Memorandum

DATE: January 2, 2019

TO: Fenner Valley Water Authority
Santa Margarita Water District

FROM: David K. Kreamer, Ph. D.

RE: Review of September 2018 Love and Zdon publication. Enclosed are my findings.

Review of "*Use of Radiocarbon Ages to Narrow Groundwater Recharge Estimates in the Southeastern Mojave Desert, USA*" by Adam H. Love and Andy Zdon in Hydrology MDPI[1]

By
David K. Kreamer, Ph.D.

In the publication, Love and Zdon 2018, the authors attempt to critically review and improve and constrain estimates of groundwater recharge in the Southeastern Mojave Desert by use of radiocarbon dating. The conclusions reached in this paper rely on previous published work in non-journal publications, and one round of radiochemical measurements made at five (5) selected springs.

Understanding groundwater recharge, subsurface water balance volumes, and average groundwater residence time is a crucial aspect in defining the sustainability of springs throughout the world, and particularly in the Mojave Desert. Springs in arid lands are precious and are the focus of ecologic system health, cultural heritage, drinking water supply, and regional stability, and therefore have attracted much scientific study (LaMoreaux et all 2001; Chapelle et al. 1997; Manga 2001; Kreamer et al. 2015; Meinzer 1927; Kreamer and Springer 2008). Environmental studies in this sensitive, vulnerable region need to be robust, based on solid literature, and quantitatively define uncertainties in their conclusions and interpretation.

While the publication by Love and Zdon in Hydrology MDPI adds data to study of springs in the Mojave Desert, the conclusions reached by the authors are seriously flawed, contain both citations and self-citations from non-refereed work, do not adequately describe limitations or uncertainties

[1] https://www.mdpi.com/2306-5338/5/3/51.

in their work, fail in some cases to consider the possibility of local spring recharge beyond surface catchments, use different areas and basins for their comparison of annual recharge volumes, and neglect the incorporation of standard methodologies to interpret their data.

The conclusions articulated by the authors are tenuous at best. Problems with the publication's format, methodologies, omissions, and interpretations, (many of them major flaws), include:

1. Springs are very poor locations to attempt to calculate average groundwater residence time.
2. The authors, Love and Zdon, confuse the concept of the generally accepted "*average groundwater residence time*" with their use of the more misleading term "*apparent groundwater age.*"
3. The paper's "*Site Description" and "Geologic and Hydrogeologic Setting*" sections contain no citations of literature, except a self-citation addressing their previous characterization of the source of Bonanza Spring.
4. The paper does not adequately map or quantitatively define "*Southeastern Mojave Desert*" in the article's title and appears to use different, non-equivalent areas and basins when comparing annual recharge volumes.
5. The work compares five annual recharge estimates, with three estimates from Technical Memoranda or Reports. Two other estimates are veiled, apparently not externally refereed, self-citations in letter and report form, and in one instance is self-congratulatory. This is generally considered a poor practice in cited literature. Memoranda and Reports are often not readily available for external review, and the rigor of their peer review is not always apparent. The obfuscation exhibited by unclear referencing exhibited in the self-cited work is also considered a poor practice in cited literature**.**
6. The publication does not indicate correction of tritium values with helium-3 analysis.
7. The authors do not use any of the standard methodologies to correct carbon-14 values for interaction with "dead" geologic inorganic carbon, not atmospherically derived.
8. The publication does not consider the effect of groundwater's interaction with organic carbon.
9. Concerning Love and Zdon's (2018) tritium and ^{14}C analyses of spring water, the authors fail to report duplicate or replicate analyses critical to establishing the limits of uncertainty in their findings.
10. For their tritium and ^{14}C analyses of spring water, there is poor reporting of the sampling date, exact location of the sampling points, ambient air temperatures and other meteorological conditions, antecedent precipitation, and many other factors which could influence radiological measurements – these are not detailed in the manuscript.
11. The authors do not report additional sampling or results from local wells or springs to support their findings.
12. Other indicators of average groundwater travel time to springs and recharge (e.g. chloride mass balance studies, chloroflourocarbons (CFCs), trace elements) are not fully investigated.

13. The authors make a refutable, *a priori* presumption that Bonanza Spring is "in hydraulic communication with the basin-fill aquifer system surrounding the Clipper Mountains".
14. The publication does not consider or analyze the possibility of fracture flow.
15. The publication lacks an associated quantitative groundwater transport model.

These weaknesses in the publication are elaborated below.

1. **Springs are poor locations to attempt to calculate average groundwater residence time.**

According to the International Atomic Energy Agency's (IAEA) "Isotope Methods for Dating Old Groundwater" (2013), "*Springs probably are the least desirable sources for sampling 'old' groundwater because their discharge can represent a mixture of many waters of generally unknown origin (and age).*" Wells are considered far superior. This is a caution about over interpretation of estimates of average groundwater residence time for spring flow.

