Isotopic Evaluation of Groundwater Recharge and Flow in Indian Wells Valley

Jenny B. Chapman
James M. Thomas

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Publication No. 41281

Prepared by

Division of Hydrological Sciences, Desert Research Institute
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EXECUTIVE SUMMARY

The isotopic composition of groundwater and surface water in and around Indian Wells Valley in southeastern California is used to evaluate the hydrologic conceptual model in terms of sources of groundwater recharge and the flow paths and ages of the groundwater. An isotope has the same chemical properties as an element but a slightly different mass due to the different number of neutrons in the atom's nucleus. Isotopes are used as tracers for groundwater and the radioactive isotope of carbon-14 (^{14}C) can also be used to calculate age, which is the time since the water was removed from contact with the atmosphere.

In 2019, the Groundwater Authority for Indian Wells Valley collected surface water and groundwater in Indian Wells Valley and analyzed the samples for hydrogen, oxygen, and carbon isotopes. The data collected were combined with similar analyses published during the previous decades. Data from precipitation, and from surface waters and springs in the canyons draining the highland recharge areas surrounding Indian Wells Valley, define the hydrogen and oxygen isotopic composition of water that could be currently recharging the groundwater system. Much of the groundwater in Indian Wells Valley has a hydrogen and oxygen isotopic composition consistent with that defined for modern recharge, but some groundwater has a different composition consistent with recharge during cooler and wetter conditions. Cooler and wetter conditions occurred in the region during the last pluvial ("ice age") period, prior to 12,000 years ago, in the Pleistocene epoch. The groundwater consistent with recharge in the current climate is most common in the shallow parts of the aquifer system and groundwater with a Pleistocene character tends to occur in deeper parts of the system and closer to the discharge zone (the farthest reaches of the flow paths), but groundwater of both types can be found in other areas.

Travel times calculated from the 2019 ^{14}C data range from 3,000 to 6,000 years for groundwater flow from the western range front to relatively shallow, central Indian Wells Valley wells. Previous data identify some groundwater with ages of 12,000 to 30,000 years, which are generally in deeper horizons and areas closer to the discharge zone. These ^{14}C age dates are consistent with the recharge climates interpreted from the oxygen and hydrogen isotopes. Although the oxygen, hydrogen, and carbon isotopes support a general interpretation of groundwater throughout much of the valley being recharged during the current climate of the most recent 12,000 years and groundwater deep and close to the discharge area being recharged in a cooler and wetter climate more than 12,000 years ago, this depiction is not uniformly true and differences occur. These differences can be attributed to the variable hydrologic nature of the alluvium-filled valley, where interconnected units of high-permeability sand may create fast pathways for current recharge and pockets of low-permeability silt and clay may hold old, slow-moving groundwater.

The conceptual and numerical models of groundwater flow in Indian Wells Valley presented in the Groundwater Sustainability Plan are consistent with the isotopic results. These models depict recharge into the valley groundwater system from the surrounding mountain ranges, which is supported by the oxygen and hydrogen isotopic composition of much of the valley groundwater and the 2019 ^{14}C travel times being within the period of post-Pleistocene climate. The numerical flow model simulates travel times in the shallow model layer from the Sierra Nevada range front to the discharge zone in the China Lake area of 4,000 to 12,000 years and in the deeper model layers of 10,000 to 35,000 years, which is supported by the 2019 and previously published ^{14}C data.

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ABSTRACT

The isotopic composition of groundwater and surface water in and around Indian Wells Valley in southeastern California is used to evaluate the sources and ages of groundwater. The goal is to build added confidence in the hydrologic conceptual model and related numerical groundwater flow model supporting sustainable management of the valley. Recent analyses of the stable isotopes of hydrogen, oxygen, and carbon and of the radioactive isotope of carbon are evaluated in combination with a substantial existing isotopic dataset. Analysis of surface waters and springs in the Indian Wells Valley watershed, combined with published research of precipitation in Southern California, leads to a characterization of recent recharge by a δ^2H composition of -100 to -85 permil (‰). Many groundwaters in the valley are consistent with this range, and therefore are consistent with recharge during current climate conditions. Isotopically lighter groundwater is also found, occurring most frequently in deeper wells and geographically distant from the recharge areas. This lighter water may indicate recharge during cooler and wetter climate conditions such as occurred at several intervals in the Holocene and during the Pleistocene. Stable inorganic carbon isotopic composition for some waters in Indian Wells Valley is unusually enriched in the heavy isotope, which is explained as the result of dissolution of trona or nahcolite dust deposited by winds from area playas. Dissolution of trona, nahcolite, or other carbonates—indicated by the stable inorganic carbon isotopic composition of many of the groundwater samples—has added "dead" radioactive ^{14}C, complicating calculations of groundwater age. One creek sampled in a recharge area has an apparent (uncorrected) inorganic ^{14}C age of 5,800 years, whereas an organic ^{14}C age unaffected by mineral dissolution is 510 years. Reaction path modeling with NETPATH to correct for carbonate mineral reactions finds a range of travel times from recharge zone to central Indian Wells Valley of 3,000 to 6,000 years for the recently analyzed groundwater samples. Applying similar reaction path models to the previous dataset identifies some groundwater samples consistent with recharge in the late Pleistocene. The older water tends to occur in the deeper portions of the basin and in areas closer to the discharge zone, but the spatial distribution is complex. The hydrologic conceptual model developed for the Indian Wells Valley Groundwater Sustainability Plan (Indian Wells Groundwater Authority, 2020) is consistent with recharge under the current climate, as suggested by the isotopic data, and the range of ^{14}C-based travel times are similar to those simulated by the Plan's groundwater flow model.

ACKNOWLEDGEMENTS

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CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF ACRONYMS

CSUB	California State University, Bakersfield
DI $\delta^{13}C$	dissolved inorganic carbon-13/carbon-12
$DI^{14}C$	dissolved inorganic carbon-14
DIC	dissolved inorganic carbon
DOC	dissolved organic carbon
$DO^{14}C$	dissolved organic carbon-14
ET	evapotranspiration
FMC	Fraction of Modern Carbon
GMWL	Global Meteoric Water Line
IWV	Indian Wells Valley
PMC	Percent Modern Carbon
SGMA	Sustainable Groundwater Management Act
Stetson	Stetson Engineers
TDS	total dissolved solids
USGS	U.S. Geological Survey
VPDB	Vienna Peedee Belemnite
VSMOW	Vienna Standard Mean Ocean Water
YBP	years before present

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INTRODUCTION

The hydrogeologic system of the Indian Wells Valley (IWV), located in the Basin and Range province of southeastern California, has been studied for a hundred years, attesting to the importance of groundwater to the valley's inhabitants. Recent droughts and evidence of long-term climate change have spurred renewed evaluations as the basin endeavors to comply with the California Sustainable Groundwater Management Act (SGMA).

The Indian Wells Valley alluvial basin is bounded on the west by the Sierra Nevada Mountains, the Coso Range to the north, the Argus Range to the east, and the El Paso Mountains to the south (Figure 1). Recharge enters the valley groundwater system primarily as mountain block recharge from the surrounding highlands, with the largest contribution originating in the Sierra Nevada Mountains. Although a minor amount of groundwater flow may exit the basin to the east, under the current climate the basin is largely closed, with discharge by evaporation and transpiration in the eastern valley around the China Lake playa. Human development in the valley since the beginning of the twentieth century has led to overdraft of groundwater resources and chronic decline of groundwater levels. A full description of the hydrogeology of Indian Wells Valley, and the groundwater model simulating the system as part of SGMA, can be found in McGraw *et al*. (2016) and IWVGA (2020a).

The objective of this isotopic analysis is to provide information regarding the sources of groundwater and the age of groundwater within Indian Wells Valley to build added confidence in and identify potential improvements for the hydrologic conceptual model. A key topic of concern in terms of sustainability is the current status of recharge to the basin hydrologic system and determining if groundwater is being recharged during the current climate or is relic of a past, wetter period.

The isotopic composition of water provides an approach for estimating recharge characteristics, flow paths, and travel times, independent of hydraulic-based approaches. The following analysis concentrates on data recently collected by the Groundwater Authority for IWV, as well as places these data and interpretations in the context of the substantial body of work previously published. The recent sampling was directed at establishing baseline water quality conditions for monitoring, but locations were also targeted to address data gaps.

The stable isotopes of the water molecule, $^{2}H/^{1}H$ and $^{18}O/^{16}O$, are considered first, followed by evaluation of the stable carbon isotope, $^{13}C/^{12}C$, and radioactive carbon isotope, ^{14}C. The stable isotopes are measured and reported as the abundance of the heavier isotope (^{2}H, ^{18}O, ^{13}C) relative to the lighter isotope (H, ^{16}O, ^{12}C) in a delta notation relative to a standard (Vienna Standard Mean Ocean Water [VSMOW] for hydrogen and oxygen, and Vienna Peedee Belemnite [VPDB] for carbon). The calculation specific to hydrogen is:

$$\delta\,^{2}H(‰_{VSMOW}) = \frac{\left[(\,^{2}H/H)_{sample} - (\,^{2}H/H)_{VSMOW}\right]}{(\,^{2}H/H)_{VSMOW}} \times 1000 \qquad (1)$$

The term "isotopically light" will be used here to refer to lower delta values and "isotopically heavy" refers to higher delta values. Explanations of the systematics of these isotopes and their application to hydrogeology can be found in numerous references, such as Clark and Fritz (1997).

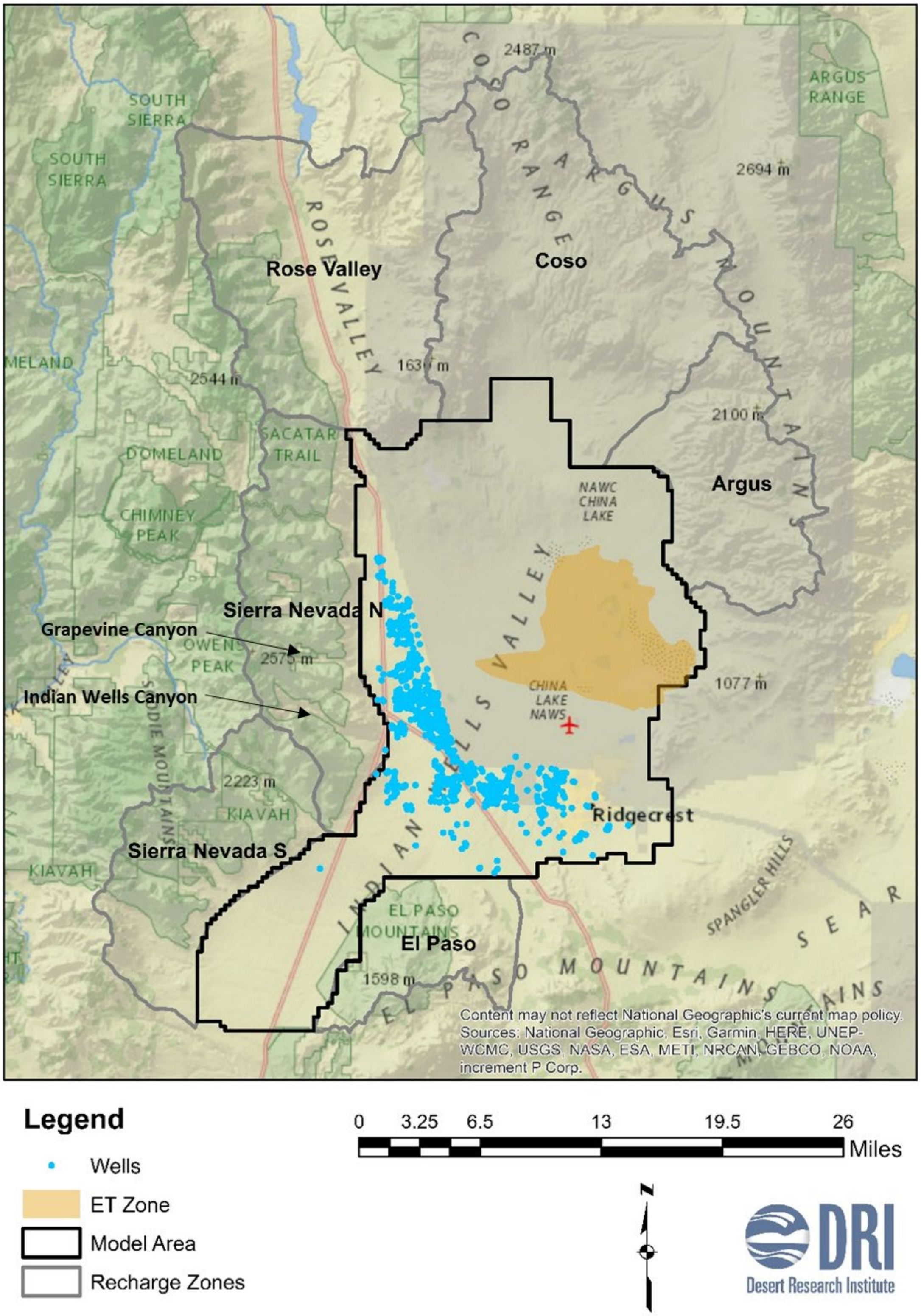

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Figure 1. Hydrographic study area of Indian Wells Valley showing the surrounding recharge areas in the highlands and evapotranspiration (ET) discharge zone. The boundary encompassing Indian Wells Valley corresponds to the GSP model domain boundary.

PUBLISHED HYDROGEN, OXYGEN, AND CARBON ISOTOPIC DATA AND INTERPRETATIONS

Recent water sampling by Stetson Engineers (Stetson) adds to the considerable amount of isotopic data available for IWV and its recharge areas, gathered as a result of efforts by the U.S. Geological Survey (USGS), the U.S. Navy, the State of California through its AB 303 grant program, and academic researchers at the Colorado School of Mines and California State University, Bakersfield (CSUB). The majority of the analyses are for δ^{2}H and δ^{18}O. Standard uncertainty bounds for these types of analyses are generally ±2 permil (‰) for δ^{2}H and ±0.2 ‰ for δ^{18}O (USGS, 2020).

