	0.1
LBPC-1	2.93 ± 0.10	0.36 ± 0.02	13.3 ± 1.5	18.4 ± 2.9	0.079 ± 0.008	18	52	-	-	
LBPC-2	2.26 ± 0.42	1.61 ± 0.24	13.9 ± 1.6	6.20 ± 1.3	0.262 ± 0.041	3.5	2.2	1	2.1	4.8
LBPF-1	-	-	41.7 ± 4.7	59.5 ± 7.5	0.127 ± 0.013	41	26	0.08	2.1	0.4
LBPF-2	-	-	82.4 ± 9.2	259 ± 21	-	204	-	0.006	-	

Notes: Ω = Ratio of the activity of a radionuclide in solution (λN_d), to its production rate, *P*; k_1 = first order adsorption rate constant; k_2 = first order desorption rate constant; R_f = Retardation Factor, calculated from k_1/k_2 .

The ²²⁴Ra/²²⁸Ra activity ratios provide a measure of the adsorption and desorption rate constants for radium [15,21]. Within host rocks that are in secular equilibrium, ²²⁴Ra/²²⁸Ra = 1. The ²²⁴Ra/²²⁸Ra activity ratios in the groundwater samples (Table 6) varied between 0.36 (LBPC-1) and 3.34 (LWEB-2). While in general the fresh groundwater ²²⁴Ra/²²⁸Ra ARs fall in a reasonably narrow range (0.5–2.0; [15,60,67]), but much higher values have also been observed [61]. Typically, higher ²²⁴Ra/²²⁸Ra ARs occur in groundwaters where steady state conditions have not yet been reached or in transitional coastal groundwater systems that are variably affected by seawater mixing [38]. In these groundwater samples (e.g., LBCH-2, LWEB-1,4,3), observed elevated ²²⁴Ra/²²⁸Ra ARs may identify waters that have recently been mixed with seawater.

Due to their short and similar half-lives ($t_{1/2} = <4$ days), the activities of ²²⁴Ra and ²²²Rn are expected to be in steady state in most groundwater. From the host rock ²³²Th/²³⁸U activity ratio, ²²⁴Ra/²²²Rn activity ratios can be used to calculate recoil and sorption rate constants [21]. The observed ²²⁴Ra/²²²Rn activity ratios (Table 6) varied between 1.34×10^{-5} to 3.9×10^{-4} (average = 1.25×10^{-4}) and agree well with other reported values ($0.2-4.4 \times 10^{-4}$; [15,60,67]). The measured range in ²²⁴Ra/²²²Rn activity ratios reflects the natural variability of these radionuclides in this groundwater system. The activity ratio of the two longest lived Ra isotopes, ²²⁸Ra/²²⁶Ra, provides a measure of the relative recoil rates of radionuclides from two decay series [21]. The observed ²²⁸Ra/²²⁶Ra activity ratios (Table 6) ranged between 1.1 and 5.7 (average = 2.3). Because ²²⁶Ra is the product of three α decays, while ²²⁸Ra is produced by one single α decay, ²²⁶Ra may be more mobile than ²²⁸Ra, resulting in lower ²²⁸Ra/²²⁶Ra activity ratios. Differences in the activity ratios can be attributed to variations in the distribution of U and Th in host rocks.

5.8. Adsorption-Desorption Rate Constants and Retardation Factors

The production rates for Ra isotopes were calculated using ²²²Rn as the recoil flux monitor and is based on the relation [15]:

$$F_i = F_r \left(Q_i / Q_r \right) \varepsilon \tag{6}$$

where F_i and F_r are the recoil supply rates of Ra isotopes (²²⁴Ra and ²²⁸Ra) and ²²²Rn to the groundwater respectively; Q_i and Q_r are the production rates of Ra isotopes and ²²²Rn in the aquifer solids; and ε is the rate of recoil supply of ²²⁴Ra and ²²⁸Ra relative to the ²²²Rn recoil supply. The term ε depends on where the radionuclide is positioned in the decay series, the α particle energy released during its production, and the scavenging capability of its immediate radiogenic parent. The value of ε can vary from a steady state value of ~1.5, if all the ²²⁶Ra recoiled into the groundwater remains in solution, to 0.86 if all the recoiled ²²⁶Ra is adsorbed onto the aquifer grain surfaces [15]. For the derivation of F_i and F_r , we assumed a ε value of 1.0.

