PLOS Water

Contemporary and Relic Waters Strongly Decoupled in Arid Alpine Environments

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Abstract

Deciphering the dominant controls on interconnections between groundwater, surface water, and climate is critical to understanding water cycles in arid environments, yet persistent uncertainties in the fundamental hydrology of these systems remain. The growing demand for critical minerals such as lithium and associated water demands in these arid environments has amplified the urgency to address these uncertainties. We present an integrated hydrological analysis of the Dry Andes region utilizing a uniquely comprehensive set of tracer data (^{3}H, ^{18}O/^{2}H) for this type of environment, paired directly with physical hydrological observations. We find two strongly decoupled hydrological systems that interact only under specific hydrogeological conditions where preferential conduits have developed. The primary conditions in these conduits form are when laterally extensive fine-grained evaporite and/or lacustrine units or perennial flowing streams exist in connection with groundwater discharge sites. These conduits which efficiently capture and transport modern or "contemporary" water (weeks to years old) within the system control the interplay between modern hydroclimate variations and groundwater aquifers. Modern waters account for a small portion of basin budgets but are critical to sustaining surface waters due to the existence of these conduits. As a result, surface waters near basin floors are disproportionally sensitive to short-term climate and anthropogenic perturbations. This framework describes a new understanding of the dominant controls on natural water cycles intrinsic to these arid high-elevation systems which improves our ability to manage critical water resources.

1. Introduction

Water is a scarce but essential resource for human societies and ecosystems in Earth's driest regions (Gleeson et al., 2020). Due to the nature of water cycles and hydrogeological systems in these environments, groundwater is an especially critical freshwater resource for both humans and ecosystems (Bierkens & Wada, 2019; Immerzeel et al., 2020). This is particularly true of arid, high-elevation regions where steep gradients in topography and climate develop deep water tables and long transit times leading to the increased importance of multi-decadal groundwater storage in water budgets (Haitjema and Mitchell-Bruker 2005; Gleeson et al. 2011). In many of these regions direct (i.e. water extraction) and indirect (i.e. global climate change) anthropogenic impacts are increasing and threatening the quantity and quality of both groundwater and surface water (Wang et al., 2018; Zipper et al., 2020). The resulting relative and in some cases absolute scarcity can increase social tension among riparian parties including communities, governmental authorities, and industry users (Mehran et al., 2017; Mehran et al., 2015; AghaKouchak et al., 2015). In addition, responses to natural perturbations (i.e. droughts) are often not well understood in these environments (Gleeson et al., 2012; Ashraf et al., 2021) making sustainable and equitable water management challenging. In arid, remote regions, limited precipitation and the importance of basin-scale groundwater flow systems together with a lack of long-term, high-quality instrumental records make responsibly allocating water resources challenging (Somers & McKenzie, 2020; Moran et al., 2022). These conditions also mean that surface water is scarce and groundwater discharge sourced from relic water (100s to 1000s of years old) often underpins the hydrological cycle, acting as critical buffers to hydrological systems from large inter-annual fluctuations (Fan et al., 2013; Bierkens & Wada, 2019; Mcknight et al., 2023). Fundamental questions remain to be answered about the hydrological functioning of these systems perpetuating persistent uncertainties around water sources and transport in these environments. This raises important questions about water scarcity issues in the face of increasing water resource development and the likely consequences of global climate change.

The Dry Andes of South America, marked by one of Earth's highest and broadest plateaus on the margin of the driest nonpolar desert, is one of the most extreme places on the planet (Hartley & Chong, 2002; Rech et al., 2019). This region is often referred to as the "Lithium Triangle" as it holds a majority of the world's reserves of the battery component metal in the form of Li-bearing brines under its salt flats or "Salares" (Munk et al., 2016). The exploitation of this resource has rapidly expanded in the push to decarbonize the global economy, highlighting concerns over the sustainability of intensive groundwater extraction (Gajardo & Redón, 2019; Gutiérrez et al., 2018; Sonter et al., 2020), equitable water management, and the tradeoffs of water allocation and water management decisions (Crawford et al., 2021; Diaz Paz, et al. 2023). This landscape is composed of many adjoining endorheic basins with hyper-arid to arid conditions (<50 mm of precipitation/year) on their basin floors where groundwater recharge occurs primarily at the highest elevations near watershed divides (Houston, 2002, 2007, 2009; Boutt et al., 2021). Thick vadose zones (>100 m) across nearly the entire landscape and intense solar insolation create conditions where actual groundwater recharge and evaporation rates are difficult to quantify and sources of water difficult to trace (Rissmann et al. 2015; Scheihing et al. 2018; Viguier et al. 2020). Where water tables reach the surface near basin floors, large evaporite deposits, and persistent saline water bodies have formed (Corenthal et al., 2016; Munk et al., 2021). Persistent surface water features (saline/brackish lagoons, vegetated wetlands, and perennial and intermittent streams) and their interconnections are controlled by a combination of lithology, topography, and structure, yet deciphering the specific controls on connectivity between these features, the modern hydroclimate and regional groundwater remains elusive (Munk et al., 2021). In addition, paleoclimate records indicate that at least four major pluvial periods have occurred over the past