The USGS used stable isotopes to evaluate the source of water for the Coso geothermal area, reporting results for 39 samples from wells and springs (Fournier and Thompson, 1980) and subsequently compiling them with additional data in a regional context (Gleason *et al*., 1992). Berenbrock and Schroder (1994) followed up these efforts with a broad geochemical evaluation of IWV that included a δ^{2}H and δ^{18}O evaluation, providing 55 new groundwater analyses and additional surface-water and spring analyses.

The U.S. Navy supported collection of surface water and groundwater samples in May, June, and August of 1996, including eight groundwater samples for δ^{2}H and δ^{18}O (Houghton HydroGeo-Logic, 1996). A large Navy Basewide Hydrogeologic Characterization effort (TtEMI, 2003a) included dissolved inorganic carbon-13/carbon-12 (DI δ^{13}C) and dissolved inorganic carbon-14 (DI^{14}C), along with δ^{2}H and δ^{18}O. Isotopic results are reported for a February/March 2000 sampling campaign of 45 wells and several surface-water and spring locations, and for a February 2002 sampling of 32 wells.

Two rounds of investigation were conducted under the auspices of the AB 303 grant program. The first summarized and interpreted previous isotopic analyses, particularly those of the Basewide Navy effort, but apparently did not conduct additional sampling and analysis (TtEMI, 2003b). The second investigation emphasized sampling and analysis of groundwater in the western and southwestern portions of IWV, identified in the previous work as a data gap. There are 48 δ^{2}H and δ^{18}O results and 20 DI δ^{13}C and DI^{14}C analyses (IWVCGTAC, 2008).

The academic research includes δ^{2}H and δ^{18}O, but not carbon isotopes. A student thesis from California State University, Bakersfield, reports analyses from 45 surface-water samples and 18 well samples collected in IWV and the recharge area to the west of the valley during 1995 and 1996 (Ostdick, 1997). These data and more (a total of up to 167 samples) were reported and interpreted in Thyne *et al*. (1999) and Williams (2004). The data are also included in Güler (2002), although he only used chemical data for interpretations.

The stable isotopic dataset has no obvious quality issues; the δ^{2}H and δ^{18}O are reasonable for meteoric water and within ranges observed in other regional studies (e.g., Smith *et al*. [1992] and Smith *et al*. [2002]). Some δ^{2}H and δ^{18}O indicate water has undergone evaporation, but evaporation of surface waters and minor evaporation during recharge processes of groundwater are common in arid environments. The quality of some of the DI δ^{13}C data were questioned by the original investigators because the values are isotopically heavier (less negative to positive values) than often encountered in groundwater studies, particularly in non-carbonate terrain. The recent Stetson sampling and analysis—duplicated by two separate, high-quality laboratories—indicates these isotopically heavy values are in fact real and not a data quality issue. A separate problem is the absence of reported DI $\delta^{13}C$ data and Fraction of Modern Carbon (FMC) or Percent Modern Carbon (PMC) values for some samples. Instead, only "corrected" ages are provided and the correction performed is unclear. Working with the University of Arizona and in cooperation with the U.S. Navy, many of the missing data were located and are included here.

In some cases, the references above include isotopic values for locations that are outside the IWV and nearby recharge areas, and IWV well samples for which the depth is not readily available. These isotopic values are not used in the analysis conducted here.

Previous Interpretations of Hydrogen and Oxygen Isotopes

Previous hydrogen and oxygen isotope investigations often share the observation that some groundwaters in the IWV are isotopically lighter than others, and that these lighter waters tend to be samples from the deeper aquifer units. The corollary to that is the other shared observation of shallow groundwater being isotopically heavier in $\delta^{2}H$ and $\delta^{18}O$, interpreted as similar to modern recharge. The isotopic composition of recharge is generally associated with analyses of surface water and springs in the Sierra Nevada canyons on the western valley margin, although some workers also have $DI^{14}C$ ages of water samples to demonstrate recent groundwater age (discussed in next section). The isotopic results for the canyon waters exhibit large variations from one sampling campaign to another, and variations from one position in a canyon to another position in the same canyon during a single sampling campaign (this variability is demonstrated primarily by the sampling conducted by CSUB and recorded in the appendix of Williams [2004], which also includes some grab samples of precipitation).

The majority of previous investigators attribute isotopically light results to groundwater recharged during the cooler climatic conditions of the last Pleistocene glaciation. The last glacial maximum is approximately 20,000 years before present [YBP], but major glacial advances in the Sierra Nevada during the Tioga glaciation are constrained from 30,500 to 15,000 YBP, and during the Recess Peak glaciation from 14,000 to 12,000 YBP (Clark and Gillespie, 1997; Bischoff and Cummins, 2001; Phillips, 2016, 2017). Several workers also acknowledge that recharge from higher elevation could account for the lighter isotopic composition and would be consistent with a deep position in the groundwater basin (consistent with the classic Toth [1963] basin flow lines). Thyne *et al*. (1999) and his students (Ostdick, 1997; Williams, 2004) concluded the light groundwater values in the southwestern portion of the IWV, where low total dissolved solids (TDS) groundwaters are also found, indicate recharge from the higher elevation Kern Plateau west of IWV, but their interpretation was partially based on faulty tritium data (IWVCGTAC, 2008). Other researchers have identified trends of isotopically lighter values (more negative) with increasing depth of groundwater (Berenbrock and Schroder, 1994; TtEMI, 2003a) and increasing isotopically lighter values in wells located in the northern part of the valley (Berenbrock and Schroder, 1994).

Previous Interpretations of $DI^{14}C$ Data

Two investigations report and interpret $DI^{14}C$ analyses; the first of these is TtEMI (2003a). Very old $DI^{14}C$ groundwater ages (~30,000 YBP) are observed in samples from every hydrogeologic zone (shallow, intermediate and deep, defined by TtEMI as coarser sediments of higher permeability for the shallow and deep zones, with the intermediate zone comprised of low-permeability silts and clays), although the set of samples from the shallow zone has the lowest median age and ages increase with increasing depth. Along with age increasing with depth below ground surface, age is observed to increase with distance from the Sierra Nevada range front in the deeper aquifer. In apparent contradiction to this, TtEMI (2003a) observed that in the shallow zone, the oldest ages are along the western margin of the basin and youngest are to the south. The oldest ages were for water collected from the intermediate zone, from discontinuous sands and gravels. These were interpreted as possibly "connate" water from time of deposition. Using NETPATH modeling to determine flow velocities, they concluded that carbon geochemical reactions have a minimal effect on DI^{14}C determined ages. (TtEMI [2003a] does not report DI δ^{13}C values for their samples. These data were found by Dr. Thomas, working with the University of Arizona and with permission of the U.S. Navy, and are added to the dataset here.)

The subsequent AB 303 (2008) report (IWVCGTAC, 2008) uses the DI^{14}C to evaluate several pathways from the Sierra Nevada range front into the valley. They observed isotopically heavier DI δ^{13}C values for some samples and concluded they were not reasonable. These data included isotopically heavier DI δ^{13}C for samples from canyons north of Indian Wells Canyon. Rather than using the entire data set to correct DI^{14}C data for carbonate water-rock reactions, they used a DI δ^{13}C of -10.4 ‰ from springs in canyons to the southwest. They calculate a corrected age of the groundwater from well Father Crowley West of 2,846 YBP, as compared to the uncorrected age of 7,780 YBP calculated directly from the DI^{14}C measured value. The correction for Navy Well 15 is smaller, 7,845 YBP compared to 8,485 YBP, because they used an isotopically heavier DI δ^{13}C of -7.9 ‰ from Indian Wells Canyon as their initial DI δ^{13}C value. The corrected age for well 21 L1 is 6,301 YBP compared to the uncorrected age of 7,821 YBP (using an initial DI δ^{13}C of -10.4 ‰).

ISOTOPIC SAMPLING CAMPAIGN IN 2019

Stetson conducted a surface- and groundwater-sampling campaign in IWV in 2019 with the primary objective of establishing baseline water quality conditions for monitoring trends and assessing the performance of basin groundwater management activities. Specific details about the wells sampled, along with many other wells in the IWV, can be found on the interactive map interface hosted by the IWV Groundwater Sustainability Plan website at https://iwvgsp.com/map/map.php. Considering their target monitoring locations, samples were prioritized for δ^{2}H and δ^{18}O analysis based on whether or not those data already exist for the location, the consistency of data with repeat samples (if applicable) and with other analyses in the nearby area, and the location relative to other analyses (data gaps). Carbon isotopic data collection was prioritized by identifying well pairs located along flow paths suggested by the steady-state potentiometric contour map.

Samples from 10 locations were analyzed for δ^{2}H and δ^{18}O, three of which were surface-water samples. Seven of these samples, including all the surface water samples, were also analyzed for DI δ^{13}C and DI^{14}C. Dissolved organic carbon isotopes were additionally determined for the Grapevine Canyon Creek and Means Well samples. Major-ion analyses were performed for all the samples. Tables 1 and 2 present the general chemistry and isotopic results.

Table 1. Major ion analyses for samples collected in 2019.

Well	**Ca (mg/L)**	**Mg (mg/L)**	**Na (mg/L)**	**K (mg/L)**	**HCO_3 (mg/L)**	**Cl (mg/L)**	**F (mg/L)**	**SO_4 (mg/L)**
Grapevine Canyon Creek	110	29	73	6.2	390	12	0.77	120
Indian Wells Creek	110	25	44	3.0	220	16	0.87	200
Sand Canyon Creek	82	24	78	4.9	320	18	1.70	76
Fields Well	58	13	110	4.4	140	88	0.75	190
Means Well	68	25	95	6.2	380	17	0.61	67
USBR-01 S/M	0.63	0.022	94	0.3	110	7	0.62	9.5
USBR-04	1.4	0.045	65	0.2	61	13	0.93	12
Baker Range	42	34	120	15.0	290	60	0.66	140
Sandquist Spa	65	9.5	52	3.0	130	70	0.51	77
Charley Tower	37	23	180	14.0	300	120	0.70	150
25S/38E-03B01	86	35	64	6.8	350	26	0.72	120

Table 2. Isotopic analyses for samples collected in 2019. UA indicates analysis by the University of Arizona and UCD indicates analysis by the University of California, Davis. Two standard deviation accuracy reported by the lab for is 1.0‰ for δ^{2}H, 0.16‰ for δ^{18}O, and 0.26‰ for DI δ^{13}C.

	δ^{2}H (‰VSMOW)	**δ^{18}O (‰VSMOW)**	**DI δ^{13}C (‰VPDB) UCD**	**DI δ^{13}C (‰VPDB) UA**	**FMC DI^{14}C**	**DI^{14}C apparent age, years**	**DO δ^{13}C (‰VPDB) UCD**	**DO $\delta^{13}C_{VPDB}$ (‰VPDB) UA**	**FMC DO^{14}C**	**DO^{14}C apparent age, years**
Grapevine Canyon Creek	-85.5	-11.72	-1.58	-1.6	0.4878 ±0.0018	5,767 ±29	-25.81	-27.7	0.9386 ±0.0029	509 ±25
Indian Wells Creek	-86.6	-11.37	-14.44	-13.7	1.0168 ±0.0031	modern				
Sand Canyon Creek	-84.4	-11.17	-8.85	-8.6	0.8116 ±0.0033	1,677 ±33				
Fields Well	-94	-12.28								
Means Well	-87.1	-11.51	-0.24	-0.2	0.3057 ±0.0013	9,520 ±34	-22.35	-26.3	0.6042 ±0.0064	4047 ±85
USBR-04	-104.4	-13.9								
Baker Range	-91.5	-11.9	-1.5	-1.2	0.2354 ±0.0016	11,619 ±56				
Sandquist Spa	-92.5	-12.35	-10.69	-10.6	0.6143 ±0.0028	3,914 ±36				
Charley Tower	-89.3	-11.55	-3.57	-3.1	0.3335 ±0.0019	8,822 ±45				
25S/38E-03B01	-90.1	-12								

INDIAN WELLS VALLEY GROUNDWATER RECHARGE CHARACTERISTICS FROM HYDROGEN AND OXYGEN ISOTOPIC DATA

The stable isotopes of hydrogen and oxygen are characteristic of groundwater recharge because they are controlled by the atmospheric source of moisture, conditions of condensation, and conditions of infiltration (all processes that can involve phase changes) and they are generally unmodified by water-rock reactions in the aquifer (except under high-temperature conditions such as occur in geothermal reservoirs) (Clark and Fritz, 1997). Comparing a groundwater isotopic composition with that of water in recharge areas and other aquifers can identify recharge sources and mixing components. Important for such interpretations is identification of the isotopic characteristics of recharge.

Despite numerous analyses of water from the recharge areas around IWV, δ^2H and δ^{18}O have not been sampled in a methodical and comprehensive manner in recharge source areas and analyses of precipitation are few. Rather, stable isotopic data are from grab samples of surface water and spring samples, which are known to vary seasonally. Four rigorous studies of the hydrogen and oxygen isotopic composition of precipitation and groundwater regionally have been performed by the USGS (Friedman *et al.*, 1992, 2002; Smith *et al.*, 1992, 2002). In these, precipitation collection networks were established in southeastern California and in the Great Basin, allowing definition of the integrated isotopic composition of precipitation throughout a year and across multiple years. Friedman *et al*. (1992) monitored stations at Inyokern, Walker Pass, Randsburg, and Trona for seven years and these data were used by Smith *et al*. (1992) in combination with stream samples to estimate that average waters recharging IWV have δ^2H values near -95 ‰. Friedman *et al*. (2002) documented annual variability in δ^2H of up to 13 ‰ and seasonal differences of almost 20 ‰. For example, at Walker Pass, the summer weighted mean (weighted by amount of precipitation) δ^2H is -70 ‰ and the winter weighted mean δ^2H is -87 ‰; the predominance of winter precipitation is evident in the annual weighted mean value for Walker Pass precipitation of -85 ‰.