2. **The authors confuse the concept of the generally accepted "*average groundwater residence time*" with their use of the misleading term "*apparent groundwater age*".**

Groundwater scientists have generally agreed for many years that the concept of "groundwater age" is flawed. Fontes (1983) notes "*Owing to dispersion, the 'age' of a groundwater sample corresponds generally to a time distribution of many elementary flows. Thus, except in the theoretical case of a pure piston flow system, or of stationary waters entrapped in a geological formation, the concept of groundwater age has little significance.*"

3. **The paper's "*Site Description*" and "*Geologic and Hydrogeologic Setting*" sections contain no citations of literature, except a self-citation addressing their previous characterization of the source of Bonanza Spring.**

It is typical in publications to do comprehensive literature searches, from extensive source material. Love and Zdon (2018) describe the region's geologic and hydrogeologic features in detail without citation of a single source. However, notable is an absence of specific description of geologic structures, exact locations of faults, orientation of geologic contacts, rock porosities and permeabilities, and other characteristics crucial to interpretation of spring flow.

Three figures are shown in this section with sources cited in the captions; one figure is a small portion of a much larger, generic map of California's surface geology from a State government website (Geological Map of California. California Geological Survey, Geologic Data Map No. 2. 2010. Available online: https://maps.conservation.ca.gov/cgs/gmc/). A second figure is a conceptual geologic cross-section drawn from another publication on the hydrogeology underlying White Pine County on the northern Utah-Nevada border about 350 miles away and distant from the Mojave Desert (U.S. Geological Survey. Water Resources of the Basin and Range Carbonate-Rock Aquifer System, White Pine County, Nevada, and Adjacent Areas in Nevada and Utah. Scientific Investigations Report 2007–5261; Welch, A.H., Bright, D.J., Knochenmus, L.A.,

Eds.; U.S. Geological Survey: Reston, VA, USA, 2007; Figure 16; p. 37.) The third is a small portion of a California state website map of groundwater basins (California Department of Water Resources. Groundwater Basin Boundary Assessment Tool. Division of Integrated Regional Water Management. 2018. Available online: https://gis.water.ca.gov/app/bbat/).

4. **The paper does not adequately map or quantitatively define "*Southeastern Mojave Desert*" in the article's title, and appears to use different, non-equivalent areas and basins for comparison of annual recharge volumes.**

One of the key elements of this publication is comparison of groundwater volumes in five annual recharge estimates. These values are compared in the paper's Figure 6. It is not reported, however, that the location and areal extent/ boundaries that are the basis for these recharge estimates are vaguely described and from dissimilar areas. The five recharge estimates compared in this publication are from: the Geoscience Support Services (1999), the U.S. Geological Survey (2000), the Lawrence Livermore National Laboratory which is the Davison and Love (2000) including a personal communication, CH_2M Hill (2011), and Johnson Wright Inc. (2012) by A. Zdon.

According to the publication's authors Love and Zdon, Geoscience Support Services (1999) and the USGS (2000) estimates are for the area comprised of the Bristol, Cadiz and Fenner Basins. The "Lawrence Livermore National Laboratory (2000)" (by Davisson and Love) recharge estimate contains anecdotal personal communication, with the recharge area under consideration being the Fenner Watershed. The Fenner Watershed includes the Clipper Valley according to the California Department of Water Resources. CH_2M Hill (2011) also bases its estimate on only Fenner and the Orange Blossom Wash. In the Love and Zdon (2018) publication, the Johnson Wright (by Zdon letter) recharge estimate is unclear about the area which it represents. The current publication only mentions the Bristol and Cadiz playas.

Also, some of the comparisons in Love and Zdon are between quantities of dissimilar (a.) "recoverable" water and (b.) groundwater recharge. Comparisons should be made between similar parameters and study areas.

5. **The work compares five annual recharge estimates, with three estimates from Technical Memoranda or Reports. Two other estimates are veiled, apparently not externally refereed, self-citations in letter and report form, and in one instance is self-congratulatory. This is generally considered a poor practice in cited literature. Memoranda and Reports are often not readily available for review, and the rigor of their peer review is not always apparent and often not critically externally reviewed. The obfuscation exhibited by unclear referencing exhibited in the self-cited work is also considered a poor practice in cited literature.**

The first three Technical Memoranda and Reports are from Geoscience Support Services (1999), CH_2M Hill (2011), and the USGS (2000). Of the remaining two, one of the self-citations is from a seven page government report (Davisson and Love, 2000) listed in the MDPI Hydrology

publication as Lawrence Livermore National Laboratory (2000), the other from a non-refereed letter written by one of the authors (Zdon), listed as Johnson Wright Inc. (2012). The authors use anecdotal information from the first (personal communication) and self-congratulate the quality of their own recharge estimate from the second. For the latter self-citation, Love and Zdon (2018) present, without support, that Zdon's (Johnson Wright Inc.) non-refereed recharge estimate, "*resulted in more consistent and generally improved estimates of groundwater discharge than in previous studies*". It should be noted that the Johnson Wright Inc. (2012) letter by Zdon only suggests a single value with no error bars in Figure 6, not a range of values, and Zdon's letter based evaporation estimates on interpretation of data from the topographically lower, hotter Death Valley, CA and may not represent all evaporation values for the study area near the Cadiz, Bristol basins.