~100 ka, increasing precipitation by a factor of 2-3 times modern rates (Gayo et al. 2012; Placzek et al. 2013). These wet periods dramatically altered the hydrological and ecological conditions (Pfeiffer et al., 2018), and the effects are likely still evident in the modern hydrological system in the form of transient groundwater storage changes within the deep and extensive regional aquifers responding over 100-10,000-year time scales (Moran et. al., 2019). These conditions have accentuated distinctions between the regional groundwater system and surface waters, making it an ideal testing ground to address these persistent questions in arid hydrology.

The challenge of hydrological budget closure in these environments has been well documented worldwide and highlights the uncertainties that remain to be addressed (van Beek et al. 2011; Liu et al., 2020; Boutt et al., 2021). Imbalances where calculated inflows are smaller than outflows are observed in nearly every arid region worldwide (Belcher et al., 2009; Ge et al., 2016; Wood et al., 2015; Kröpelin et al., 2008; Wheater et al., 2007), including in the massive Salar de Atacama basin on the western edge of the Andean plateau (Corenthal et al., 2016; Munk et al., 2018). Major unresolved questions include groundwater transit time characteristics, surface water sources and residence times, and interconnectivity between groundwater, surface hydrology, and climate (Favreau et al., 2009; Gleeson et al., 2011; Walvoord et al., 2002). Recent work in the basins of the Dry Andes has shown that true hydrological catchments often cross topography and include substantial inputs from relic groundwater sourced from long-flow paths and/or groundwater storage head-decay (Jordan et al., 2015; Corenthal et al., 2016; Moran et al., 2019). Therefore, modern water budgets do not come close to closure at steady-state with modern climate inputs (Boutt et al., 2021). Though the inputs from modern precipitation are relatively small, large infrequent precipitation events play an important role in sustaining salar floor water bodies in these environments through preferential recharge and areas of restricted vertical infiltration (Boutt et al., 2016; Munk et al., 2021). Other work shows the critical role that evaporite stratigraphy has on the expression of surface water features and their connection to modern precipitation inputs and groundwater discharge (Mcknight et al., 2021; Munk et al., 2021). Recent work by Moran et al., (2022) establishes that modern water accounts for a relatively small portion of water budgets but is critical to sustaining surface water bodies and wetlands, as a result, these arid systems are uniquely sensitive to climate (drought) and anthropogenic perturbations on short time scales. Much of this work has been focused on the western edge of the Dry Andes, while other work has explored these issues in basins further east (Godfrey et al., 2013; Gamboa et al., 2019; Frau et al., 2021) but a mechanistic framework to explain our observations region-wide has not been established.

Substantial gaps remain in our understanding of the time scales and spatial definition of primary interconnections that constitute water cycles in these environments, specifically the controls on groundwater, surface water, and modern climate interactions (Masbruch et al., 2016). We investigate these remaining uncertainties using a large dataset of tritium activity in water paired with stable oxygen and hydrogen isotope signatures, and hydrophysical and hydrogeochemical field observations. Utilizing a new approach to integrating and interpreting the well-established systematics of these tracers we present a process-based conceptual framework that describes two dominant archetypes of flow systems in these environments and the controls on connections between their constituent parts. This new framework provides critical insight into expected responses to perturbations (natural and anthropogenic) in the Dry Andes and describes intrinsic hydrological processes for arid alpine systems worldwide.