The calculated values of Ω_{224} , Ω_{228} , k_1 , k_2 , and R_f are given in Table 6. The adsorption rate constants (k_1) calculated based on the ²²⁴Ra and ²²⁸Ra concentrations varied between 0.006 to 1.70 min⁻¹, with an average value of 0.55 min⁻¹ and co-varied positively (R = 0.71, n = 7) with Na⁺ concentration if one excludes the three highest Na⁺ values (LBPF-1,2, Wilmington-2#5). This observation is intriguing, as one might expect an inverse correlation, as higher Na⁺ would imply more Na⁺ available for exchange, and thus, longer Ra residence time (or smaller k_1 values). More studies need to be conducted to validate this observation. The corresponding residence times, calculated for an irreversible adsorption model $(1/k_1)$ ranged from 0.59 to 20.0 min (average = 6.62 min). The desorption rate (k_2) constant varied between 0.56 and 121×10^{-4} min⁻¹, with a mean value of 14.8×10^{-4} min⁻¹. The corresponding average residence time with respect to desorption was expectedly much greater. Faster sorption (k_1) of Ra injected into the water and slower desorption (k_2) from the host rock has been previously documented [15,17,18,67]. This range in values is in contrast with the values reported for subsurface brines, where k_1 and k_2 values are typically comparable [16,68]. As k_1 is always much greater than k_2 for these groundwater samples, the ratio k_1/k_2 can be used as a measure of the retardation factor, R_f [15], which here ranged from 0.1 to 11.5 × 10³ (average = 3.5 × 10³). Such R_f values are on the same order of magnitude as has been reported for other groundwater systems [15,16,60,67].

6. Conclusions

Stable- and radio-isotopes, as well as a complementary suite of water quality parameters, were utilized to assess groundwater properties from select wells in the Los Angeles Basin–Dominguez Gap area. Groundwater resources in this region have been extensively developed and managed since the late 1800s. In the study area, groundwater resides in multiple aquifer systems that are complexly mixed with seawater, non-native water that is used to stave off saltwater intrusion, and oil-field related brine waters. Elevated Cl⁻ concentrations are observed in some nearshore wells (LBPF-2, Wilmington-2 #5) and in the Dominguez Gap area. The δ^{18} O composition observed in select wells provides a measure of saltwater and oil-field brine mixing. Tritium data from these wells reveal that recent (less than 50 years old) groundwater was present only in a few select wells in the Upper and Lower aquifer systems close to the Dominguez Gap area (Wilmington-1 #4, Wilmington-1 #5, and Wilmington-2 #5) where the

seawater barrier injection wells may introduce additional ³H. The $\delta^{13}C_{DIC}$ composition in groundwater ranged from -18.9% to + 6.3% and provides an indication of the evolution of this groundwater system; some well water exhibited considerably lower $\delta^{13}C_{DIC}$ values and in the absence of SO₄²⁻ may reflect a contribution of enhanced ¹³C from microbial methanogenesis under anoxic conditions. Lastly, $\delta^{18}O$ (-9.77‰ to -0.42‰) and deuterium (-3.65‰ to -77.5‰) in these well waters provide information on the likely quantification of water balance and interaction within adjacent groundwaters.

From a series of well cuttings, aquifer host rock ²³⁴U and ²³⁸U are expectedly in secular equilibrium. In contrast, U- and Th-series radionuclides exhibit strong fractionation in groundwaters from select wells. Such radiogenic disequilibria are used to assess fundamental aquifer properties, such as the retardation factor R_f and adsorption/desorption rate constants, k_1 and k_2 , respectively. While we cannot quantify a relative groundwater age from the Ra isotopes alone, the calculated adsorption rate constant (k_1) is markedly higher than the desorption rate constant (k_2), which implies that the residence time of dissolved Ra must be very short (average ~7 min).

In combination, this suite of isotopic and elemental tracers can provide valuable information on complex groundwater mixing scenarios and provenance, which are useful to assess groundwater vulnerability to current and future external stressors, such as groundwater withdrawals, contamination, and sea level rise.