In fairness to the authors, there are not an abundance of recharge estimates in the Eastern Mojave Desert, and their choices for comparison are limited. Even so, annual groundwater recharge comparisons should normalize to equivalent areas, self-citation should be made more transparent, and it is suggested that authors should refrain from self-promotion.

6. The publication does not indicate correction of tritium values with helium-3 analysis.

Tritium was measured in this study at five springs and used to represent apparent groundwater age. There are natural limits to this method because the atmospheric tritium bomb pulse caused by nuclear testing and associated tritium in the atmosphere, precipitation, infiltrating waters, and groundwater has been greatly reduced in recent decades because of: (a.) lower amounts of tritium in precipitation in the Mojave Desert relative to points further inland and other locations in California (Stewart and Farnsworth 1968; Harms 2015), (b.) tritium decay, which has brought tritium levels in precipitation close to pre-bomb levels for several decades, and (c.) dispersion and mixing of groundwater of different ages. Because of tritium's short half-life it has been increasingly difficult to identify a "bomb peak" in groundwater and distinguish between pre-bomb pulse and post-bomb pulse waters. These challenges can be overcome by measuring tritium concentrations in concert with its decay product helium-three or ^3He ($^3He_{trit}$) as first suggested by Tolstykhin and Kamensky (1969) and experimentally confirmed by Torgersen et al. (1979). Measuring tritium and tritiogenic ^3He together supports identification of the tritium peak as the sum of tritium and ($^3He_{trit}$), even if most of the tritium has decayed. It also allows direct calculation of average groundwater residence time from the mother/daughter ratio (tritium/^3He). This is advantageous because it removes the requirement to ascertain the exact time-dependent tritium delivery to the aquifer (Clark et al. 1976). $^3H/^3He$ analysis can also be compared to studies of chlourofluorocarbons and krypton-85. ^3He analysis was not presented in the current paper by Love and Zdon.

Through radioactive decay, post bomb pulse tritium levels in precipitation have approached pre-bomb levels since the 1980s around the world, and the mean tritium concentration in California precipitation is 11.4 pCi/L, or 3.5 Tritium Units (TU) (Harms 2015). With even lower than average tritium in the precipitation in Mojave Desert relative to inland and mountainous areas in California and on the West Coast, for as much as approximately 35 years or almost 3 half-lives, some groundwater which originated as post-bomb precipitation contains tritium concentrations

now approaching detection limits of analytical equipment. This diminishment reduces the strength of conclusions in Love and Zdon (2018) based on single measurements of tritium alone.

Without helium-three analysis the tritium result of Love and Zdon (2018) are less useful. Also, there is only one value of tritium measurement for each spring listed in the Hydrology MDPI publication. This lack of confirmatory replicate sampling will be discussed further below.

7. **The authors do not use any of the standard methodologies to correct carbon-14 values for interaction with "dead" geologic inorganic carbon, not atmospherically derived.**

Probably one of the greatest flaws is the radioactive carbon-14 (^{14}C) "age dating" work by Love and Zdon (2018) and their inadequate discussion of, and correction for, groundwater interaction with carbonate geologic materials. These carbonate rocks have been in the ground millennia and have totally depleted ^{14}C (sometimes referred to as "dead" carbon), thus reducing the radioactive carbon signal in the adjacent and interacting groundwater and producing a false indication of a lengthy average groundwater travel time to a spring.

According to Phillips and Castro (2003), "*Natural radiocarbon was first detected by Libby in the mid-1940s (Arnold and Libby, 1949; Libby, 1946), but the first applications to subsurface hydrology were not attempted for another decade (Hanshaw et al., 1965; Munnich, 1957; Pearson, 1966). These early investigators discovered that radiocarbon shows clear and systematic decreases with flow distance that can be attributed to radiodecay, but also exhibits the effects of carbonate mineral dissolution and precipitation reactions.* ***Quantification of residence time is not possible without correction for additions of nonatmospheric carbon***." (My emphasis).

It is a major error in the Hydrology MDPI manuscript that the authors do not adequately correct their data for interaction with "dead" carbonate species. These adjustments can be major. From IAEA (2013), "*the extent to which recharge waters evolve in isotopic equilibrium with soil gas (open system evolution) or react with carbonates following recharge (closed system evolution) (Clark and Fritz 1997; Deines et al. 1974) can lead to uncertainties in 14C model age of old groundwater.*" Love and Zdon do not include uncertainty analysis in their publication.