Recharge occurs principally along the northern and western margins of the valley. Underflow from Rose Valley may be approximated by the isotopic composition of groundwater in the Little Lake area. These waters are relatively isotopically light, with δ^2H values as light as -111 ‰ (Williams, 2004). Although some spring samples from the Coso and Argus Ranges overlap in isotopic composition with the Sierra Nevada canyons, as a group, they are more depleted, with δ^2H values as low as -102 ‰ (Berenbrock and Schroder, 1994).

The grab samples collected by previous workers from the Sierra Nevada canyons along the western margin of IWV generally range from δ^2H values of -100 to -85 ‰, and δ^{18}O values of -12.5 to -11 ‰ (Figure 2). The majority of values plot to the right of the Global Meteoric Water Line (GMWL) defined by Craig (1961). The GMWL expresses the equilibrium fractionation of hydrogen and oxygen during condensation, and deviations are caused by kinetic processes that affect the heavier oxygen atoms more than hydrogen. Evaporation is one such process and some of the samples from the canyons that plot far to the right of the GMWL may represent evaporation. However, the preponderance of the population being offset from the GMWL is likely to be the result of the combined effect of

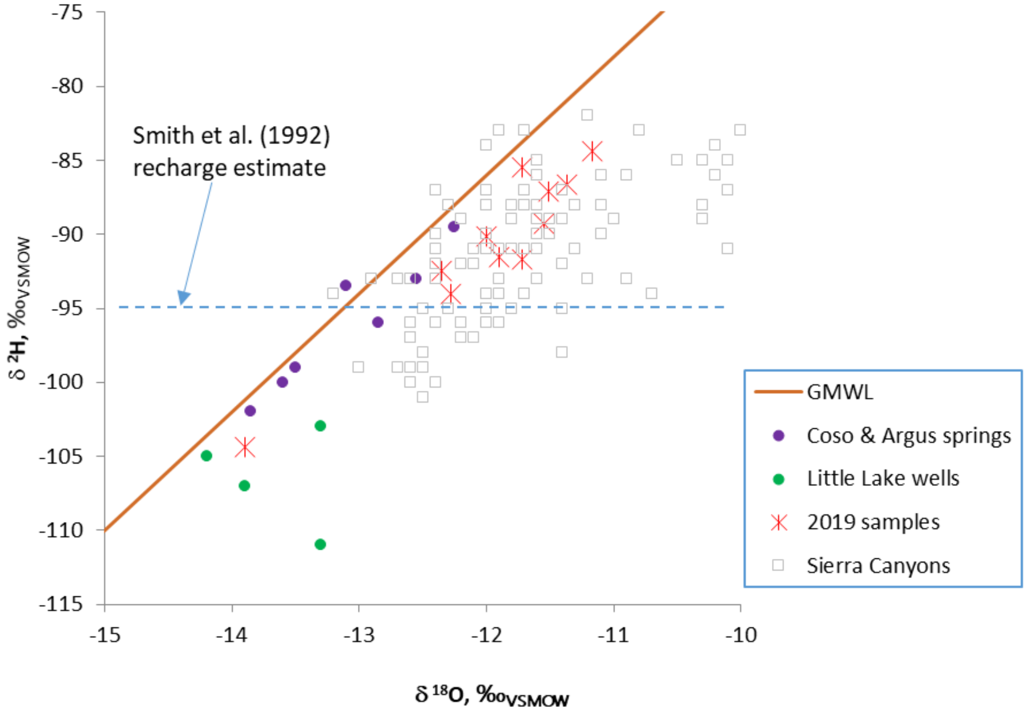

Figure 2. The δ^{2}H and δ^{18}O composition of samples collected from recharge areas of IWV (Williams, 2004), shown with samples collected in 2019 (surface water and groundwater). The δ^{2}H value estimated for recharge to IWV by Smith *et al*. (1992) is shown by the dashed line. The Global Meteoric Water Line (GMWL) (Craig, 1961) is also shown for reference.

sublimation, partial melting and refreezing, and exchange with atmospheric water vapor of the snowpack (Earman *et al*., 2006) providing water to the canyons. The closer alignment of the spring samples from the Coso and Argus Ranges with the GMWL (Figure 2) may reflect less input of snowmelt and/or less long-term exposure of snow to the atmosphere prior to melting on these lower elevation ranges.

As noted previously, the grab samples also indicate variability based on position in a given canyon (from several CSUB sample sets that appear to be intra-canyon transects) and on season of collection. The grab sampling from Indian Wells Canyon has identified δ^{2}H values varying from -99 to -84 ‰, suggesting that seasonality has the potential to affect the isotopic composition of recharge. Samples collected during the early summer from the canyons tend to be isotopically lighter, similar to the -95 ‰ δ^{2}H value suggested by Smith *et al*. (1992), representing the snowmelt of winter precipitation entering the system. Williams (2004) identifies the isotopic content of water in the southern part of the watershed (the canyons from Indian Wells Canyon and south) as averaging several per mil lighter in δ^{2}H than water from Short Canyon north to Fivemile Canyon. However, a standard t-test finds no statistical difference between the two populations when five samples indicating evaporative enrichment are excluded (Figure 3). The three canyon surface waters sampled in 2019 (denoted by the word “creek” in the location name of Tables 1 and 2) are consistent with the Sierra Nevada canyons grab-sample dataset (Figure 2) and with the previous measurements in Indian Wells, Sand, and Grapevine Canyons (Figure 4).

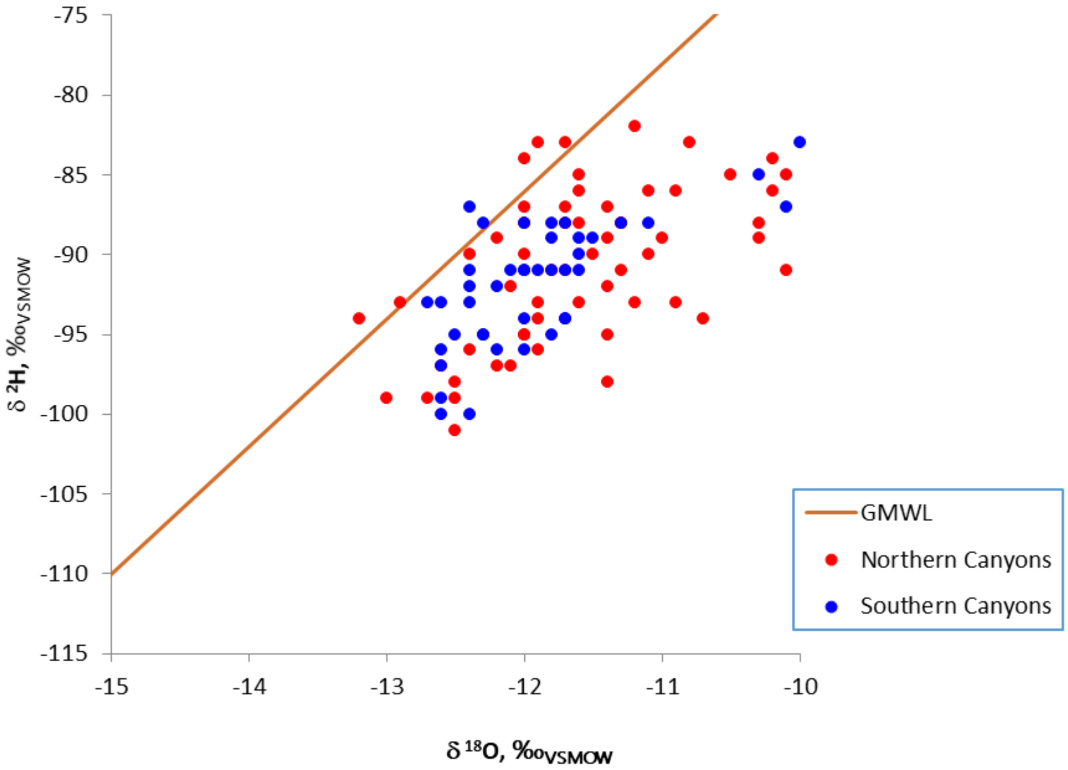

Figure 3. The δ^2H and δ^{18}O composition of Sierra Nevada canyon samples reported by Williams (2004), differentiated by northern (Short Canyon and northward) and southern (Indian Wells Canyon and southward) location. Five analyses with relative δ^{18}O enrichment (δ^{18}O values greater than -9 ‰) indicating evaporation are not shown. Excluding those five samples, there is no statistical difference, using a standard t-test, in the two populations. The Global Meteoric Water Line (GMWL) (Craig, 1961) is also shown for reference.

Summarizing the observations, there are considerable data available for waters in areas recharging IWV, but the resulting stable isotopic definition is broad. Although this is largely driven by the ad hoc sampling, it also reflects the considerable natural variability in recharge to the area, variability that occurs on seasonal (e.g., summer in contrast to winter), annual (e.g., drought years versus a year of enhanced atmospheric river flux of Pacific moisture), and over longer time scales with major hydroclimatic changes that may not be fully averaged throughout the valley’s groundwater system (e.g., the mid-Holocene warm period in contrast to wet and/or cooler periods in the Holocene at ~8,000-6,000, 3,600, 800, and 600-150 YBP) (Bacon *et al.*, 2020). The observed range in isotopic composition of watershed areas is also biased to measurements in seasons other than winter and does not focus on peak snowmelt (most sampling has been conducted during the autumn). Winter precipitation in this region is generally 20 to 30 ‰ isotopically lighter than summer precipitation (Friedman *et al.*, 1992). Surface-water sources are also subject to evaporation prior to sampling, again biasing toward more isotopically heavy compositions.

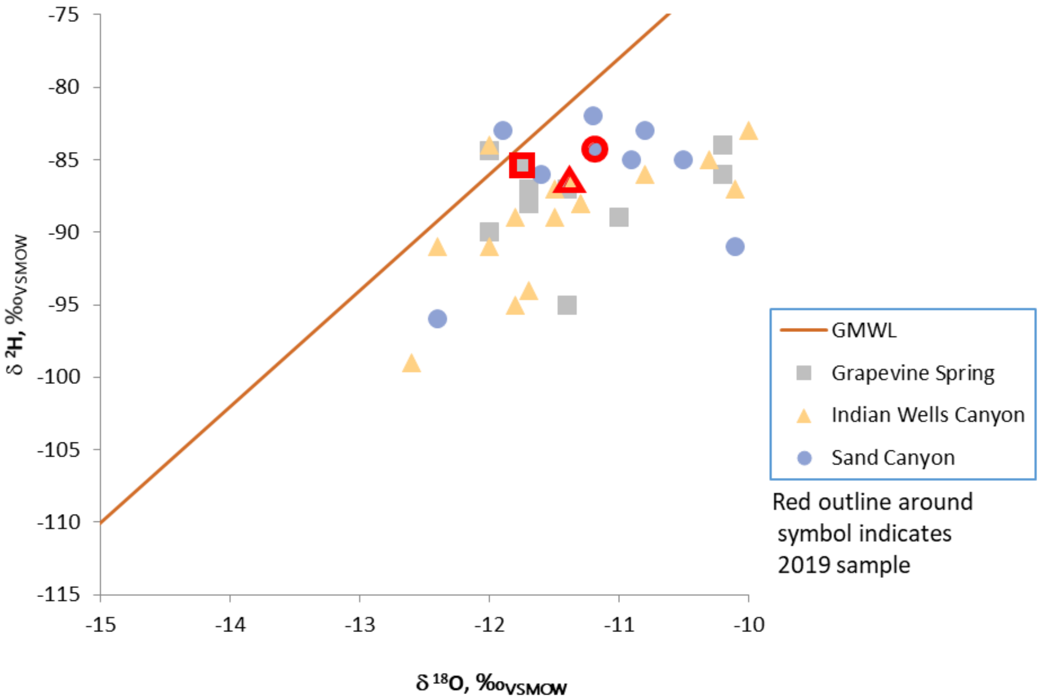

Figure 4. The δ^2H and δ^{18}O composition of 2019 surface-water samples in context of previous analyses from the same canyons. The Global Meteoric Water Line (GMWL) (Craig, 1961) is also shown for reference.

Keeping the limitations in mind, the existing data suggest that recharge from the area of the Sierra Nevada canyons bounding IWV is consistent with δ^2H values roughly ranging from -100 to -85 ‰. Recharge from the Coso and Argus Ranges is defined by δ^2H values of generally -100 to -90 ‰, and underflow from Rose Valley is isotopically lighter with δ^2H values lower than -100 ‰ (groundwater in Rose Valley has δ^2H values ranging from -100 to -115 ‰, with a trend of lower values to the north) (MHA Environmental Consulting, 2008).

Comparison of Valley Groundwater to Recharge

Many groundwaters in IWV have isotopic compositions consistent with the range observed for waters from the Sierra Nevada canyons (δ^2H values of -100 to -85 ‰) and similarly plot to the right of the GMWL (Figure 5). This means these groundwaters are consistent with recharge under current climate conditions. Such groundwater is present throughout the aquifer system, from shallow to deep (Figure 6).

Some groundwaters in IWV have isotopic compositions that are isotopically lighter relative to the values observed for surface waters in the surrounding uplands. Acknowledging the uncertainty from the ad hoc sampling of springs and surface water regarding the definition of modern recharge, the values lower than -100 ‰ in δ^2H may indicate recharge during different climate conditions. The Pleistocene climate in the Great Basin is believed to have been colder and wetter than present because it was dominated by storm tracks from the north/northwest, with relatively fewer storm tracks originating in the tropical Pacific compared to today (Smith *et al.*, 2002).