Acknowledgements

We thank John Haines of the USGS Coastal and Marine Geology (CM&G) Program for continued support in coastal groundwater studies. Nancy Prouty, Renee Takesue, and Christopher Conaway provided thoughtful reviews of an earlier version of this manuscript. The authors are also thankful for the four constructive reviews that greatly improved the manuscript. The use of trade, product, or firm names in this publication is for descriptive purposes only and does not imply endorsement by the U.S. government.

References

- 1. Mendenhall, W.D. Development of Underground Waters in the Eastern Coastal Plain Region of Southern California; Water-Supply Paper 137; U.S. Geological Survey: Reston, VA, USA, 1905.
- California Department of Water Resources. Planned Utilization of the Groundwater Basins of the Coastal Plain of Los Angeles Country, Appendix A: Ground Water Geology; Bulletin 104; California Department of Water Resources: Sacramento, CA, USA, 1961.
- 3. Los Angeles County Department of Public Works Web Page. Seawater Barriers. Available online: http://dpw.lacounty.gov/wrd/Barriers/ (accessed on 1 March 2013).
- Reichard, E.G.; Land, M.; Crawford, S.M.; Johnson, T.; Everett, R.R.; Kulshan, T.V.; Ponti, D.J.; Halford, K.L.; Johnson, T.A.; Paybins, K.S.; *et al. Geohydrology, Geochemistry, and Ground-Water Simulation-Optimization of the Central and West Coast Basins, Los Angeles County, California*; Water-Resources Investigations Report 03-4065; U.S. Geological Survey: Reston, VA, USA, 2003.
- Land, M.; Everett, R.R.; Crawford, S.M. Geologic, Hydrologic, and Water-Quality Data from Multiple-Well Monitoring Sites in the Central and West Coast Basins, Los Angeles County, California; Open-File Report 01-277; U.S. Geological Survey: Reston, VA, USA, 2002.

- Land, M.; Reichard, E.G.; Crawford, S.M.; Everett, R.R.; Newhouse, M.W.; Williams, C.F. Ground-Water Quality of Coastal Aquifer Systems in the West Coast Basin, Los Angeles County, California, 1999–2002; Scientific Investigations Report 2004–5067; U.S. Geological Survey: Reston, VA, USA, 2004.
- 7. Clark, I.; Fritz, P. *Environmental Isotopes in Hydrogeology*; Lewis Press: Boca Raton, FL, USA, 1997.
- 8. Kendall, C.; McDonnell, J.J. *Isotope Tracers in Catchment Hydrology*; Elsevier Science: Amsterdam, The Netherlands, 1998.
- 9. Hem, J.D. *Study and Interpretation of the Chemical Characteristics of Natural Water*, 4th ed.; Water-Supply Paper 2254; U.S. Geological Survey: Reston, VA, USA, 1992.
- 10. Gat, J.R.; Gonfiantini, R. Stable Isotope Hydrology—Deuterium and Oxygen-18 in the Water Cycle; International Atomic Energy Agency: Vienna, Austria, 1981.
- Kendall, C.; Mast, M.A.; Rice, K.C. Tracing Watershed Weathering Reactions with δ¹³C. In *Water-Rock Interactions*, Proceedings of the 7th International Symposium, Park City, UT, USA, 13–18 July 1993; Kharaka, Y.K., Maest, A.S., Eds.; Balkema: Rotterdam, The Netherlands, 1993; pp. 569–572.
- 12. Rozanski, K.; Araguas-Araguas, L.; Gonfiantini, R. Isotopic patterns in modern global precipitation, in climate change in Continental Isotopic Records. *Geophys. Monogr.* **1993**, *78*, 1–36.
- Izbicki, J.A., Danskin, W.R., Mendez, G.O. Chemistry and Isotopic Composition of Groundwater along a Section near the Newmark Area, San Bernardino County, California; Water-Resources Investigations Report 97-4179; U.S. Geological Survey: Reston, VA, USA, 1998.
- Szabo, Z.; Rice, D.E.; Plummer, L.N.; Busenberg, E.; Drenkard, S.; Schlosser, P. Age dating of shallow groundwater with chlorofluorocarbons, tritium/helium 3, and flow path analysis, southern New Jersey coastal plain. *Water Resour. Res.* 1996, *32*, 1023–1038.
- 15. Krishnaswami, S.; Graustein, W.C.; Turekian, K.K.; Dowd, J.F. Radium, thorium, and radioactive lead isotopes in groundwaters: Application to the *in-situ* determination of adsorption-desorption rate constants and retardation factors. *Water Resour. Res.* **1982**, *18*, 1633–1675.
- 16. Krishnaswami, S.; Bhushan, R.; Baskaran, M. Radium isotopes and ²²²Rn in shallow brines, Kharaghoda (India). *Chem. Geol.* **1991**, *87*, 125–136.
- 17. Copenhaver, S.A.; Krishnaswami, S.; Turekian, K.K.; Shaw, H. ²³⁸U and ²³²Th series nuclides in groundwater from the J-13 well at the Nevada test site: Implications for ion retardation. *Geophys. Res. Let.* **1992**, *19*, 1383–1386.
- Copenhaver, S.A.; Krishnaswami, S.; Turekian, K.K.; Epler, N.; Cochran, J.K. Retardation of ²³⁸U and ²³²Th decay chain radionuclides in Long Island and Connecticut aquifers. *Geochim. Cosmochim. Acta* 1993, *57*, 597–603.
- 19. Hussain, N. Supply rates of natural U-Th series radionuclides from aquifer solids into groundwater. *Geophys. Res. Let.* **1995**, *22*, 1521–1524.
- Ku, T.-L.; Luo, S.; Leslie, B.W.; Hammond, D.E. Decay-series disequilibria applied to the study of rock-water interaction and geothermal systems. In *Uranium-series Disequilibrium*; Ivanovich, M., Harmon, R.S., Eds.; Clarendon Press: Oxford, England, 1992; pp. 631–688.
- 21. Porcelli, D.; Swarzenski, P.W. The behavior of U- and Th-series nuclides in groundwater. *Rev. Mineral. Geochem.* **2003**, *52*, 317–361.