2. Methods

2.1. Water sample analysis

To assess spatially explicit water residence times within these hydrological systems we utilize stable ($\delta^{18}O$ & $\delta^{2}H$) and radiogenic (^{3}H) isotopic tracer measurements in 142 water samples collected across the Dry Andes. These include surface and groundwaters collected during numerous field campaigns between October 2011 and March 2021 in Salar de Atacama (data first presented in Moran et al. 2022) and from 2019 and 2020 on the Puna Plateau. Samples were collected with a consistent, standardized procedure and in-situ measurements of temperature, specific conductance, and pH were made at each sampling location during collection. Tritium activity in water samples was measured at the Dissolved and Noble Gas Laboratory, University of Utah. Samples were collected in 1 L HDPE bottles with minimal headspace. In the lab, 0.5 L aliquots were distilled to remove dissolved solids. These water samples were then degassed in stainless steel flasks until <0.01% of dissolved gas remained and sealed to ingrow helium. ^{3}H concentrations were measured by helium ingrowth (Clarke et al., 1976); 6–12 weeks is typically adequate to ingrow sufficient ^{3}He from the decay of ^{3}H ($t^{1/2}$ = 12.32 yr.; Lucas & Unterweger, 2000) for analysis. ^{3}He concentrations were then measured on a MAP215-50 magnetic sector mass spectrometer using an electron multiplier to measure low abundance ^{3}He, which was directly correlated with the amount of ^{3}H decayed. Data are reported in tritium units (TU) on the date of sampling, where one TU is equivalent to one tritium atom per 10^{18} hydrogen atoms ($^{3}H/H*10^{18}$) (Kendall & Caldwell, 1998). Several duplicate analyses of the same sample were conducted to confirm important values, and the reproducibility for these samples is of the same order as the precision of the measurement. The analytical error associated with each sample is reported along with the full dataset in the supplemental material.

Water samples were analyzed for δ^2H and $\delta^{18}O$ using wave-length scanned cavity ring-down spectroscopy (Picarro L-1102i); samples were vaporized at 120°C (150°C for higher salt content waters) in the Stable Isotope Laboratory at the University of Alaska Anchorage. International reference standards (IAEA, Vienna, Austria) were used to calibrate the instrument to the VSMOW-VSLAP scale and working standards (USGS45: δ^2H = -10.3‰, $\delta^{18}O$ = -2.24‰ and USGS46: δ^2H = -235.8‰, $\delta^{18}O$ = -29.8‰) were used with each analytical run to correct for instrumental drift. Long-term mean and standard deviation records of a purified water laboratory internal QA/QC standard (δ^2H = -149.80‰, $\delta^{18}O$ = -19.68‰) yield an instrumental precision of 0.93‰ for δ^2H and 0.08‰ for $\delta^{18}O$. The full dataset is provided in the supplemental material.

2.2. Tritium Age Tracing Approach

The hydrological system in this region is complex and heterogeneous on all scales, and large gaps exist in hydrogeological and hydroclimatological data coverage, especially above the basin floors at the higher elevation plateaus and mountain peaks. Very deep water tables (100s of meters) and rugged terrain make direct observation of the groundwater system impractical across much of the landscape. Long-term high-quality terrestrial monitoring of climatology and streamflow flow is also sparse. Therefore, highly parameterized models and tracers that require additional assumptions are not the most effective tools to assess water flux rates or transit times in this environment. Tracing signatures recorded in the water molecule itself most reliably integrate small-scale variability with large-scale processes and can be captured with individual water samples (Birkel et al., 2015; Buttle, 1994). Stable isotope ratios ($\delta^{18}O$, δ^2H) and radioisotopes (^3H) in water offer many unique advantages in these systems (Cook & Bohlke, 2000; Kendall & Caldwell, 1998). Besides the well-understood influence (fractionation) from low and high-temperature water-rock interaction and evaporation, signatures of $\delta^{18}O$ & δ^2H in groundwater recharge remain unchanged from infiltration until re-emergence from the ground (Beria et al., 2018; Clark & Fritz, 1997; Kendall & McDonnell, 1998). Geothermal water-rock interactions cause a pronounced "oxygen shift" in $\delta^{18}O$ & $\delta^{2}H$ cross-plot space and a trend line with a slope approaching zero (Panichi and Gonfiantini, 1977). Evaporation causes the signature of a water parcel to increase in deuterium-excess and deviate from the GMWL along a steep, positive linear slope. Deuterium excess (d-excess) is the deviation from the global meteoric water line defined as d-excess = δ2H-8*δ18O (Dansgaard, 1964). These fractionation processes both act to progressively increase the d-excess value in a sample or group of samples but can be reliably differentiated from each other through comparison of the slopes of the apparent local evaporation line trends (LEL) defining groups of samples (Rissmann et al., 2015, Moran et al., 2019).