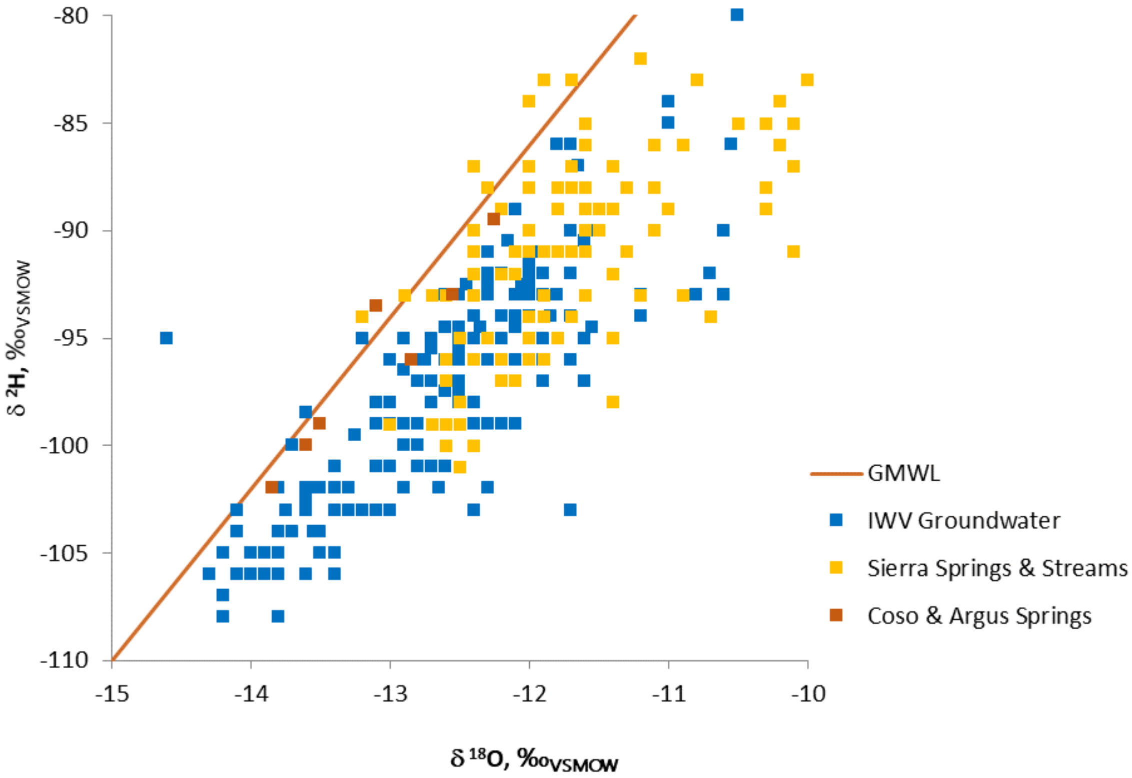

Figure 5. The δ^2H and δ^{18}O composition of IWV groundwater and springs and streams from surrounding recharge areas. The Global Meteoric Water Line (GMWL, Craig, 1961) is also shown for reference.

These lighter values are found in shallow, intermediate, and deep wells, although a larger proportion of the intermediate and deep groundwaters are at or below -100 ‰ in δ^2H than the shallow groundwater (Figure 6). The lighter values are primarily clustered in the southeastern portion of the valley, in the general Ridgecrest area (Figure 7). This geographic distribution of greater prevalence of lighter values, in deeper horizons and in the southeastern area, indicates that groundwater farther from the recharge areas is more likely to have an isotopic content consistent with Pleistocene recharge. A few of the groundwater samples, primarily from the deep wells, are noticeably more displaced from the GMWL than the rest, which would be consistent with evaporation, perhaps from a Pleistocene lake.

All of the 2019 samples have stable isotopic compositions consistent with their depth-based aquifer grouping (Figure 8), although the intermediate layer sample is on the isotopically heavy end of the range and the deep layer sample is on the lighter end. The shallow layer corresponds to wells completed in the upper layer of the GSP groundwater model, the intermediate layer combines wells completed in model layers 2 and 3, and the deep layer wells are completed in model layers 4, 5, or 6 (IWVGA, 2020a). The one 2019 sample with a relatively depleted δ^2H value (-104.4 ‰), from well USBR-04, is located mid-valley and completed at a depth of 1,200 feet in the deep layer.

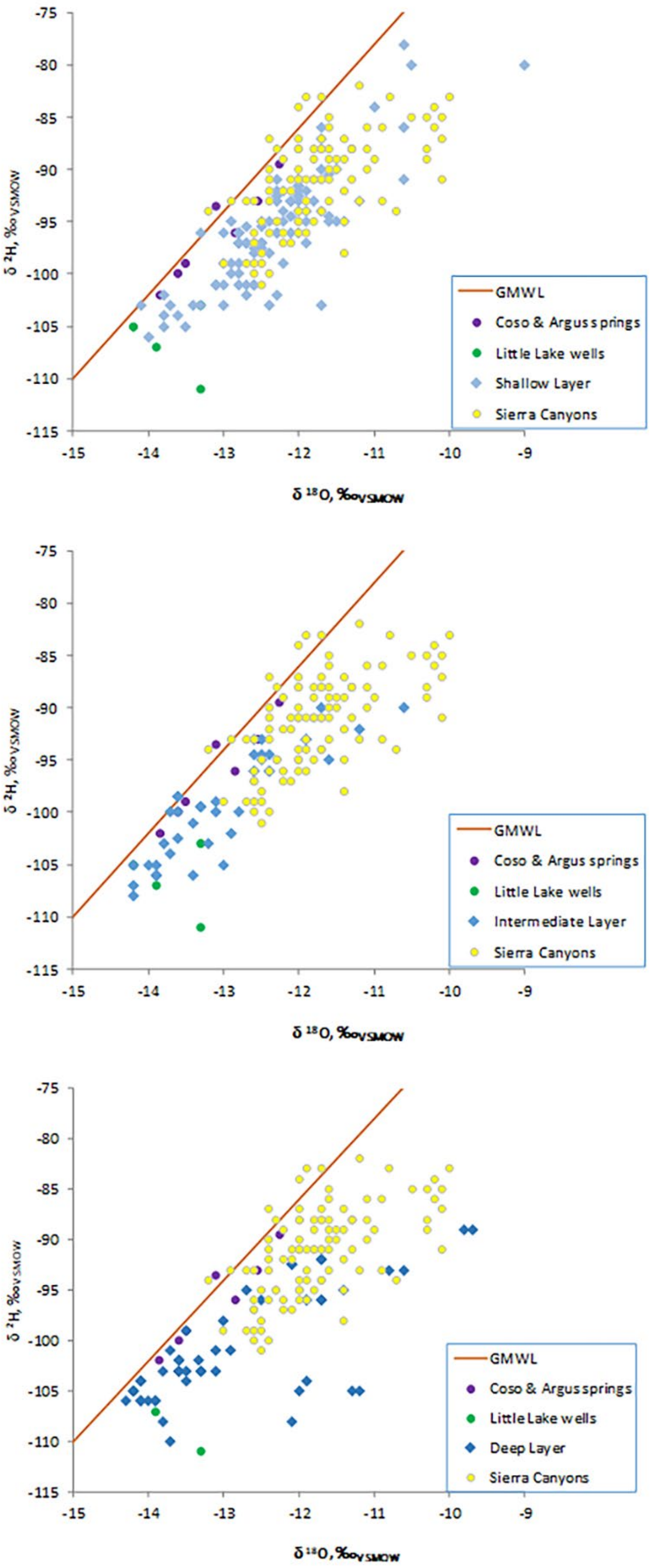

Figure 6. The δ^2H and δ^{18}O composition of IWV groundwater, differentiated by depth, compared to recharge water. The Global Meteoric Water Line (GMWL, Craig, 1961) is also shown for reference.

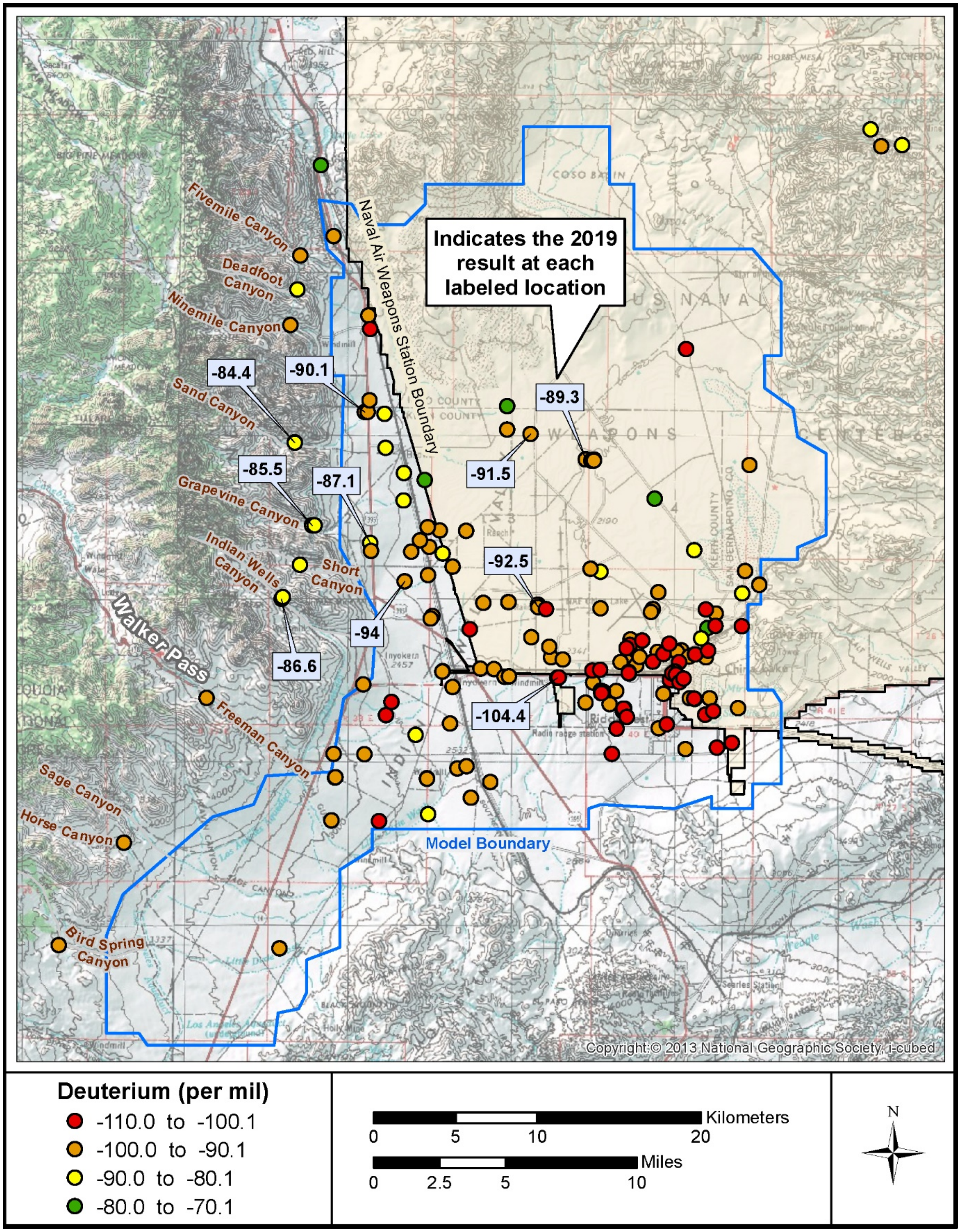

Figure 7. Geographic distribution of δ^2H of IWV groundwater.

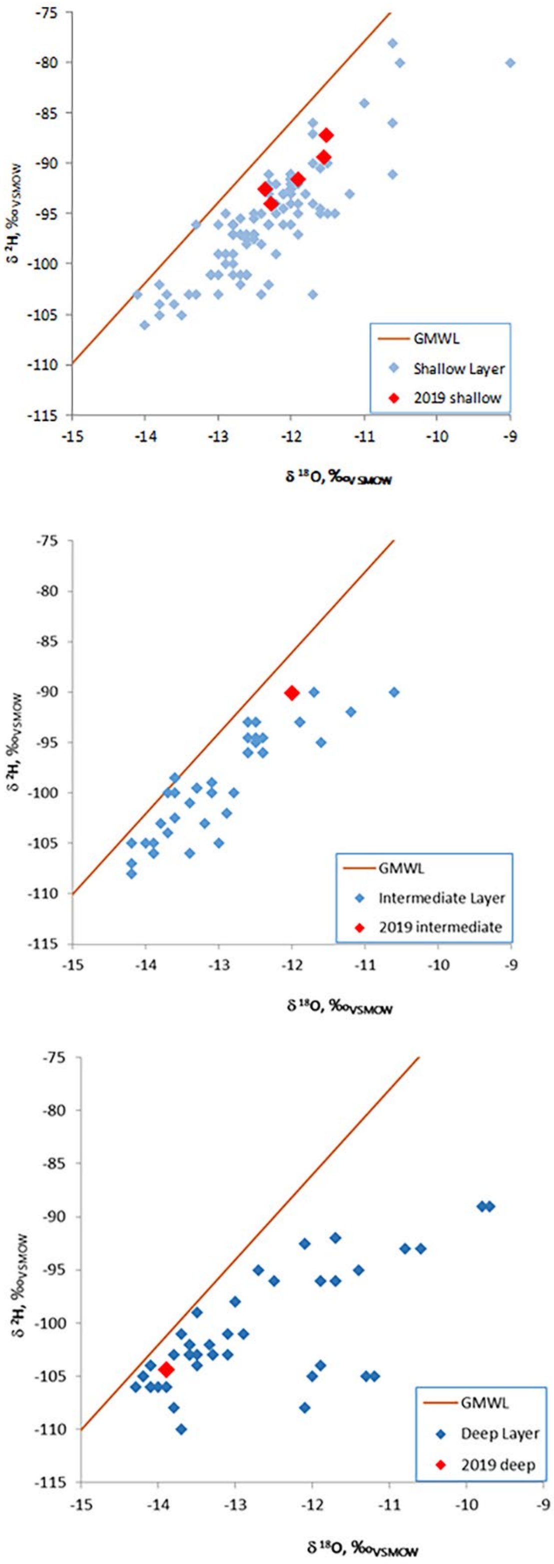

Figure 8. The δ^2H and δ^{18}O of the 2019 groundwater samples relative to other valley groundwaters in the same depth range. The Global Meteoric Water Line (GMWL) (Craig, 1961) is also shown for reference.