Not only do Love and Zdon (2018) not adjust for non-atmospheric carbon, they make no distinction between dissolved inorganic carbon (DIC) and dissolved organic carbon (DOC) or address other complicating factors. Along these lines the International Atomic Energy Agency describes inorganic carbon and its effects, "*The two most significant geochemical processes are dilution of dissolved inorganic 14C (DI^{14}C) from dissolution of carbonates and formation of DIC from microbial degradation of old organic carbon within the aquifer. Thomas et al. (2001) found unadjusted ^{14}C model ages of DIC in groundwater from Nevada as much as 20 ka, that, when corrected on the basis of δ13C for carbonate rock recrystallization in this tectonically active aquifer, were in the range of 1–7 ka and similar to ^{14}C model ages of DOC in the aquifer.*"

Other typical chemical reactions, such as de-dolomitization (Plummer et al. 1990) or weathering of feldspars, cause chemical precipitation of calcium carbonate which leads to an isotopic fractionation influencing the concentrations of both ^{13}C and ^{14}C. Also, noted by IAEA (2013),

"*uptake of magnesium and/or calcium on exchangers, such as clay minerals, permits additional dissolution of carbonate minerals (calcite and/or dolomite), which dilutes the ^{14}C reservoir in groundwater. If not corrected for cation exchange, the 'adjusted' C model age is too old*." Love and Zdon make no such correction.

It is clear that calcium carbonate exists in rocks, fractures and groundwater in the study area. In the upgradient Clipper Mountains Mine, according to Minedata.org, the rock contains "small, thin lenses of limestone in the schist" and "limestone near the quartz diorite contains small, discontinuous bodies of friable, granite-rich tactite." Limestone is largely calcium carbonate rock in which ^{14}C is absent, and whose interaction with groundwater would artificially increase the apparent average groundwater travel time – "apparent age". There are also documented calcium mine prospects in the study area (e.g. Unnamed Prospect at 34° 48' 8" North , 115° 22' 25" West). Importantly, Zdon et al. (2018) in major ion analysis show 30% to 70% carbonate and bicarbonate species in water from many springs and wells in and around the study area. The serious omission of ^{14}C adjustment for non-atmospheric carbon in Love and Zdon (2018) is unexplained.

8. **The publication does not consider the effect of groundwater's interaction with organic carbon.**

Love and Zdon (2018) do not make clear distinctions between the impact of inorganic carbon and organic carbon, or many of the other complicating factors in ^{14}C analysis of groundwater. Although organic material is sparse in the present Mojave Desert, past climate supported abundant plant life which could be incorporated into the study site's subsurface. Discussing the impact of DOC on ^{14}C in groundwater, IAEA (2013) notes, "*Owing to the many geochemical interactions that can lower the 14C content of DIC and, if not quantified, limit the usefulness of radiocarbon dating of DIC in groundwater, the feasibility of radiocarbon dating of DOC in groundwater was investigated in a series of studies (Drimmie et al. 1991; Hendry and Wassenaar 2005; Long et al. 1992; Murphy et al. 1989; Murphy et al. 1989; Purdy et al. 1992; Tullborg and Gustafsson 1999; Wassenaar et al. 1989; Wassenaar et al. 1991).*"

IAEA (2013) continues, "*Many more geochemical and isotopic reactions occur in groundwater systems that are not considered by any of the traditional adjustment models. The most important of these pertain to the presence of organic carbon*", and "*old organic carbon is oxidized in the aquifer, which dilutes the ^{14}C reservoir, and if not accounted for, the adjusted age is too old*." IAEA concludes. "*There are two main sources of DOC in groundwater: (i) particulate organic carbon (POC) in the soil zone and unsaturated zone that can have radiocarbon ages of zero to at least several thousand years; and (ii) sedimentary organic matter (SOM) such as lignite, peat or other forms of POC buried with the aquifer sediment that typically is radiocarbon-'dead'. Both sources of DOC can dilute the ^{14}C content of DOC in an aquifer.*"

The net result of decades of research and study on the use of dissolved ^{14}C to assess average groundwater residence time is that adjustments must be made to any calculation of "apparent age" for the contribution of non-atmospheric carbon. These indispensable and fundamental adjustments are not included in Love and Zdon (2018). Love and Zdon acknowledge these possible complications but take no steps to correct their data.

9. **Concerning Love and Zdon's (2018) tritium and ^{14}C analyses of spring water, the authors fail to report duplicate or replicate analyses critical to establishing the limits of uncertainty in their findings.**

An essential element of almost all scientific studies is to evaluate the representativeness of sampling, the extent of uncertainties in results and conclusions (error bars), and to identify and quantify sensitivities in parameters used for calculation. Core to this are duplicate and replicate analyses, to determine the accuracy and precision of measurements. These standard methods were not reported by Love and Zdon, and goodness and validity of their "one shot" tritium and ^{14}C analyses remain in question.

10. **For their tritium and ^{14}C analyses of spring water, there is poor reporting of the sampling time of day, exact location of the sampling points, ambient air temperatures and other meteorological conditions, antecedent precipitation, and many other factors which could influence radiological measurements – these are not detailed in the manuscript.**

For an external reviewer to determine the representativeness of a sampling regimen, important information, such as ambient and preceding meteorological conditions, aids in interpretation. The authors briefly describe their sampling and analytical methodologies, but leave out important details on the actual field sampling, chain-of-custody protocols, exact location of sampling, and other important details. The exact location of sampling is important in this case as Bonanza Spring is actually two springs, Upper and Lower, and has a long surface flow above ground in between where ambient air temperatures could affect water temperatures and chemistry. The "one shot" nature of the sampling, coupled with a paucity of field information make further interpretation of seasonal or diurnal variation particularly difficult. The authors speculate on seasonal variability for Theresa Spring, but provide no overwhelming evidence of temporal variation. It should be noted that the study/sampling area receive scant to no rain in the many months preceding sampling.