Radioisotope signatures (^{3}H) are also conservative but follow a predictable decay (half-life of 12.32 years) during transit. To effectively utilize this tracer, we must constrain the ^{3}H content of modern precipitation, this defines the signature of direct modern inputs to the hydrologic system. Widespread atmospheric nuclear bomb testing in the late 1950s and early '60s created a large and unmistakable peak in global atmospheric ^{3}H concentrations which increased activities in precipitation globally by greater than an order of magnitude (Cartwright et al., 2017). We assume the modern value in precipitation described above is representative of average precipitation from about 2000 to the present since the bomb peak signature is no longer resolvable after that date in the Southern Hemisphere (Rooyen et al., 2021). This modern signature is also representative of precipitation before the mid-1950s since the bomb peak had not yet occurred (Houston, 2007; Jasechko, 2016). This period of high ^{3}H activity in precipitation and therefore in recharge during that time allows for reliable differentiation between water recharged post-1955 and that before 1955 because if this strong signature is not observed in water (very low ^3H activity), very little if any of that water is composed of recharge after the bomb peak. Since the ^3H activity in any given sample is a bulk sample representing mixtures of unknown sources and respective amounts, we must also be careful not to over-interpret specific ^3H activities in individual samples without proper physical constraints. Therefore, to ensure a reliable and conservative interpretation of this broad dataset we determine a simple"percent modern water" ratio in each sample as the ratio of modern precipitation input activity to the activity measured in the sample. Using the ^3H activity in modern precipitation, we determine the proportion of modern or "contemporary" and pre-modern or "relic" water components in the sample according to the formula: $Percent\ Modern\ Water\ in\ Sample = \frac{3_H \text{ Activity in Sample}}{3_H \text{ Activity in Modern Precipitation}}$.

The ^3H activities in modern precipitation over the region, also presented by Boutt et al. (2016) and Moran et al. (2019), are determined to be 3.17 ± 0.53 TU from 5 amount-weighted rain and snow samples collected between 2013 and 2014 in the western part of the region (Chile); and determined to be 4.54 ± 1.34 TU from 3 amount-weighted rain and snow samples collected between 2018 and 2019 in the eastern region (Argentine Puna) (**Figure 1**). These values are within the range reported by others in the region (Cortecci et al., 2005; Grosjean et al., 1995; Herrera et al., 2016; Houston, 2002, 2007). Consistent with other studies in this region and

Figure 1. Surface and groundwaters in the Dry Andes analyzed for ^3H, $\delta^{18}O$, and δ^2H in this study (n=142). Pie charts represent percent modern content, colored outlines show general water type groupings and colored dots show sample sites and their physical water type. The black crosses are precipitation sample sites used in ^3H analysis. Black outlines show internally drained basins, blue solid lines are perennial streams, and blue dashed lines are intermittent streams. Important features (salars, mountains, rivers) are noted along with their elevations. (a) Map of the Salar de Atacama basin and the the northern Puna region to the east, where pie charts represent average content of inflow zones and surface waters in order to display all data (see Moran et al., 2022). (b) Map of the southern Puna where each pie chart represents one sample. (c) A schematic cross-section of salar-basin floor hydrogeological systems describing the physical water classifications.