Carbon Isotopic Characteristics of Indian Wells Valley Water

The interest in ^{14}C for IWV is for determining the age of groundwater to assess sustainability of the resource. Unfortunately, determining groundwater age using $DI^{14}C$ requires correcting for carbon introduced to the water after it is recharged. These carbon sources can be identified by their stable carbon isotope ratios, expressed as DI $\delta^{13}C$. Nonetheless, using DI $\delta^{13}C$ for identifying and correcting for "dead" ^{14}C (dead in the sense that mineral carbon sources will be older than 50,000 years and have essentially zero fraction modern carbon) is nontrivial and nonunique. This led Smith *et al*. (2002) to conclude that "recalculation of ^{14}C ages has not yet reached a level where results are meaningful," causing them to not subscribe to either "original" (uncorrected) or recalculated (corrected) groundwater ages. With fewer subsurface sources of organic carbon, dissolved organic carbon-14 ($DO^{14}C$) has been developed as an alternative for ^{14}C measurements and groundwater age determinations.

Until the 2019 sampling campaign, all ^{14}C data are for $DI^{14}C$. Interpreting these data, despite the skepticism of Smith *et al*. (2002), requires evaluation of the DI $\delta^{13}C$. The DI $\delta^{13}C$ data from IWV and its recharge areas are unusual because several waters are quite isotopically heavy in DI $\delta^{13}C$. Considerable variability has also been recorded, which has led to discounting of the isotopically heavy DI $\delta^{13}C$ measurements. The AB 303 final report (2008) concluded that the "positive values for $\delta^{13}C$ are not reasonable except under extremely unusual conditions. Therefore, because of the improbable results and inability to replicate the measurements, these are deemed unreliable."

Recharge water begins with a DI $\delta^{13}C$ of approximately -15 ‰, based on the soil gas composition from plant root respiration (e.g., Quade *et al*. [1989]). As that relatively acidic water infiltrates into the subsurface, it dissolves solid phase carbonate (carbonate dust, pedogenic carbonates, marine bedrock carbonates) that has an average DI $\delta^{13}C$ composition close to zero (Clark and Fritz, 1997). The water's DI $\delta^{13}C$ value increases from the initial recharge value and some mineral carbon dissolution may occur under open CO_2 conditions, meaning that the atmospheric ^{14}C FMC of 1.0 (or slightly higher) may apply to water with a DI $\delta^{13}C$ composition somewhat heavier than -15 ‰. Nonetheless, within the recharge area, with little residence time for water-rock reactions, the DI $\delta^{13}C$ is expected to be relatively light (DI $\delta^{13}C$ of -10 ‰ or less). This is the reason the heavy DI $\delta^{13}C$ values (-1.6 to +2.5 ‰) of canyon surface waters reported in the AB 303 final report (2008) were considered unreliable. Carbon-13 measurements for water samples collected in the Sierra Nevada canyons are summarized in Table 3.

The 2019 sampling substantiates the validity of an unusually isotopically heavy DI $\delta^{13}C$ composition for some waters in the canyon recharge areas. Analysis of DI $\delta^{13}C$ was performed by two independent and highly qualified laboratories, resulting in validation of the measurements. Of particular note is the DI $\delta^{13}C$ composition measured for Grapevine Canyon Creek. This location is in the recharge zone but it has a heavy DI $\delta^{13}C$ of -1.6 ‰. This result suggests that similar values reported previously for Grapevine Canyon, Sand Canyon, and Ninemile Canyon should not be discounted. The canyon data exhibit a spatial

Table 3. Surface water $\delta^{13}C$ measurements.

Location	**Date**	**DI $\delta^{13}C$, ‰**
Ninemile Canyon	Sample date not specified in IWVCGTAC (2008)	+2.5
Sand Canyon	Sample date not specified in IWVCGTAC (2008)	-1.0
Sand Canyon Creek	2019	-8.85, -8.6
Grapevine Canyon	3/10/1999	-0.2
Grapevine Canyon Creek	2019	-1.58, -1.6
Indian Wells Creek	2019	-14.44, -13.7
Indian Wells Canyon	Sample date not specified in IWVCGTAC (2008)	-10.1
IWVBCS1 (TTEMI)	2001	-7.9
Cow Haven Canyon	7/9/2007	-11.3
Sage Canyon	7/9/2007	-10.3
Horse Canyon	7/9/2007	-9.3

trend, with the heavy DI $\delta^{13}C$ waters observed in the canyons north of Indian Wells Canyon and the canyons south of Indian Wells Canyon having DI $\delta^{13}C$ published values ranging from -14 to -7.9 ‰. However, temporal variation is also exhibited at Sand Canyon, where a previous measurement was -1.0 ‰, whereas the 2019 value is -8.7 ‰ (Table 3).

The origin of the enriched DI $\delta^{13}C$ values may be explained by the dissolution of trona or nahcolite (suggested as a source of Na-HCO_3 water in Owens Valley) and probably secondary calcite sourced from lacustrine sediment deposited in Pleistocene shallow lakes and playas in the valley. As these lakes evaporated, the trona and calcite that precipitated from saturated lake waters would become progressively more isotopically heavy. Therefore, trona and secondary calcite deposited in sediments in the valley could be quite isotopically heavy in DI $\delta^{13}C$ in some areas. For waters in the canyons to have these heavy DI $\delta^{13}C$ values, dust containing trona and/or calcite particles sourced from dry lake beds in either IWV or nearby Searles Valley, or southern Owens Valley, would have to be initially blown into the canyons in the northern part of the IWV, incorporated into hillslope deposits, followed by leaching into the groundwater system. Measurements of DI $\delta^{13}C$ in trona in other environments find heavy isotopic enrichment: approximately -1.9 ‰ for trona from Cameroon, West Africa (Fantong *et al*., 2019) and +10.5 ‰ for Crater Lake trona (Earman *et al*., 2005). The geothermal system in the IWV region also presents another possible source of heavy carbon isotopes (Chiodini *et al*., 2010).

There are some groundwaters sampled from IWV that have DI $\delta^{13}C$ compositions consistent with the range assumed for recharge (-10 ‰ or less), indicating minimal reactions with carbonate minerals. A larger number of groundwater samples are heavier in DI $\delta^{13}C$, indicating dissolution of mineral carbonate along the flow path.

Carbon-14 in Indian Wells Valley Water

The FMC for dissolved inorganic carbon (DIC) for water in the recharge areas is available from the 2019 samples of Indian Wells Canyon, Grapevine Canyon, and Sand Canyon creeks. Although previous workers occasionally measured DI δ^{13}C for water collected from the recharge areas, no previous ^{14}C measurements have been identified. Rather, the assumption in previous analysis and modeling has been for the FMC to be 1.0, or nearly so, for recharge water flowing into the valley. Although this assumption is logical given the hydrogeology, the 2019 samples reveal that the FMC of water from one of the sampled Sierra Nevada canyons is considerably less than one. This has significant implications for estimating the age of groundwater in the valley. If it is assumed that recharge has an FMC near 1.0 when in fact it is much less than 1.0, a computed groundwater residence time will be thousands of years longer than the actual time.

Given the apparent similarity in watershed environments, the range of FMC is striking, varying from 0.49 at Grapevine Canyon to 1.02 at Indian Wells Canyon. The Indian Wells Canyon measurement is "modern," which is indicative of a water in equilibrium with atmospheric ^{14}C. There is a very strong, linear relationship between DI δ^{13}C and DI^{14}C for the three samples collected in 2019 (Figure 9). This relationship along with the hydrogeologic environment demonstrate the dilution of FMC that can be caused by dissolution of mineral carbon in the recharge areas. The heavy isotopic enrichment of Grapevine Canyon Creek, with a DI δ^{13}Cof -1.6 ‰, indicates dissolution of carbonates (likely including trona) and this addition of "dead" carbon accounts for the recharge area water having an apparent age of 5,800 years based on the DI^{14}C (FMC of 0.49). Sand Canyon Creek lies between Indian Wells and Grapevine canyons in terms of carbonate reactions, with its DI δ^{13}C of -8.75 ‰ reflecting dissolution of less carbonate material than Grapevine Canyon creek water and an apparent, decay-only, age of 1,700 years (FMC of 0.81). The modern age of Indian Wells canyon water with an FMC of 1.02 has an average DI δ^{13}C of -14.1 ‰, indicating little reaction of this water with carbonate minerals (Table 2; Figure 9).

Although the residence time of water within each watershed likely varies depending on a number of factors, an age of thousands of years is not reasonable for Grapevine and Sand Canyon Creeks. The dissolved organic carbon (DOC) data collected in 2019 for Grapevine Canyon Creek underscores this. The DOC is unaffected by dissolution of mineral carbon. The FMC_{DOC} for Grapevine Canyon Creek is 0.94, in contrast to the FMC_{DIC} of 0.49, with the age derived from the DOC being 510 years. These results emphasize the need for correction of any DI^{14}C based groundwater ages because uncorrected ages will be significantly older than actual ages.

It is possible that the FMC_{DOC} for Grapevine Canyon Creek should be essentially 1.0, as observed for FMC_{DIC} at Indian Wells Canyon, and that some "dead" organic carbon is added in the watershed. Such an addition is small, but nonetheless suggests that even the DO^{14}C ages should be considered maximum ages, potentially older than actual.

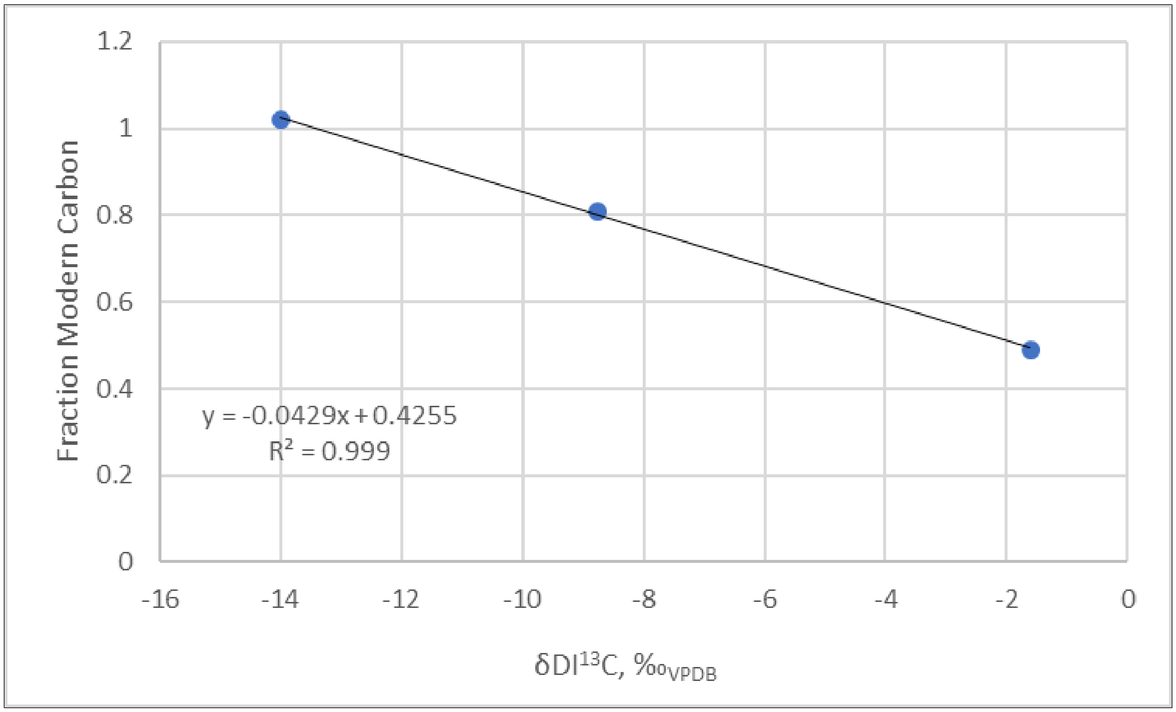

Figure 9. The relationship between DI δ^{13}C and FMC for the three Sierra Nevada canyon samples collected in 2019.

The FMC measured in IWV groundwater varies from less than 0.1 to almost 0.9. The deeper portions of the flow system have smaller amounts of DI^{14}C, whereas shallow groundwater (defined here as occurring in the upper groundwater model layer) has DI^{14}C contents running the full range of very low to high (Figure 10). With one exception, the 2019 groundwater analyses have FMC values of approximately 0.3 or less, equating to decay-only ages of 9,000 to 12,000 years (calculated solely considering the half-life of ^{14}C). Sandquist Spa is the exception with an FMC of 0.6 (decay age of approximately 4,000 years). Again, with the exception of Sandquist Spa, the DI δ^{13}C values are all relatively heavy, indicating addition of mineral carbon. As a result, dead DI^{14}C has been dissolved in the groundwater and the decay-calculated ages are assuredly too old.

As with Grapevine Canyon, the DO^{14}C analysis for the Means Well is in stark contrast to the DI^{14}C analysis. The 4,000-year DO^{14}C age for Means, calculated solely using radioactive decay, is less than half the 9,500-year apparent DI^{14}C age. Regardless, the lower DO^{14}C age demonstrates how misleading an uncorrected DI^{14}C age can be.

Old, “dead,” organic carbon can be dissolved in groundwater and alter ages, just as inorganic carbon can, but organic carbon is less common in most aquifer environments. Nonetheless, an area of fine-grained, organic-rich sediments has been encountered in the subsurface in the North Brown Road area and could be a source of dissolved organic carbon in groundwater downgradient of it. The Means Well is located upgradient of, but close to, this organic deposit.