This problem could be easily resolved. Attendant field information could be made available in either an Appendix or via a publicly accessible URL.

11. **The authors do not report additional sampling or results from local wells or springs to support their findings.**

Zdon et al. (2018) and other literature sources provide hydrochemical information from many wells and springs in the same study area as this publication, but Love and Zdon (2018) make very few, and in some instances, no comparisons with this available water quality information. For example, trace elements, measured by the authors previously for this study's five springs, are not reported or interpreted. Also, as mentioned above, the past information on the carbonate concentrations in the five springs sampled in the current publication are directly relevant to interpretation of ^{14}C, and many other parameters are germane. Past spring water temperatures, major ions, stable isotope similarities between spring water and precipitation all are applicable to current interpretation. The lack of complete and holistic treatment of available data can lead to

erroneous interpretations, if they are just based on the small body of field measurements presented in Love and Zdon (2018).

12. **Other indicators of average groundwater travel time to springs and recharge (e.g. chloride mass balance studies, chloroflourocarbons (CFCs), trace elements) are not fully investigated.**

There are many other ways to ascertain groundwater recharge volumes and average groundwater travel time to springs. These include many environmental tracers in soil and groundwater. Some of these proven methodologies include chloride mass balance techniques, measurement of chlorofluorocarbons (e.g. Freon CFC-12, SF6, Halon 1301, CFC-11, CDC-113) and sulfur hexafluoride (SF_6), trace element analysis, and other indicators. Multivariate analysis of these many parameters, including techniques like Principal Component Analysis (PCA) serial correlation, are often fundamental in interpretation.

Several authors stress the importance of using more than one approach for estimating recharge, and underscore the need to employ various techniques (Scanlon et al. 2002). Concerning the use of chloride balance in arid lands IAEA notes that, "*In semi-arid to arid regions, the distribution of recharge is usually quite heterogeneous, occurring mainly in the mountains or along mountain fronts or ephemeral streams during intermittent runoff events. Local measurement techniques can be useful in areas of focused recharge. In broad areas between mountain ranges or away from streams, recharge can be nearly zero or essentially zero, as can be determined by the accumulation of solute tracers within the unsaturated zone which occurs through continued conditions where evaporation removes the water but not the solutes. The chloride mass balance technique (Wood and Sanford 1995) is one method that has proven useful under such conditions.*"

Use of CFCs, SF_6, ^{85}Kr, and $^{3}H/^{3}He$ to date and track subsurface fluid flow has proven valuable in many studies (Busenberg and Plummer, 1992; Dunkle et al, 1993; Kreamer et al. 1988; Busenberg et al., 1993; Plummer et al., 1993; Ekwurzel et al., 1994; Reilly et al., 1994; Katz et al., 1995; Cook et al., 1995, 1996; Cook and Solomon, 1995, 1997; Szabo et al., 1996; Oster et al., 1996; Johnston et al., 1998; Plummer et al., 1998 a,b). The U.S. Geological Survey (2018) notes, "*The feasibility of using CFCs as tracers of recent recharge and indicators of groundwater age was first recognized in the 1970s (Thompson et al., 1974; Schultz et al., 1976; Randall and Schultz, 1976; Thompson, 1976; Hayes and Thompson, 1977; Randall et al., 1977; Thompson and Hayes, 1979; Schultz, 1979*)." Love and Zdon (2018) did not investigate these approaches.

The use of trace elements, rare earth element, and statistical analytical interpretation (including multivariate analysis) has also been used to great advantage to understand groundwater flow and recharge, including in the desert Southwest (Kreamer et al 1996; Johannessonn et al. 1997; Asante et al. 2018; Asante and Kreamer 2018; Asante and Kreamer 2015). Multivariate analysis was not included in the Love and Zdon (2018) publication.

13. **The authors make a refutable *a priori* presumption that Bonanza Spring is "in hydraulic communication with the basin-fill aquifer system surrounding the Clipper Mountains."**

Love and Zdon (2018) state that Bonanza Spring is sourced from regional groundwater distantly sourced and in direct connection with basin groundwater that, immediately below, is over one thousand feet lower than the elevation of the spring's issuance. The basis for this assertion, that Bonanza "*has previously been identified as being in hydraulic communication with the basin-fill aquifer system surrounding the Clipper Mountains [2]"* is a self-citation (Zdon et al 2018). This speculative assertion by the authors is unlikely and refutable based on field measurements, some made by the authors themselves. Love and Zdon (2018) rule out the possibility that recharge to the spring could be locally sourced from higher elevations in the Clipper Mountains themselves, and assert that any local recharge contribution to spring flow could only come from a small surface water catchment immediately above the spring.