- 22. Olsen, C.R.; Cutshall, N.H.; Larsen, I.L. Pollutant-particle associations and dynamics in coastal marine environments: A review. *Mar. Chem.* **1982**, *11*, 501–533.
- 23. Dickson, B.L. Radium isotopes in saline seepages, south-western Yilgarn, Western Australia. *Geochim. Cosmochim. Acta* **1985**, *49*, 361–368.
- Dickson, B.L.; Wheller, G.E. Uranium-series disequilibrium exploration geology. In *Uranium-Series Disequilibrium: Applications to Earth, Marine, and Environmental Sciences*; Ivanovich, M., Harmon, R.S., Eds.; Clarendon Press: Oxford, UK, 1992; pp. 704–730.
- 25. Rama; Moore, W.S. Mechanisms of transport of U-Th series radioisotopes from solids into groundwater. *Geochim. Cosmochim. Acta* **1984**, *48*, 395–399.
- 26. Poland, J.F.; Piper, A.N. *Groundwater Geology of the Coastal Zone, Long Beach-Santa Ana Area, California*; Water-Supply Paper 1109; U.S. Geological Survey: Reston, VA, USA, 1956.
- Yerkes, R.F.; McCulloh, T.H.; Schoellhamer, J.E.; Vedder, J.G. *Geology of the Los Angeles Basin, California: An Introduction*; Professional Paper 420-A; U.S. Geological Survey: Reston, VA, USA, 1965.
- Davis, T.L.; Namson, J.; Yerkes, R.F. A cross section of the Los Angeles area: Seismically active fold and thrust belt, the 1987 Whittier Narrows earthquake and earthquake hazard. *Geophys. Res.* 1989, *94*, 9644–9664.
- Wright, T.L. Structural geology and tectonic evolution of the Los Angeles Basin, California. In Active Margin Basins; Memoir 52; Biddle, K.T., Eds.; American Association of Petroleum Geologists: Tulsa, OK, USA, 1991; pp. 35–134.
- Ponti, D.J.; Ehman, K.D.; Edwards, B.D.; Tinsley, J.C., III; Hildenbrand, T.; Hillhouse, J.W.; Hanson, R.T.; McDougall, K.; Powell, C.L., II; Wan, E.; *et al. A 3-Dimensional Model of Water-Bearing Sequences in the Dominguez Gap Region, Long Beach, California*; Open-File Report 2007-1013; U.S. Geological Survey: Reston, VA, USA, 2007.
- Nishikawa, T.; Siade, A.J.; Reichard, E.G.; Ponti, D.J.; Canales, A.G.; Johnson, T.A. Stratigraphic controls on seawater intrusion and implications for groundwater management, Dominguez Gap area of Los Angeles, California, USA. *Hydrol. J.* 2009, *17*, 1699–1725.
- 32. Woodring, W.P.; Bramlette, M.N.; Kew, W.S.W. *Geology and Paleontology of Pales Verdes Hills, California*; Professional Paper 207; U.S. Geological Survey: Reston, VA, USA, 1946.
- Epstein, S.; Mayeda, T. Variation of O¹⁸ content of water from natural sources. *Geochim. Cosmochim. Acta* 1953, *4*, 213–224.
- 34. Coplen, T.B.; Wildman, J.D.; Chen, J. Improvements in the gaseous hydrogen-water equilibration technique for hydrogen isotope ratio analysis. *Anal. Chem.* **1991**, *63*, 910–912.
- 35. Burnett, W.C.; Taniguchi, M.; Oberdorfer, J.A. Assessment of submarine groundwater discharge into the coastal zone. *J. Sea Res.* **2001**, *46*, 109–116.
- 36. Burnett, W.C.; Dulaiova, H. Estimating the dynamics of groundwater input into the coastal zone via continuous radon-222 measurements. *J. Environ. Radio.* **2003**, *69*, 21–25.
- Swarzenski, P.W.; Orem, W.G.; McPherson, B.F.; Baskaran, M.; Wan, Y. Biogeochemical transport in the Loxahatchee river estuary: The role of submarine groundwater discharge. *Mar. Chem.* 2006, 101, 248–265.
- 38. Swarzenski, P.W. U/Th series radionuclides as tracers of coastal groundwater. *Chem. Rev.* 2007, 107, 663–674.