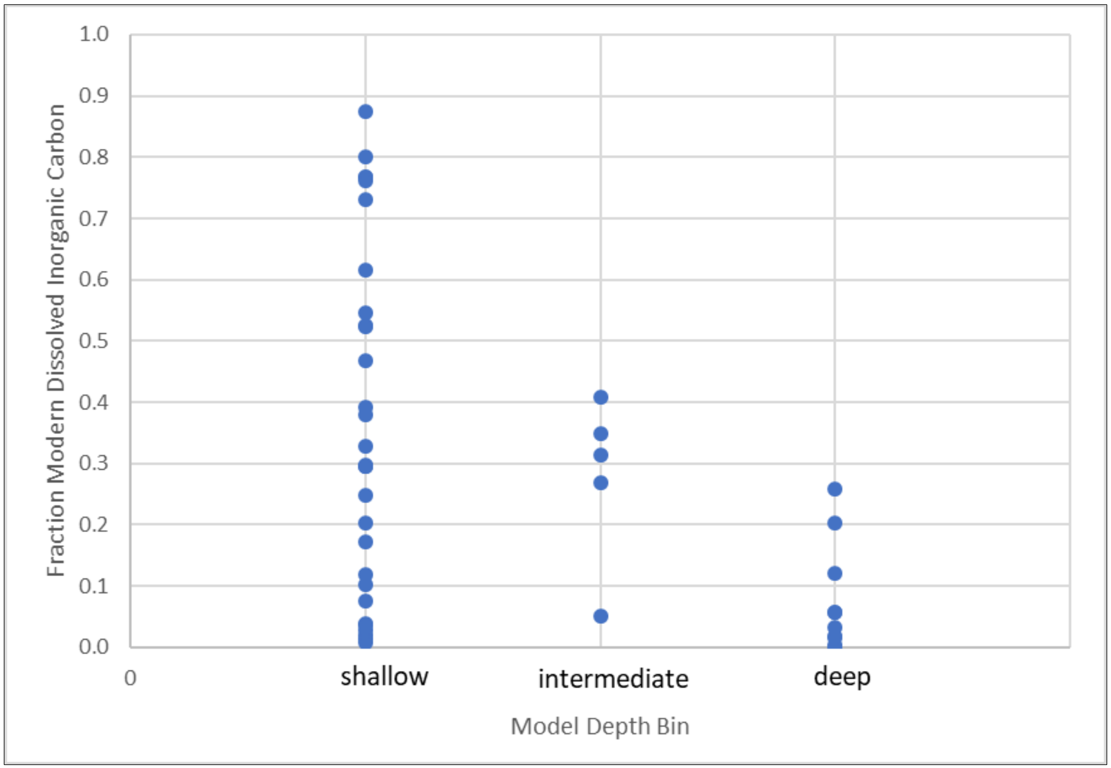

Figure 10. Fraction Modern Carbon DIC ^{14}C measured in samples from wells completed at different depth horizons in the groundwater model.

Geochemical Modeling of Groundwater Age

The geochemical reactions involving water and minerals can be simulated and used to correct ^{14}C ages for the addition of mineral carbon. The USGS Program NETPATH (Plummer *et al*., 1994) is well suited for this because it includes associated carbon isotopic fractionation between water and solid phases during the mineral reactions.

Minerals assumed to interact with valley groundwater are albite, anorthite, calcite, halite, gypsum, montmorillonite clays, and trona, as well as CO_2 gas, and cation exchange between calcium and magnesium in the groundwater with sodium on clay surfaces (Table 4). Other assumptions used for the NETPATH simulations are that the DI $\delta^{13}C$ of CO_2 gas is -18.0 ‰ and that of calcite is -2.0 ‰, which is consistent with a secondary or pedogenic calcite, in contrast to a marine calcite (which would be a value of 0 ‰). The carbon in trona is assumed to have a DI $\delta^{13}C$ value of +5.0 ‰.

The models each explore a flow path and if a solution can be found for evolving a starting water chemistry to a downgradient water chemistry, and then the travel time between the points is calculated from the DI^{14}C data. Solutions are constrained by geochemical thermodynamics, the chemical composition of the waters and some controls on the solubility of minerals (for example, halite is only allowed to dissolve, not precipitate), and evaluated based on the match between calculated and measured DI $\delta^{13}C$. For a model to be valid, the model calculated DI $\delta^{13}C$ needs to be within one permil (‰) of the measured value in the downgradient water.

Table 4. NETPATH model results for the 2019 samples.

Phase "+" dissolution "-" precipitation mmoles/L	**Grapevine Canyon to Means**	**Grapevine Canyon to Charley Tower**	**Indian Wells Canyon (62%) plus Means Wells (38%) to Charley Tower**	**Grapevine Canyon to Baker Range**	**Indian Wells Canyon Creek to Sandquist Spa**
Anorthite		0.7			
Albite					
Calcite	-0.5	-1.7	-1.4	-1.9	-0.4
CO_2 gas	-0.4			-0.4	-1.0
NaCl	0.14	3.1	2.9	1.36	1.5
Gypsum	-0.6	0.3		0.21	-1.3
Na-Mont			-1.5		
Exchange		0.5			-0.6
Trona	0.27		0.9	0.2	
DI $\delta^{13}C_{meas}$, ‰	-0.29	-3.1	-3.1	-1.2	-10.6
DI $\delta^{13}C_{model}$, ‰	-1.45	-2.8	-3.4	-1.7	-11.1
Travel time, years	2,900	2,800	2,500	5,100	4,200
$\delta^{2}H$ initial, ‰	-85.5	-85.5	-86.8	-85.5	-86.6
$\delta^{2}H$ final, ‰	-87.1	-89.3	-89.3	-91.5	-92.5

The identification of flow paths for geochemical modeling should always be viewed with some skepticism. The paths are constrained by the few locations where the geochemical data are available and may not represent true locations where water passes from one place to another. The three dimensionality of groundwater flow in the basin, with downward directed flow in the western and northern regions closer to recharge and upward flow in the eastern discharge area, is another important factor controlling actual flow paths that is masked by considering flow vectors on a two-dimensional map. The heterogeneity of the alluvium-filled basin dictates flow along more permeable beds that are layered and connected in complex ways between less permeable horizons, and interrupted by fault zones that cross the groundwater basin. These complications are important considerations when evaluating the geochemical model results.

The Grapevine Canyon to Means Well flow path has the benefit of both DI^{14}C and DO^{14}C data and is a good pathway to consider first. Using the apparent ages (radioactive decay only), the difference in DI^{14}C between the locations suggests a travel time of 3,800 years. This compares favorably to the apparent DO^{14}C age travel time of 3,500 years. Both of these travel times must be considered maximums, given the addition (albeit probably minor amount) of dead DI^{14}C suggested by the 1.4 ‰ heavier DI δ^{13}C at Means Well and the proximity to old organic-rich material in the subsurface, but the coincidence of the ages suggests those interferences are minor. The concentration of dissolved organic carbon in the Means Well groundwater is low (0.2 mg/L, less than that of the Grapevine Creek water at 2.8 mg/L), so it does not appear to be affected by dissolution of organic carbon in the subsurface.

Including the effects of geochemical reactions, NETPATH calculates a travel time of 2,900 years for Grapevine Canyon Creek to Means Well (Table 4), but struggles to simulate the evolution of Means Well water within the chemical and DI $\delta^{13}C$ model constraints. The difficulty lies with the different chemical compositions of Grapevine Canyon Creek and the Means Well, which require simulation of gypsum precipitation along the flow path, which is not reasonable at the observed salinity. The surface water samples in the creek may not be representative of the underflow recharging the valley from the canyon and/or groundwater flow from the north may contribute to the groundwater in the Means Well area. The $\delta^{2}H$ and $\delta^{18}O$ do not indicate evaporative effects to the Grapevine Canyon water, but it may dissolve windblown dust sourced from playa surface efflorescent crusts (primarily gypsum) that may increase its dissolved ion concentration relative to the bulk of recharge.

Continuing downgradient, simulated flow in the upper portion of the steady-state, pre-development, groundwater model indicates that Charley Tower well is downgradient of the general Grapevine Canyon and Means area, although it may also receive flow from the south (Figure 11). All of these flow paths to Charley Tower require groundwater flow across the Little Lake Fault. A travel time of approximately 2,800 years is calculated by NETPATH for flow from Grapevine Canyon to Charley Tower well (Table 4). Models from the Means Well to Charley Tower well do not meet the acceptable criterion for a DI $\delta^{13}C$ match, but mixing Means Well groundwater (38%) with Indian Wells Canyon water (62%) achieves a good NETPATH simulation for Charley Tower well water with a travel time of 2,500 years (Table 4). These results show consistency in travel time to Charley Tower well from the Sierra Nevada canyon recharge zone.

North of the Charley Tower well, groundwater at Baker Range well originates from the west and northwest (Figure 11). No suitable geochemical model can be developed for evolving Baker Range well water from Sand Canyon water because the decrease in HCO_3 from Sand Canyon to Baker Range inhibits dissolution of isotopically heavy carbonate so that the modeled DI $\delta^{13}C$ for that flow path is too isotopically light compared to that measured at Baker Range. If a composition represented by Grapevine Canyon is used rather than Sand Canyon (Grapevine Canyon has a higher HCO_3 concentration than Sand Canyon and Baker Range), a travel time of 5,100 years is calculated (Table 4).

The groundwater model indicates that flow to Sandquist Spa Well comes from the southwest (Figure 11), south of Indian Wells Canyon. If the Indian Wells Canyon Creek sample is allowed to stand in for recharge entering the basin from the canyons to the south of it (none of which have ^{14}C data), a travel time of 4,200 years is calculated for flow from recharge area to Sandquist Spa (Table 4).

The historic Indian Wells Spring, located at the current brewery at the mouth of Indian Wells Canyon, with an analysis reported in TTEMI (2003), provides a contrast between surface water in the canyon and water that has infiltrated into the groundwater system. Indian Wells Canyon Creek has a DI $\delta^{13}C$ of -13.7 ‰ and FMC of 1.0, whereas IWVBCS1 (Indian Wells Valley Brewing Company Spring 1) has a DI $\delta^{13}C$ of -7.9‰ and an FMC of approximately 0.9. The $\delta^{2}H$ of the canyon surface water is -86.6‰ and that of the brewery spring is -94.0 ‰. The apparent age of IWVBCS1 is approximately 900 years (decay alone), but a travel time of approximately 100 years results when NETPATH accounts for carbonate reactions between the 2019 Indian Wells Canyon sample and the spring (a lower SO_4 concentration water must also recharge in the canyon because this model requires gypsum precipitation that is unreasonable at these salinities) (Table 5).

Hydrologically, a canyon-mouth spring is a better integrator of recharge water composition than a surface water sample, with the spring representing the infiltration and mixing of water throughout the catchment area. The importance of assumptions of recharge composition can be seen by comparing NETPATH models for travel time between the Indian Wells Canyon Creek sample to Navy Well 15 (location 26 on Figure 12), with that of IWVBCS1 to Navy Well 15. The geochemical reactions are more reasonable and the DI $\delta^{13}C$ match superior for the IWVBCS1 starting composition, and the calculated travel time is 4,000 years shorter for IWVBCS1 than for the creek as a starting point (Table 5). Similarly, calculating travel time from IWVBCS1 to Sandquist Spa provides a 3,300-year time (Table 5), in contrast to the 4,200 years calculated using the creek (Table 4), and the deuterium values are in better agreement for the IWVBCS1 pathway.

Table 5. NETPATH model results using 2019 and previous analyses.

Phase "+" dissolution "-" precipitation mmoles/L	**Indian Wells Canyon Creek to IWVBCS1**	**Indian Wells Canyon Creek to Navy Well 15**	**IWVBCS1 to Navy Well 15**	**IWVBCS1 to Sandquist Spa**
Anorthite				
Albite				
Calcite	0.3		-1.7	
CO_2 gas	-2.1	-1.9	0.8	0.3
NaCl	0.2	0.6	0.3	1.3
Gypsum	-1.3	-0.7	0.6	0.1
Na-Mont		-4.5		-4.6
Exchange	-0.5	0.9		0.7
Trona			0.4	
DI $\delta^{13}C_{meas}$, ‰	-7.9	-7.3	-7.3	-10.6
DI $\delta^{13}C_{model}$, ‰	-7.1	-8.2	-7.3	-9.4
Travel time, years	113	9,000	5,000	3,300
$\delta^{2}H$ initial, ‰	-86.6	-86.6	-94	-94
$\delta^{2}H$ final, ‰	-94	-95	-95	-92.5

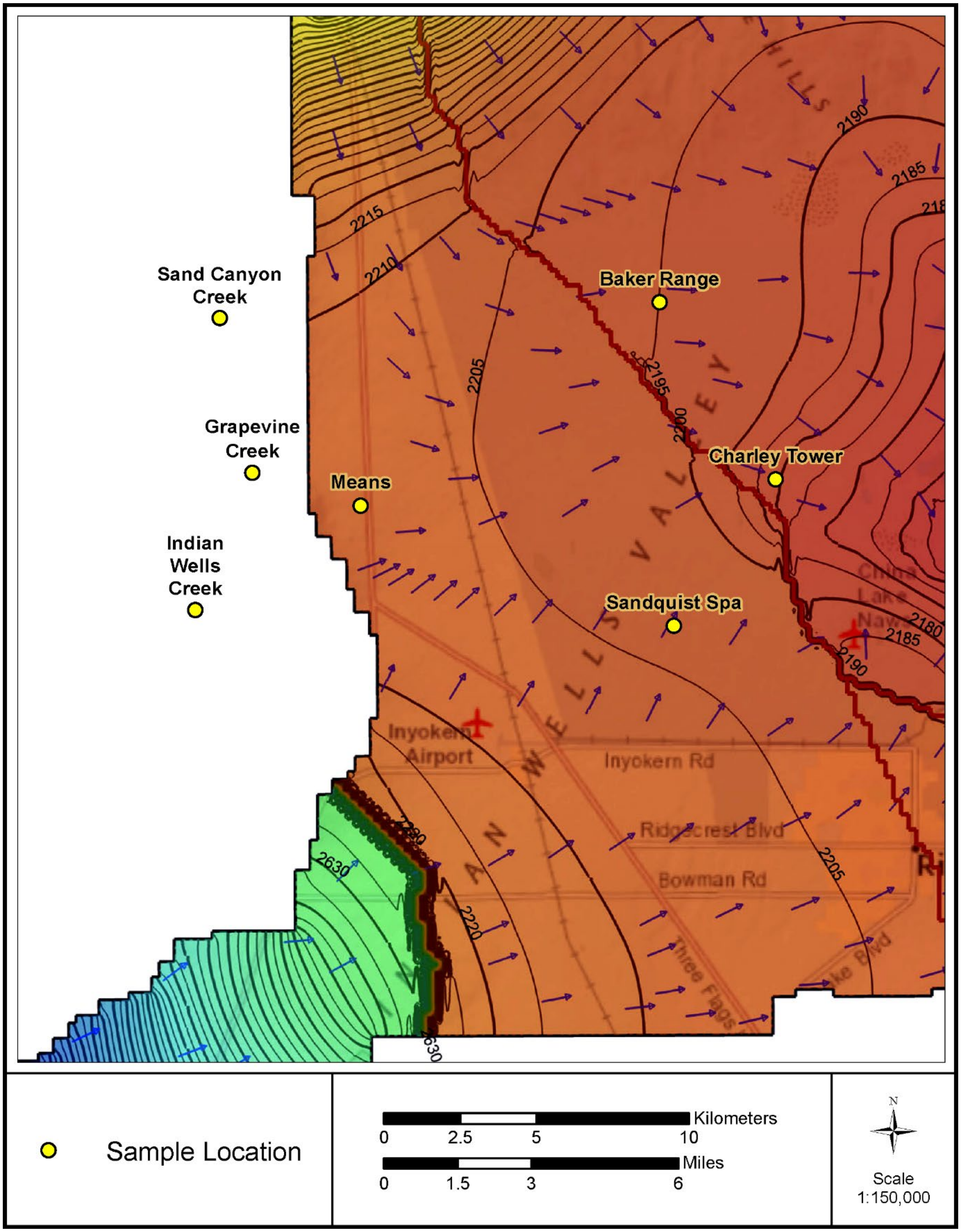

Figure 11. Flow paths (vectors and potentiometric contours) in the upper layer of the steady-state groundwater model simulating groundwater flow prior to the start of pumping in the valley in 1921. The contour interval for the potentiometric contours is five feet and units are feet above mean sea level. Faults are shown as red solid lines.