across the southern hemisphere, the 3H activities in precipitation have now stabilized to reflect modern production and so this value accurately reflects (within uncertainty) any recharge that occurred within the last few decades (Basaldúa et al., 2022). Water recharged in 1955 before the bomb peak with a ^{3}H activity of 3.17 ± 0.53 TU would have between 0.07 and 0.10 TU in June 2020, or about 2-3% of the modern precipitation input; water with a ^{3}H activity of 4.54 ± 1.34 TU would have between 0.08 and 0.15 TU in June 2020, also about 2-3% of the modern precipitation input (Stewart et al., 2017). Due to the small but non-negligible analytical uncertainty (~0.02-0.07 TU at low activities), samples with these very small activities are herein considered to be effectively ^{3}H-dead waters or indistinguishable from zero. Waters registering such low activities are assumed to contain negligible volumes of water recharged post-bomb peak (1955), as even small amounts of water with these higher activities would heavily skew resultant activities in these ^{3}H-dead samples to appear to contain high levels of modern water. Since most of the waters measured in this environment contain effectively no ^{3}H, our objective is not to directly estimate discrete mean residence time distributions but instead to describe the relative proportions of ^{3}H-dead to recent recharge (<65 years old) in these waters (Cartwright et al., 2017). This relative water age value allows for the reliable interpretation of connections to modern precipitation inputs, as well as the lack thereof.

3. Results & Discussion

3.1. Physical water-type groupings

Sampled waters were grouped into seven physical water types. These distinctions are based on extensive knowledge of the regional hydrogeology gathered during more than ten field campaigns in Salar de Atacama on the Puna Plateau, previously published works, and scrutiny of geochemical signatures (Munk et al., 2021). A schematic cross-section describing these water groupings is shown in **Figure 1c**. Nucleus Brines are groundwaters from the core of the halite-dominated brine aquifer, sampled at shallow depths <13 meters below ground level (mbgl), Marginal Brines are groundwaters from the margins of the brine aquifer, sampled at the water table (<2 mbgl). Transitional Pools are highly saline, shallow pools that form at the margin of the halite crust that grow and shrink rapidly primarily in response to precipitation events. These are often adjacent to (~1-2km away) but distinct from the Lagoons (saline lakes). Many of these Lagoon water bodies also grow and shrink seasonally and after precipitation events but are perennially extant. They are also quite shallow (<1m) but much less saline than the Transitional Pools. In Salar de Atacama we were able to access groundwater wells, whereas, in the Puna region, these brine bodies are present in the vicinity of the salars indicated in **Figure 1**, there are currently very few accessible groundwater wells that could be sampled. In addition, on the high-elevation plateau, there are no true Transitional Pools as there are in Salar de Atacama. The waters classified as "inflows" are separated into three groups; Streams are perennially and intermittently flowing fresh surface waters, Inflow Groundwaters (Inflow Gw) are fresh to brackish waters sampled from wells and from persistent springs that we define as groundwater outcrops, and Transition Zone Groundwaters are brackish to saline waters sampled at the water table within the transition zone between the inflow water bodies and the brines.

3.2. Water transit time partitioning

We assess tritium (^3H) activities in 142 samples representing all major physical water types covering a large swath of the Dry Andes. In this environment where modern water and pre-modern water appear to be strongly decoupled in terms of where they exist on the landscape, determining the relative proportion of each in a sample is a highly effective way to define the relative transit age and therefore sources of water to different water bodies. A detailed summary of this analysis and the raw and derived data presented in the results is provided in the supplemental material (**Table S1**).

The geographical distribution of relative water age across the region highlights important results concerning surface and groundwater on basin floors and inflow waters to the basins (**Figure 1**). First, in the Salar de Atacama basin, all basin inflow waters (streams, springs, and groundwaters) are principally composed of pre-modern water (ie. 0-5% modern; Moran et al., 2022). Relative modern water components in inflow waters are consistent across several years, and in different seasons of site repeat sampling, larger river waters show higher seasonal and yearly variability due to their direct and more rapid interaction with modern precipitation inputs (**Figure S1**). Waters at the basin floor, in saline surface waters, and brine groundwaters also show consistently larger components of modern water. In addition, two high-elevation (4100 masl) fresh-to-brackish lakes near the watershed divide contain ~30% modern water, similar to the basin floor surface waters. These results demonstrate the strong distinctions that exist between overall inputs to these basin water budgets and the near-surface waters at the basin floors, especially since recent inflow waters are critical to sustaining these surface waters. These general observations also describe the higher-elevation plateau endorheic basins to the east. Inflow groundwaters, which here consist of spring complexes that are effectively “outcrops” of and discharge from the groundwater system to the surface, have very low modern water content (0-2%). Basin floor waters on the plateau (saline surface waters) also have substantially higher modern water content than the nearby groundwaters.