- 39. Moore, W.S.; Arnold, R. Measurements of ²²³Ra and ²²⁴Ra in coastal waters using a delayed coincidence counter. *J. Geophys. Res.* **1996**, *101*, 1321–1329.
- 40. Moore, W.S. Sampling ²²⁸Ra in the deep ocean. Deep Sea Res. Oceanogr. Abstr. 1976, 23, 647–651.
- 41. Drever, J.I. *The Geochemistry of Natural Waters*, 2nd ed.; Prentice Hall: Upper Saddle River, NJ, USA, 1988.
- 42. Back, W.; Hanshaw, B.B.; Pyler, T.E.; Plummer, L.N.; Weide, E. Geochemical significance of groundwater discharge in Caleta Xel Ha, Quintana Roo, Mexico. *Water Resour. Res.* **1979**, *15*, 1521–1535.
- 43. Ponti, D. U.S. Geological Survey, Menlo Park, CA, USA. Personal communication, September 2012.
- 44. Izbicki, J.A. Source, Movement, and Age of Groundwater in a Coastal California Aquifer; Fact Sheet FS126-96; U.S. Geological Survey: Reston, VA, USA, 1996.
- 45. Michel, R.L. *Tritium Deposition in the Continental United States*, *1953–1989*; Water-Resources Investigations Report 89-4072; U.S. Geological Survey: Reston, VA, USA, 1989.
- 46. Craig, H. Isotopic variations in meteoric waters. Science 1961, 133, 1702–1803.
- 47. Dansgaard, W. Stable isotopes in precipitation. Tellus 1964, 16, 436-468.
- 48. Williams, A.E.; Rodoni, D.P. Regional isotope effects and application to hydrologic investigations in southwestern California. *Water Resour. Res.* **1997**, *33*, 1721–1729.
- 49. Taylor, C.B. On the isotopic composition of dissolved inorganic carbon in rivers and shallow groundwater: A diagrammatic approach to process identification and a more realistic model of the open system. *Radiocarbon* **1997**, *39*, 251–268.
- Claypool, G.E.; Kaplan, I.R. The origin and distribution of methane in marine sediments. In *Natural Gases in Marine Sediments*; Kaplan, I.R., Ed.; Springer: Berlin, Germany, 1974; pp. 99–139.
- Grossman, E.L. Stable carbon isotopes as indicators of microbial activity in aquifers. In *Manual of Environmental Microbiology*; Hurst, C.J., Ed.; American Society for Microbiology: Washington, DC, USA, 1997; pp. 565–576.
- Hellings, L.; van den Driessche, K.; Baeyens, W.; Keppens, E.; Dehairs, F. Origin and fate of dissolved inorganic carbon in interstitial waters of two freshwater intertidal areas: A case study of the Scheldt estuary, Belgium. *Biogeochemistry* 2000, *51*, 141–160.
- 53. Landmeyer, J.E.; Vroblesky, D.A.; Chapelle, F.H. Stable carbon isotope evidence of biodegradation zonation in a shallow jet-fuel contaminated aquifer. *Environ. Sci. Technol.* **1996**, *30*, 1120–1128.
- Conrad, M.E.; Daley, P.F.; Fischer, M.L.; Buchanan, B.B.; Kashgarian, M. Combined ¹⁴C and δ¹³C monitoring of *in situ* biodegradation of petroleum hydrocarbons. *Environ. Sci. Technol.* 1997, *31*, 1463–1469.
- 55. Marfia, A.M.; Krishnamurthy, R.V.; Atekwana, E.A.; Panton, W.F. Isotopic and geochemical evolution of ground and surface waters in a karst dominated geologic setting: A case study from Belize, Central America. *Appl. Geochem.* **2004**, *19*, 937–946.
- 56. Nascimento, C.; Atekwana, E.A.; Krishnamurthy, K.V. Concentrations and isotope ratios of dissolved inorganic carbon in denitrifying environments. *Geophys. Res. Lett.* **1997**, *24*, 1511–1514.
- Rosenthal, E.; Vinokurov, A.; Magaritz, M.; Moshkovitz, S. Anthropogenically induced salinization of groundwater: A case study from the coastal plain aquifer of Israel. *Contamin. Hydrol.* 1992, *11*, 149–171.