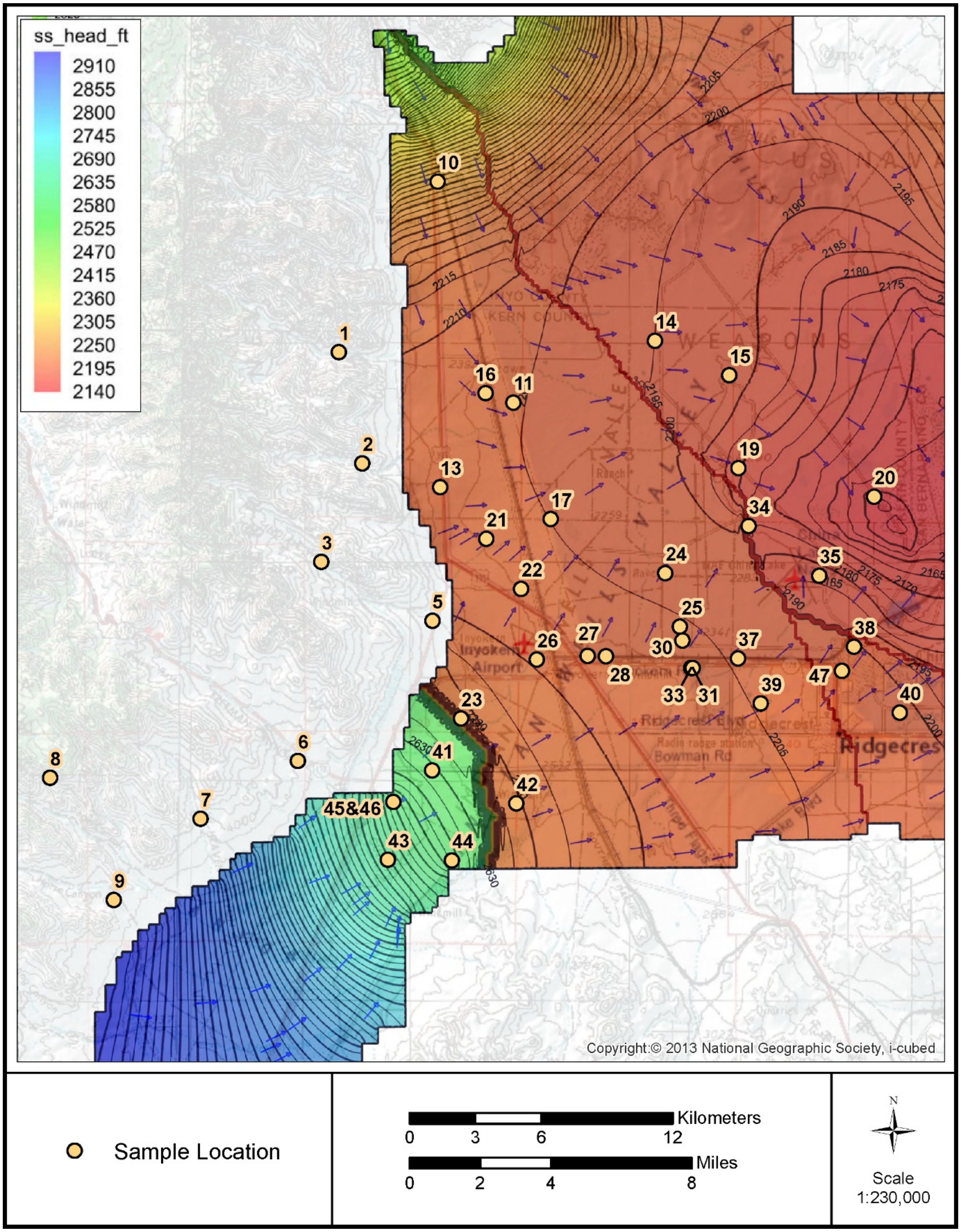

Figure 12. Flow paths in the upper layer of the groundwater model as indicated by steady-state vectors and contours of hydraulic head. Wells previously sampled for carbon isotopic analysis are shown. Faults are shown as red solid lines. A key for the well numbers is provided in Table 6 and analytical data are in Appendix A.

Table 6. Key to locations shown on the map in Figure 12.

1	Sand Canyon
2	Grapevine Canyon
3	Indian Wells Canyon
5	IWVBCS1
6	Freeman Canyon
7	Cow Heaven
8	Sage Canyon
9	Horse Canyon
10	Sawmill Well
11	25S/38E 13J01
12	25S/38E 13J01 USGS
13	Means Well
14	Baker Range Well
15	Navy Well 22
16	Childers Well
17	25S/39E 31R01 1988
18	25S/39E 31R01 2007
19	Charley Tower Well
20	TTBK-MW13
21	Field Well
22	Campbell Well
23	Marquart Well
24	Sandquist Spa Well
25	26S/39E 14P01
26	Navy 15
27	Navy 30
28	Navy 31
29	Navy 31
30	Navy 28
31	TTIWV-MW01-D
32	TTIWV-MW01-I
33	USBR-4
34	26S/40E 06C01
35	26S/40E 09 1983
36	26S/40E 09 USGS 1987
37	TTIWV-MW02 D
38	MW07-14
39	26S/40E 31A01
40	26S/40E 35H02
41	27S/38E 10C2
42	SWCB01
43	27S/38E 21L1
44	USBR-01 S/M
45	Father Crowley West
46	Father Crowley East
47	TTIWV-MW07

Although no comprehensive interpretation of flow paths involving published DI^{14}C data for IWV was performed, it is important to recognize that some of the previous samples indicate much older groundwater than sampled in 2019. Most of these locations are in the southeastern part of the valley. Given the DI δ^{13}C and salinity of some of these samples, considerable water-rock reactions have occurred and the apparent DI^{14}C ages are likely much older than actual. However, some of these low FMC groundwaters also have depleted δ^{2}H compositions (Figure 13), which indicate a residence time coinciding with recharge during the last glacial period of the Pleistocene (ranging from 12,000 to 30,000 YBP).

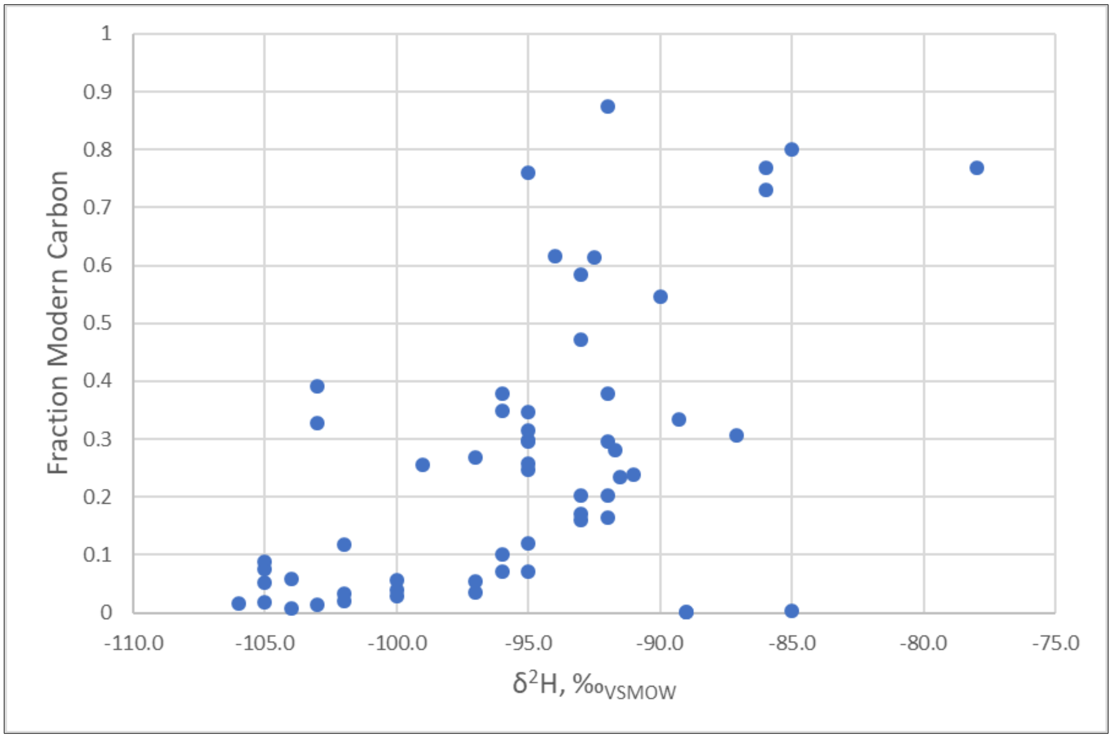

Figure 13. Relationship between δ^2H and fraction of modern carbon in groundwater samples.

Pleistocene-age groundwater may have been recharged by inflow from the Sierra Nevada canyons with greater snow accumulations than the present climate, or by infiltration from the paleo-Owens River system and associated China Lake that occupied IWV as recently as 6,400 YBP (Bacon *et al.*, 2020). In either case, the recharge occurred during cooler and wetter conditions and likely was lower salinity than measured today in the Sierra Nevada canyons.

The most dilute canyon water analysis for the IWV watershed today is from Cow Heaven Canyon. There is no DI^{14}C measurement for the canyon, so an FMC range of 0.5 (as measured in Grapevine Canyon today) to 1.0 (consistent with infiltration from a paleo lake) is assumed, with the Cow Heaven measured DI δ^{13}C value of -11.3 ‰. This assumed Pleistocene recharge composition is used in NETPATH to estimate travel time to some of the low FMC and light δ^2H groundwaters previously sampled in IWV (Table 7). Calculations for TTIWV-MW02D (denoted as number 37 on Figure 12) yield a range of travel times from 19,000 to 25,000 years, with the range defined primarily by the range in assumed FMC for the Pleistocene recharge. Travel times to well TTIWV-MW01D (number 31 on Figure 12) range from 16,000 to 22,000 years. Closer to the discharge area, travel time to well MW07-14 (number 38 on Figure 12) is longer, at 25,000 to 37,000 years, in this case with the range resulting primarily from different chemical reactions. Collectively, these groundwater ages suggest long travel and/or residence times in portions of the deep aquifer, times that generally coincide with the latest periods of major glacial advances in the Sierra Nevada and overflow from Owens Lake via the paleo-Owens River into IWV (e.g., Phillips [2016] and [2017], and Bacon *et al*. [2020]).

Table 7. NETPATH model results for a hypothetical Pleistocene recharge value, constructed using the chemistry measured in Cow Heaven Canyon and assuming FMC values of 0.5 and 1.0.

Phase "+" dissolution "-" precipitation mmoles/L	**Hypothetical Pleistocene recharge to TTIWV-MW02D**	**Hypothetical Pleistocene recharge to TTIWV-MW01D**	**Hypothetical Pleistocene recharge to MW07-14**	
Anorthite				
Albite	1.5	1.6		
Calcite	-1.0	-1.1	11	
CO$_2$ gas	-1.1	-0.8		3.7
NaCl	0.4	0.1	4.1	4.1
Gypsum	-0.03	0.1	-0.03	-0.03
Na-Mont			-33	
Exchange			11	1.0
Trona				3.6
DI $\delta^{13}C_{meas}$, ‰	-8.7	-8.9	-5.6	
DI $\delta^{13}C_{model}$, ‰	-7.6	-9.1	-4.2	-4.8
Travel time, years	19,000 to 25,000*	16,000 to 22,000*	25,000 to 37,000**	
δ^2H initial, ‰	Not available	Not available	Not available	
δ^2H final, ‰	-105	-105	-106	

*Range results from using an initial FMC of either 0.5 (for lower travel time) or 1.0 (for longer travel).

**Range results from two different sets of geochemical reactions, as noted by split column.

DISCUSSION AND CONCLUSIONS

The δ^2H and $\delta^{18}O$ data clearly identify much of the groundwater in IWV as consistent with the isotopic character of modern recharge. There is also groundwater that is isotopically lighter in δ^2H and $\delta^{18}O$ than modern recharge. Because modern recharge has not been systematically investigated, the exact isotopic criteria for the two groups is not well defined, but generally groundwater with a composition lighter than δ^2H of -100 ‰ and $\delta^{18}O$ of -13 ‰ may be the product of recharge during cooler and wetter conditions of the past.