There are a few important distinctions between water age distributions on the plateau and at the lower elevation of Salar de Atacama. One is that many of these higher elevation basin floor waters (brackish-brine lagoons) have modern water contents of >50%, some of the highest values observed in the region. Two exceptions to this are the lagoons at Salar del Hombre Muerto and Salar del Carachi Pampa. Another key distinction is the consistently high modern water content in streams on the Puna plateau, particularly in the large perennial rivers of Rio Los Patos and Rio Punilla which average ~22% modern, and streams in the northern Puna region which average 46%. The vegetated wetland complexes above the basin floors, common to the high elevations of this region, have consistently higher modern water content than nearby groundwaters and streams. The commonalities in transit age across the whole region and the distinctions between low-elevation and high-elevation systems are valuable in deciphering the dominant controls on water transport and interconnectivity.

Examining the distribution of these data across the region allows for further examination of common dominant controlling mechanisms across the many individual basin systems. Kruskal-Wallis tests were conducted on data groupings in each panel of **Figure 2** showing that the groupings chosen are statistically unique (P-value <0.001) except when grouped by Sample Elevation Above Basin Floor (P-value=0.09), detailed results of these tests are provided in the supplemental material (**Table S2**). **Figure 2a** shows the distribution of the water age ratios grouped by water type, a definition based on the position between recharge and discharge zone, and salinity (described schematically in **Figure 1c)**. Inflow groundwaters average <5% modern water content, similar to stream waters yet stream data skew towards very low modern water values. Importantly several stream samples show higher modern water content of between 15% and 60%, these samples are of the large perennial streams mentioned above. Saline surface

Figure 2. Statistical distributions of ^{3}H-derived percent modern water results. Grey boxes inside the polygons show the interquartile range; red dots are the median and polygons represent the frequency distribution of the data (black dots). Data grouped by (a) physical water type, where colors of polygons correspond to physical water type dots in Figure 1; (b) by elevation of sample; (c) by specific conductance of sample, where colors of polygons show fresh (blue) to brine (pink) waters; and (d) by sample elevation above the basin floor (basin floor elevations indicated in Figure 1).

waters near the basin floors average 20-30% modern while the lagoons (perennial saline lakes) in particular show a large range in values but also skew towards the lower values. The brine groundwater bodies within the salar evaporites and the brackish groundwaters in the transition zone between fresh inflow and brine (TZ Gw) show two primary groupings of relative age. One of very low modern water content and the other close to 25% modern, this younger water component is most clearly shown in the marginal brine waters but is also present in the other two water bodies. Grouped by sample elevation we observe that on average, more modern water exists near the surface above 3000 masl but also that waters with very small modern components are present at all elevations (**Figure 2b**). Importantly the lowest elevations show clusters of samples with modern content similar to the highest elevations. These characteristics can also be seen when grouped by elevation above the basin floor (**Figure 2d**), where samples collected highest above the basin floor average higher modern water content. Most samples were collected very near basin floors, which reflects the concentration of near-surface water and its absence elsewhere, and shows a wide distribution of water ages. Grouped by specific conductivity (a proxy for salinity) we see that the freshest water is predominately relic but also that there are many freshwaters with much higher modern content. Average water age generally increases with salinity but the saltiest waters (brines) also contain a range of ages from <3% modern to nearly 95% modern. These results provide many important insights into where pre-modern and modern water persist in this system, their sources, and how they interact.

These results highlight the strong influence of hydroclimate, topography, and hydrogeology on transit time and interaction with modern inputs. In this arid environment, modern water is not spatially common but differences in climate across the region have important influences on surface hydrology. Region-wide, groundwaters, and most streams have very small modern components reflecting the long transit times from their source waters. But the large perennially flowing streams that exist at the colder and slightly wetter climate at these higher elevations, have a substantial portion of their flow composed of modern water. Vegetated wetland complexes or vegas can be extensive and often form near basin floors at the periphery of salars, high elevation wetlands or peatlands referred to in this region as bofedales also occur sporadically on the Puna above 3800 masl around groundwater outcrops or springs (Marconi et al., 2022). Although these two systems are characterized by different ecology, they display similar hydrological characteristics in that they are strongly influenced by recent precipitation inputs; we refer to all these systems together herein as vegas. The consistently strong signature in surface water bodies at basin floors exists across the region but the climate at higher elevations appears to create conditions where less than half of their water is composed of regional groundwater. Specific hydrogeological and ecological conditions that allow water tables to persist close to the surface (<5m) are a shared feature of all of the water bodies mentioned above. We argue that these conditions strongly control how modern water enters and moves through this system since most precipitation either evaporates in the thick vadose zones or slowly infiltrates towards the groundwater table below.