The authors acknowledge that recharge to springs can come from areas outside surface water catchment basins but assume *a priori* that Bonanza Spring is sourced from deep subsurface basin water, derived from alluvial fill thousands of feet lower. The authors never explain the mechanism that raises water from depth. They assume that local recharge contribution to the spring could only come from its relatively small surface catchment, rather than the simpler, more likely explanation that the bulk of the recharge to Bonanza Spring flows from the fractured rocks and higher elevations in the Clipper Mountains immediately above the spring. The reasons for this assumption by Love and Zdon are articulated in Zdon et al. (2018) but are refutable.

The reasons given in Zdon et al (2018) include Bonanza Spring's temperature, discharge, major ion concentrations, trace metal concentrations, stable isotopes of hydrogen and oxygen, and one, single tritium value. These interpretations by the collective authors have other different explanations and conclusions.

Temperature

One reason the authors (Zdon et al 2018; Love and Zdon 2018) assume Bonanza spring water is sourced from deep basin fill water (and not the upgradient Clipper Mountains directly above the spring) is the water's temperature. Zdon et al. (2018) state that *"Bonanza Spring water temperature is indicative of waters that have been at depths of greater than 750 feet below the spring vent and risen to groundwater surface despite being in such a small catchment."* This is based on the author's reporting a temperature of 27.5 (or 81.5°F) for the water at Bonanza Spring in the manuscript, which they assume is geothermally influenced. This value, however, directly conflicts with a value of 14.2°C (57.6°F) reported by Andy Zdon and Associates (2016) for Bonanza Spring. This measured spring water temperature documented by Andy Zdon and Associates is less than the yearly average air temperature calculated by Zdon et al. (2018) at 21.0°C (69.8°F). Cool water documented at the spring by Andy Zdon and Associates (2016) is inconsistent with a deep source; rather this variation is indicative of a more local source, influenced by seasonal or diurnal variation.

Discharge

Another reason the authors (Zdon et al 2018; Love and Zdon 2018) give for the assumption of a deep, consistent groundwater source is their assertion of stability of spring discharge and flow. Zdon et al. (2018) reached the conclusion, *"Bonanza Spring flow has been consistent for more*

than 100 years despite multi-year wet periods and longer periods of drought (as indicated by the literature)." This is demonstrably untrue. Although Zdon et al (2018) give no numerical values for Bonanza Spring discharge in their publication, they do state, "*Thompson (1929) noted the presence of Bonanza Spring as a spring that yielded about 10 gallons per minute (similar to what it produces currently) that was piped to the community of Danby for use at the railroad."* In Andy Zdon and Associates (2016) the flow of Bonanza Spring is recorded as less than 1 gallon per minute (gpm) - significantly less than the 1929 value. On June 1, 2018, the flow of Bonanza Spring was also estimated at less than 1 gpm. This variability does not indicate "consistent" flow. Further, Rose (2017) reports an entirely different, higher flow value for Bonanza Spring. The reported flow at Bonanza Spring varies by at least an order of magnitude. Inconstant flow (particularly coupled with inconstant temperature readings) is not compatible with an assumption of a constant, sustainable deep groundwater source which is a conclusion of both Zdon et al. (2018) and Love and Zdon (2018). Additionally, the vegetation around Bonanza Spring has apparently changed in the past, sometimes dramatically, when viewing Google Earth imagery or from on the ground observations at the spring. This could be another indicator of inconstant discharge and flow at the spring, or alternatively periodic destruction of vegetation from localized flash flooding events.

Major Ions

Zdon et al. (2018) presents a Piper diagram of regional waters including selected springs, USGS wells, and Cadiz wells, showing the measured major ion aqueous chemistry of those sources. Trace element analysis of the waters was not reported. The authors state, *"Spring water at Bonanza Spring is a Na-HCO3 type (this is consistent with water at Lower Bonanza Spring as well). This is similar to most waters in the region except those waters at Hummingbird Spring (Ca-HCO3 type)."* Inspection of these data reveals that Bonanza Spring is dissimilar in its major ion chemistry from any well water sources, which primarily draw water from basin fill environments. This is particularly true with regard to major cations. The waters of Bonanza Spring are uniquely different than the surrounding regional well water with less than half the dissolved calcium of any well in the area and in some cases more than 4.5 times less. This difference is not supportive of the opinion put forth in Zdon et al. (2018) that Bonanza Spring issuance has a similar source to basin-fill well water and Cadiz wells. The discussion in Zdon et al. (2018) on this topic includes the statement *"The Bonanza Spring water is also similar in type to waters from the basin fill in the Fenner and Cadiz Valleys..."*.

Independent analysis of Bonanza Spring samples, collected February 2013 and March 2018 do show that the most abundant cation and anion are sodium and bicarbonate, respectively, similar to most basin fill well samples in the area. However, a sodium-bicarbonate chemistry is a generally common chemistry given the compositions of both local and regional source rocks, and therefore does not necessarily link the spring water to a regional source. Closer examination of the Bonanza Spring chemistry shows that this spring (and the associated Little Bonanza Spring) has a significantly higher sodium percentage than any of the other samples, as shown in the Piper diagram on Figure 4 in Zdon et al. (2018), and from other available well data surveyed among Fenner Valley and Cadiz Valley. The sulfate percentage for Bonanza Spring (approximately 30% of anions from Figure 4) is also higher than all nearby springs and wells.