Carbon-14 measurements span the full gamut from essentially zero to 1.0 for FMC, but associated DI $\delta^{13}C$ data clearly indicate that radioactively "dead" inorganic carbon has affected many of the groundwater DI^{14}C values. The impact of carbonate-mineral dissolution on the water's DI^{14}C is demonstrated by the Grapevine Canyon and Means Well samples in 2019, for which the DO^{14}C based measurements are thousands of years younger than the DI^{14}C data would suggest. Correcting for carbonate mineral reactions using the geochemical model NETPATH yields travel times to wells in central IWV on the order of 3,000 to 5,000 years. Other wells sampled previously identify some groundwater samples with very low fractions of modern carbon that indicate residence times into the late Pleistocene, even when geochemical reactions are taken into account.

Although groundwater from both populations (recent and Pleistocene recharge) occurs throughout the valley, and in all depth horizons sampled, a larger proportion of the intermediate and deep groundwater groups have Pleistocene characteristics, whereas a larger proportion of shallow groundwater is consistent with modern recharge from the highlands around the IWV. Spatially, the Pleistocene-character groundwater occurs more frequently in the southeastern part of the valley. Both conditions, deeper and located closer to the discharge zone, are consistent with residence times on the older end of the distribution for the groundwater system.

Path-line analysis of the groundwater model developed for the Groundwater Sustainability Plan (Indian Wells Valley Groundwater Authority, 2020a) calculated travel times in the shallow horizon from the Sierra Nevada canyons to the China Lake playa evapotranspiration zone of 4,000 to 12,000 years (Figure 14) (DRI, 2018). Modeled travel times through the deeper layers of the flow system are on the order of 30,000 years. The combined $\delta^{2}H$, $\delta^{18}O$, DI $\delta^{13}C$, and DI^{14}C and DO^{14}C data generally support this model depiction.

One confounding isotopic observation is the travel time indicated by both the DI^{14}C and DO^{14}C data for flow between Grapevine Canyon and the Means Well. The travel time suggested by the groundwater model is estimated at 1,500 years from Figure 14 (note the time intervals along the flow lines) but that is from the range-front fault bounding the valley groundwater system. The ^{14}C travel time of approximately 3,500 years could suggest that groundwater flow from recharge areas west of, and through, the range-front fault requires a couple of thousand years in the shallow groundwater horizon downgradient from Grapevine Canyon. However, the relatively short travel times from western recharge areas to Charley Tower and Sandquist Spa Wells indicate more rapid flow paths from recharge areas to some parts of the basin. These different observations may be the result of the three-dimensional spatial complexity of the hydrogeologic system in this alluvial basin. For example, consider the water level observed in well USBR-5 D in autumn 2019, after a very wet spring. Well USBR-5 D is located just south of the Means Well, and at roughly the same land surface elevation. The USBR-5 D well monitors a depth of approximately 1,970 feet below land surface and exhibits over a six-foot rise in water level between March and October 2019 (Indian Wells Valley Groundwater Authority, 2020b). Conversely, the record from the Means well, completed between 420 and 480 feet below land surface, shows little change between those dates. This suggests a good hydrologic connection between the recharge zone in the canyon and the relatively deep aquifer, which may facilitate groundwater flow to the east, whereas the shallower zone appears less well-connected across the fault.

Although precise interpretations of groundwater age and travel time remain elusive given the limitations of sampling and complexities of path-line definition and geochemical processes, the broad interpretation of the isotopic character of water in IWV clearly describes a basin receiving current recharge that flows into the central basin in a matter of 3,000 to 6,000 years. The basin also contains groundwater recharged during the late Pleistocene from 12,000 to 30,000 years ago. The older water tends to occur in the deeper portions of the basin and in areas closer to the discharge zone, but the spatial distribution of water recharged under the current and past climate is complex. The range of travel times inferred from the isotopic data are consistent with the groundwater flow model used by the IWV Groundwater Sustainability Plan (Indian Wells Groundwater Authority, 2020).

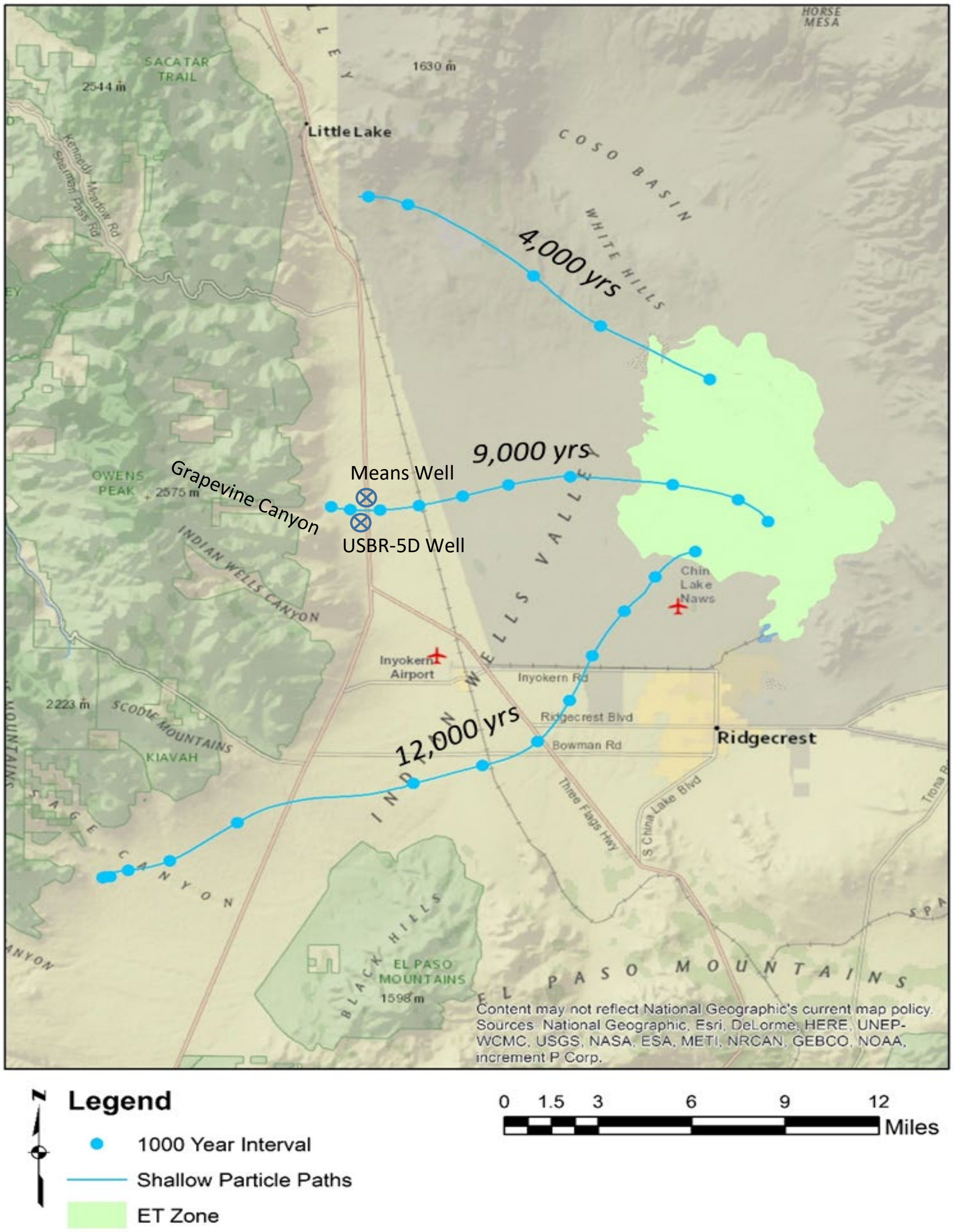

Figure 14. Path lines and travel times calculated with the Groundwater Sustainability Plan groundwater flow model for water in the upper model layer, starting at the western model boundary recharge zone and traveling to the valley discharge zone (Desert Research Institute, 2018). Locations of Grapevine Canyon, Means Well, and USBR-5D were added to the original map and are approximate.

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APPENDIX A. ANALYTICAL DATA FOR PREVIOUSLY COLLECTED SAMPLES FROM THE INDIAN WELLS VALLEY AREA.

Table A-1. Analytical data for previously collected samples from surface water locations and wells in the Indian Wells Valley area; "—" denotes no data for the parameter.

Location	**pH**	**Ca (mg/L)**	**Mg (mg/L)**	**Na (mg/L)**	**K (mg/L)**	**Cl (mg/L)**	**SO_4 (mg/L)**	**Alkalinity (mg/L)**	**$\delta^{13}C$ (‰$_{VPDB}$)**	**$DI^{14}C$ (FMC)**	**$\delta^{2}H$ (‰$_{VSMOW}$)**	**$\delta^{18}O$ (‰$_{VSMOW}$)**	**Ref.**
Indian Wells Canyon (AB 303)	8.34	100.00	26.00	41.00	3.20	15.00	190.00	240.0	-10.10	--	-86.0	-10.8	1
IWVBCS1 (TTEMI)	7.23	89.00	22.00	27.00	4.00	23.90	72.00	82.00	-7.90	0.895	-94.0	-12.3	3
Freeman (Big/Soldier)	7.82	49.00	8.90	32.00	0.29	13.00	36.00	160.00	--	--	-84.0	-11.8	3
Cow Heaven Canyon	8.22	43.00	8.90	22.00	2.40	6.30	15.00	170.00	-11.30	--	-89.0	-12.1	3
Sage Canyon	8.08	96.00	18.00	57.00	1.70	21.00	26.00	340.00	-10.90	--	-85.0	-11.4	3
Horse Canyon	7.84	57.00	17.00	47.00	2.50	17.00	36.00	260.00	-9.30	--	-86.0	-11.5	3
Sawmill Well #1 (24S38E16J02)	8.13	68.00	39.00	350.00	18.00	180.00	180.00	770.00	1.1	0.314	-95.0	-11.9	1
25S38E13J01	8.32	12.00	5.20	92.00	8.20	28.00	12.00	240	-5.8	0.768	-78.0	-10.6	1
25S38E13J01 USGS data	8.20	33.00	13.00	70.00	5.80	24.00	62.00	179	--	--	-86.0	-11.8	1&2

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Navy Well 22 (25S39E12R02)	--	--	--	--	--	--	--	--	-2.9	0.349	-96.0	-12.1	3
Childers Well (25S39E14H01)	8.18	91.00	0.10	98.00	7.00	100.00	120.00	260	-7.2	0.800	-85.0	-11.0	1
25S/39E 31R01 1988	9.20	31.00	14.00	314.00	4.90	232.00	163.00	288	-5.4	0.234	-97.5	-12.5	1
25S/39E 31R01 2007	8.04	65.00	15.00	100.00	3.70	92.00	160.00	200	-10.0	0.248	-95.0	-12.4	1
TTBK-MW13 (25S40E35D01)	--	--	--	--	--	--	--	--	-2.9	0.545	-90.0	-11.5	3
Campbell 26S38E12R1	8.16	69	12	100	3.5	130	140	150	-15.4	0.296	-95	-12.3	1
Marquardt (26/38 35L1)	8.98	1.80	0.01	65.00	0.64	5.00	14.00	110.00	-9.40	0.089	-105.0	-13.4	1
26S39E14P01	7.96	30.00	10.00	25.00	2.70	33.00	22.00	120	-17.70	0.072	-95.0	-14.6	1
Navy 15 (26/39 19P2)	8.07	44.00	6.40	65.00	2.60	36.00	130.00	88.00	-7.30	0.348	-95.0	-12.5	1
Navy Well 30 (26S39E20R01)	8.14	31.00	3.50	37.00	2.10	24.00	50.00	110	-7.50	0.203	-93.0	-12.6	1

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Navy Well 31 (26S39E21Q01) 2007	8.14	22.00	0.32	38.00	1.70	22.00	36.00	89	-10.00	0.258	-95.0	-12.7	1
TTIWV-MW01-D (26S39E26A02-D)	9.57	1.79	0.16	62.90	0.90	10.90	21.80	102.00	-8.90	0.075	-105.0	-14.2	3
TTIWV-MW01-I (26S39E26A02-I)	7.99	32.60	9.84	33.90	2.76	29.60	52.70	100.00	-5.50	0.121	-95.0	-12.9	3
26S40E06C01 USGS 5-30-87	10.10	3.10	0.75	24000.00	74.00	14000.00	5200.00	28200.00	-4.30	0.004	-85.0	-8.1	2&3
26S40E09 1983	7.45	69.00	11.00	125.00	5.00	135.00	123.00	191.00	-9.00	0.084	--	--	3
26S40E09 USGS 5-29-87	8.00	41.00	6.70	110.00	4.60	130.00	76.00	222.00	-9.00	0.106	--	--	2
TTIWV-MW02(D) (26S40E19N01)	9.66	1.37	0.132	65.1	0.42	19.1	12.1	106	-8.7	0.051	-105	-14.2	3
MW07-14 (26S40E22P1) USGS 1987	8.60	1.70	0.53	410.00	4.40	150.00	12.00	741.00	-5.60	0.006	-106.0	-13.9	2&3
26S40E31A01	--	--	--	--	--	--	--	--	-6.3	0.054	-97	-12.8	3
26S40E35H02	--	--	--	--	--	--	--	--	-3.00	0.015	-104.0	-13.7	3

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27/38 10C2	8.46	2.70	0.10	98.00	1.10	18.00	67.00	120.00	-10.00	0.269	-97.0	-12.7	1
SWCB01 (27S38E13A01)	7.7	34 .0	5.5	58	2.3	27	61	194	-5.6	0.585	-93	--	1
27/38 21L1	8.26	14.00	11.00	100.00	2.70	35.00	69.00	140.00	-8.80	0.378	-96.0	-12.6	1
Father Crowley West (27/39 9Q2)	8.32	29.00	13.00	290.00	12.00	140.00	190.00	320.00	-6.50	0.379	-92.0	-12.2	1
Father Crowley East (27/39 9Q1)	8.08	68.00	19.00	55.00	3.20	17.00	81.00	260.0	1.50	0.239	-91.0	-12.1	1
TTIWV-MW07	--	--	--	--	--	--	--	--	-3.80	0.015	-106	-14.3	3

Key for References:

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