3.3. Hydrogeological mechanisms controlling source partitioning

We further investigate mechanisms controlling the partitioning of waters in this environment using d-excess signatures paired with percent modern water content (**Figure 3a**).

Figure 3. (a) Processes controlling physical water distinctions and interactions based on ^{3}H, δ^{18}O, and δ^2H signatures. Circles are proportional to the average magnitude of discharge at each stream site, SdA streams plot within the black dashed box. The grey vertical bar is the Global Meteoric Water Line (GMWL), and the blue box at the top represents the approximate range of meteoric input waters in the region (based on Moran et al., 2019 data). Arrows depict the influence of important hydrological processes and interactions. (b) Shows these data plotted in δ^{18}O-δ^2H space relative to the LMWL (Rissmann et al. 2015) and evaporation trends of basin floor waters in Salar de Atacama and on the higher elevation Puna plateau.

The d-excess provides a reliable measure of the amount of evaporation a sampled water has undergone, placing important constraints on waters that have had little or no atmospheric interaction from that which has undergone substantial evaporation (waters with increasing negative values). We group all stream samples by average streamflow at the sample site to highlight the relative size of each stream and therefore the relative volume of modern water represented by the ratio (data provided in **Tables S3**).

The inflow groundwaters plot close to the Global Meteoric Water Line (GMWL) as they are composed of infiltration that interacted minimally with the atmosphere before becoming groundwater, and their modern water content indicates nearly all of their volume is composed of relic water. The streams also plot along the GMWL and most have similar mean age profiles to the inflow groundwaters while some have many times the amount of modern water in them. This likely reflects the fact that inflow groundwater is relic regional groundwater and provides the baseflow to streams in this environment. But some of the streams, particularly the large streams on the Puna plateau are composed of a large amount of recent meteoric water that does not show a strong evaporation signature. The vegas also have a similar signature to these large Puna streams. The other major water groupings display a few distinctive characteristics. Marginal brines and transitional pools plot in a similar position likely reflecting similar sources and interactions between these water bodies. The nucleus brine waters show less evaporation, indicating a distinct combination of sources but skew more towards the regional groundwaters than the marginal water bodies. The lagoon waters tend to fall between the nucleus brines and the marginal/transitional pool waters with a large range of modern components and are less evaporated than the other saline surface waters suggesting they are more closely connected to the inflow waters than other basin floor water bodies.

These results reiterate that most inflow is relic water but also show that large streams particularly on the higher elevation plateau can transport substantial volumes of modern water relatively quickly through these systems. These streams along with the vegetated wetland complexes appear to be the primary hydrological conditions under which fresh modern water is captured and transported within human time scales. The fact that the saline basin floor surface water bodies also contain substantial amounts of modern water and that these four water types (streams, vegas, lagoons, and transitional pools) are the only places where water tables exist near the surface in this environment demonstrates this is the primary pathway of modern hydroclimate connection to the larger hydrological cycle. We present the two principle archetypal frameworks that describe these climate-surface water-groundwater interactions in this system.

We define the archetypal flow systems in this environment which describe and integrate our observations of transit time and flow paths in the Dry Andes (**Figure 4**). The Ephemeral Surface Flow System is the more common type and is defined by steep topography and structural and hydrogeological conditions that promote infiltration and drop water tables well below the surface (**Figure 4a**). Intermittent streams do often form downgradient of spring complexes in these systems (for example in the southern and eastern parts of the Salar de Atacama and to the east of Salar de Carchi Pampa) but generally flow for short distances downgradient of spring discharge and/or intermittently during large rain events. These streams are fed almost entirely by regional groundwater and contain very small or transitory proportions of modern water. Perched

Figure 4. Conceptual model of archetypal flow regimes in the Dry Andes. Size of the ^3H symbol and pie charts show relative modern water content in major water bodies and along flow paths. Arrows show general flow paths from precipitation-to-recharge-to-groundwater colored by relative modern water content from green-to-blue with predicted presence of very old "Fossil" water in teal. Straight arrows show general modern preciptiation inputs and regional groundwaters, and zig-zag arrows represent water fluxes to and from the surface scaled by relative flux magnitude. General water body types and geology are colored and textured. (a) Represents the archetype dominated by ephemeral streams and regional groundwater fluxes, (b) represents the archetype dominated by perennial streams that act as efficient conduits for modern water.