Independent data from Bonanza Spring show the water to be undersaturated with respect

to calcite, while all other regional aquifer groundwater samples from Fenner and Cadiz Valley show saturation with this common mineral. This characteristic further supports the Bonanza Spring water reflecting a more localized source, such as the more calcite-poor rocks of the Clipper Mountains. The notably high percentages of sodium and sulfate in Bonanza Spring, along with its undersaturation with calcite, suggest a more localized source rather than a regional source, since this combination of major ion chemistry does not appear in wells of the flow regime proposed by the authors.

Trace Metals

The authors mention that trace metal analysis was carried out but no results are reported. Sample preparation was made by addition of nitric acid, but sample filtration and use of ultra pure nitric acid, which is necessary for trace analysis, is not mentioned. Trace element analysis has proven useful in source analysis of springs in Death Valley (Kreamer et al. 1996). Why the results of trace analysis were left out of the Zdon et al. (2018) publication is not explained.

Stable Isotopes

Zdon et al. (2018) presents stable isotopic data showing aqueous hydrogen and oxygen at Bonanza Spring is uniquely different than any other spring they evaluate regionally (their Figure 8). The isotopic signature is lighter (more negative) at Bonanza Spring (δD -82.1, δ_{18}O -10.25) which typically indicates water is sourced from a colder and/or higher elevation source. Surprisingly, the authors attribute this to a recharge source considerably distant (20 to 45 miles) to the north and northwest, the Providence and New York Mountains, and not to the surrounding Clipper Mountains where Bonanza is located. The authors do note, however, that previously a different assumption was made (including by one of the co-authors of Zdon et al. 2018): "*Of note is that Davisson and Rose (2000) assumed the local catchment for Bonanza Spring as being the whole of the Clipper Mountains …".* The Clipper Mountains surround the spring rising up several thousand feet higher to the north (with the spring downslope), are in close proximity and receive substantial rainfall, but the authors speculate that the spring water is sourced instead tens of miles away in more distant ranges. Without discussion or justification Zdon et al. (2018) state, "*isotopic signatures of precipitation collected in the Clipper Mountains are much higher than those at Bonanza Spring (Rose, 2017).*" The authors use this statement as part of a justification to exclude the adjacent, upgradient Clipper Mountains as potential recharge areas contributing to Bonanza Spring discharge. Inspection of the data from Rose (2017) does not support the authors' assertion.

The authors state that precipitation measurement in the Clipper Mountains are isotopically heavier and infer that this invalidates these surrounding mountains as a recharge source, supplying the Bonanza Spring. As noted in Zdon et al. (2018), these same stable isotopes of hydrogen and oxygen were measured in precipitation near Bonanza Spring from 2001 to 2005 by T.P. Rose (2017) (labeled "Clipper Mountains"). According to the latitude and longitude given, the sampling point was approximately 1000 ft north of the spring and about 300 ft higher in elevation. The "winter" (October to April) precipitation measured by Rose accounted for about 79% of the yearly rainfall summed over those years and ranged in isotopic values from δD -59.3 to δD -91.0, and from δ^{18}O -7.2 to δ^{18}O -12.6. When these values are weighted with the seasonal rainfall for each individual year, the weighted "winter", October to April, 6 month averages are δD -77.55, and δ^{18}O -10.75. These delta values are very close to the values recorded in nearby Bonanza Spring

discharge by Zdon et al. 2018 (δD -82.1, $\delta^{18}O$ -10.25), indicating that the spring could very well be in large part fed by local recharge in the Clipper Mountains.

Tritium

Tritium analysis reported in Love and Zdon (2018) for Bonanza Spring is apparently the same information reported information published on selected samples in Zdon et al. (2018). Zdon et al. states, "*Tritium (3H) analysis was conducted using the tritium enhanced enrichment (TEE) method to obtain lower reporting limits."* The authors also state that, "3*H was not detected at reporting limits of 0.56 TU in the water samples from Bonanza (and Lower Bonanza) and Hummingbird Springs*." The only laboratory for isotopic analysis mentioned in the manuscript is Isotech Laboratories for stable isotopic analysis. On the Isotech website, it is reported that they conduct liquid scintillation counting with or without electrolytic enrichment, having a detection limit of 1 Tritium Unit (TU), not 0.56 TU. Tritium electrolytic enrichment available at Isotech Laboratories, called "enhanced enrichment (TEE)" in the manuscript, allows lower reporting limits. Because the laboratory for tritium analysis was not specified in Zdon et al. (2018) and because of the discrepancy in detection limits, it is slightly unclear which laboratory was used for tritium analysis, nor are the number of duplicates, spiked samples, field or laboratory controls, or chain of custody procedures specified in the publication. Sampling dates, times, exact locations, antecedent rainfall are also not specified in the manuscript.