- Plummer, L.N.; Parkhurst, D.L.; Thorstenson, D.C. Development of reaction models for ground-water systems. *Geochim. Cosmochim. Acta* 1983, 47, 665–686.
- 59. Kigoshi, K. Alpha recoil ²³⁴Th: Dissolution in water and the ²³⁴U/²³⁸U disequilibrium in nature. *Science* **1971**, *173*, 47–48.
- 60. Tricca, A.; Wasserburg, G.J.; Porcelli, D.; Baskaran, M. The transport of U- and Th-series nuclides in a sandy confined aquifer. *Geochim. Cosmochim Acta* **2001**, *65*, 1187–1121.
- 61. Turekian, K.K.; Wedepohl, K.H. Distribution of the elements in some major units of the earth's crust. *GSA Bull.* **1961**, *72*, 175–192.
- 62. Swarzenski, P.W.; Reich, C.D.; Spechler, R.M.; Kindinger, J.L.; Moore, W.S. Using multiple geochemical tracers to characterize the hydrogeology of the submarine spring off Crescent Beach, Florida. *Chem. Geol.* **2001**, *179*, 187–202.
- 63. Krishnaswami, S.; Seidemann, D.E. Comparative study of ²²²Rn, ⁴⁰Ar, ³⁹Ar, and ³⁷Ar leakage from rocks and minerals—Implications for the role of nanopores in gas transport through natural silicates. *Geochim. Cosmochim. Acta* **1988**, *52*, 655–658.
- 64. Rama; Moore, W.S. Submicronic porosity in common minerals and emanation of radon. *Nucl. Geophys.* **1990**, *4*, 467–473.
- 65. Davidson, M.R.; Dickson, B.L. A porous flow model for steady state transport of radium in groundwater. *Water Resour. Res.* **1986**, *22*, 34–44.
- 66. Martin, P.; Akber, R.A. Radium isotopes as indicators of adsorption–desorption interactions and barite formation in groundwater. *J. Environ. Radioact.* **1999**, *46*, 271–286.
- Luo, S.; Ku, T.-L.; Roback, R.; Murrell, M.; McLing, T.L. *In-situ* radionuclide transport and preferential groundwater flows at INEEL (Idaho): Decay-series disequilibrium studies. *Geochim. Cosmochim. Acta* 2000, 64, 867–881.
- 68. Hammond, D.E.; Zukin, J.G.; Ku, T.-L. The kinetics of radioisotope exchange between brine and rock in a geothermal system. *J. Geophys. Res.* **1988**, *93*, 13175–13186.

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