If one assumes the lack of detection of ^{3}H in the single, "one shot" sample taken Bonanza and Lower Bonanza Spring, without ^{3}He comparison (Zdon et al 2018; Love and Zdon 2018), is a valid value and does not have a post bomb pulse component, this would support the authors' contention that the average residence time for groundwater emerging at the springs is more than 65 years. However, these data are not incompatible with flow from fractured Tertiary volcanic rocks immediately upgradient of the surface water catchment for these springs, in the Clipper Mountains. Flow through fractured rock can include not only fracture flow, but matrix flow which has much longer average residence time. A combination of slow flow through the vadose zone, and consequent imbibition of water into the rock matrix during groundwater flow can extend average groundwater travel and residence time, and is consistent with the geological materials upgradient of the catchment area of the springs in question. Geologic data indicate that the recharge area for the spring is much larger than the topographic surface drainage area. Tritium ages exceeding 65 years are common in saturated fractured media, which contains a mixture of transmissive fractures and very narrow micro-fracture networks that can have very slow transport velocities.

14. The manuscript does not consider or analyze the possibility of fracture flow.

As stated above, a likely source for groundwater supply to springs on mountain slopes in arid regions is precipitation, infiltration and recharge in the mountains immediately above the springs and gravity fed flow downward to the spring. This would require subsurface fracture flow through the hard rocks above the spring. (Note that even in Love and Zdon's (2018) presumption that Bonanza Spring is not fed from mountain recharge immediately above, but fed from groundwater in the alluvial fill basin up to and over 1000 feet below, constrained fracture flow would likely be required or there would be many springs along the mountain front of the Clipper

Mountains). But fracture flow is not addressed by the authors, nor tectonic structural analysis of study area conducted.

^{14}C analysis can be mathematically analyzed in fracture flow systems, but was not presented by Love and Zdon. These analyses consider both fracture flow, and flow within the rock matrix for calculation of average groundwater residence time. Several authors have modeled radiocarbon fate and transport in fractured systems, correcting for diffusion in carbon-14 dating of groundwater. For simulation of fracture flow with matrix effects work has been done by Neretnieks (1980); Neretnieks (1981); and Tang et al. (1981), then for transport through a parallel set of fractures with transverse diffusion into the intervening rock matrix Sudicky and Frind (1982); and Sudicky and Frind (1984). Also, as noted by IAEA (2013), *"A more general 3-D analysis for fractured rock media was provided by Therrien and Sudicky (1996). Although Tang et al. (1981) recognized early on the application of their analytical solution to radiocarbon dating of groundwater in a thin aquifer bounded by thick confining beds, Sanford (1997) provided an elegant analytical derivation and solution for a parallel series of stagnant and flow zones, applicable either for porous or fractured rock media."*

15. The study lacks an associated quantitative groundwater transport model.

Many representations of groundwater flow in arid regions are supported by robust numerical modeling (Belcher et al. 2017). Love and Zdon (2018) present no mathematical modeling effort to support their conclusions.

Conclusions

The publication by Adam H. Love and Andy Zdon (2018), *"Use of Radiocarbon Ages to Narrow Groundwater Recharge Estimates in the Southeastern Mojave Desert, USA"* published in Hydrology MDPI, is an interesting study of groundwater recharge and selected spring radiocarbon analyses in the Mojave Desert, but suffers from critical weaknesses which undercut and invalidate some of the conclusions of the paper. The publication only makes general statements on the geological setting, location of faults, and the hydrogeologic environment, without complete referencing or justification. Annual recharge is compared from apparently dissimilar geographical areas with dissimilar data sets. The exact sample times, number of samples, measurement error bars, ambient air temperatures, antecedent rainfall, spring discharge and other important factors which could influence results are not documented in the publication. The number of duplicates, spiked samples, field or laboratory controls, or the chain of custody procedures are not specified.

Springs in the Mojave Desert are clearly a precious resource in the region and must be protected, and estimates of groundwater recharge are important factors in predicting their sustainability. Conceptual models which support recharge estimates and help populate water balance calculations must consider all alternative explanations. However, the omission of data and misinterpretation of hydrogeology based on selective information, lead the authors of this manuscript to dubiously ascribe groundwater recharge that sustains some of these springs to far-flung areas.

The questionable speculation in the Zdon et al. (2018) manuscript supported by Love and Zdon (2018), that recharge for springs like Bonanza occurs in the distant New York or Providence

Mountains, then moves tens of miles through basin alluvium and then resurges upward over a thousand feet through undefined mechanisms, is inconsistent and incompatible with the field evidence. In the Bonanza Spring example, they do not rigorously address the likelihood of nearby recharge in the Clipper Mountains immediately upgradient of the spring surface catchment area. These closer, sustainable recharge sources for Bonanza Spring and other springs in the Clipper Mountains are the most probable explanation of subsurface flow to springs and are consistent with published, investigatory results.

Importantly, Love and Zdon (2018) contains serious methodological omissions in interpretation of recharge and average groundwater residence time, which ultimately influence their interpretation for the hydrogeology of the study area.

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