aquifers do form, in the vicinity of vegetated wetlands at elevation and particularly near the basin floors where the abundance of fine-grained deposits and evaporite precipitation prevents infiltration directly to the deeper water table, these perched aquifers allow moderately aged (years-decades) waters to feed basin floors and importantly create persistent shallow water tables that allow recent rainfall to mix with the saturated zone near the surface. We argue that these conditions are what maintain the vegetated wetlands and lagoons at elevation and allow them to capture and transmit modern precipitation. The dimensions and depth of the water table constitute the dominant control on surface water formation and modern hydroclimate connections in these systems.

The other primary archetype in this environment is a perennial surface flow system which is defined primarily by relatively large perennial streams that are also fed predominantly by regional groundwater (baseflow) but maintain consistent flow in all seasons and over large distances (30-100 km) (**Figure 4b**). Smaller topographic gradients and/or hydrological conditions that allow these streams to form create unique hydrological systems that capture more modern rainfall and move it efficiently toward basin floors. The presence of this perennial surface water itself, like shallow water tables, creates conduits that capture modern rainfall and runoff before it evaporates or begins infiltrating through the thick vadose zones. The presence of these conduits is the primary control on connections between the modern hydroclimate and surface waters in these systems. Across most of this arid landscape, when rainfall does occur, much of it rapidly evaporates at the surface and as it makes its way toward the water table, the 0.01-5% of that water that reaches the water table as groundwater recharge (now and during past climate conditions) sustains the regional groundwater system (Scanlon et al., 2006; Boutt et al., 2021). These mechanisms are also responsible for maintaining the saline water bodies near the basin floors and on the salars. Groundwater discharge is focused near the basin floor where the topography flattens and fine-grained units have accumulated, creating permeability contrasts that both force water to the surface and restrict infiltration. These conditions create persistent shallow water tables that in turn allow modern waters to efficiently mix with relic groundwaters.

3.4. Implications for society and ecosystems

The extreme decoupling between basin-to-regional scale groundwaters, which constitute the primary inflow to these endorheic basins, and local, modern precipitation inputs has major implications for the management and future sustainability of water systems in the Dry Andes and other arid mountain environments. Our results show that modern precipitation comprises only a small portion of modern hydrological budgets in these environments but is critical to maintaining surface water bodies and vegetation due to a unique but intrinsic set of hydrogeological conditions. The Sixth Assessment Report from the Intergovernmental Panel on Climate Change (IPCC) reports a high confidence projection of increased drought extent and severity in the area (IPCC 2022), which presents threats to the delicate balance of these environments and hydrological systems. Prolonged droughts have been shown to cause major and rapid changes to surface water systems in this region over the last few decades (Frau et al., 2021; Moran et al., 2022). It is critical to understand the current interplay between pre-modern and modern waters to define how human use and changing temperature and precipitation in the region could alter the integrity of these systems. We define the modern and relic water systems in this region for the first time within a framework that reconciles the prevalence of relic groundwater in these environments with the observations of rapid changes to surface waters in response to natural and anthropogenic perturbations.

A major focus in these watersheds is the interplay between competing use of water by a variety of riparian stakeholders and the policies and use rights conferred by water managers. Demands for water resources exist from current metal mines and the massive expansion of exploration for lithium among other commodities, indigenous communities, agriculture, as well as the environmental flows required to maintain existing ecosystem services and functions. There is a lack of watershed-specific knowledge of water resources in the region, meaning that water management is naïve to the pre-modern and modern water balance dynamics. If left unfilled, this knowledge gap could lead to use patterns that threaten the viability of these hydrological systems. Moreover, there is limited regional coordination and oversight related to water management in the area which exacerbates the sustainable water management challenge.

The work presented in this study provides an important starting point for filling the technical knowledge gap surrounding water balances in these environments. The present work develops a general framework for users of water in these basins and presents the opportunity to revise water budgets within scientifically justifiable frameworks that do not require steady-state closure of basin budgets to allocate water resources more responsibly. In addition, this new understanding can greatly improve our ability to attribute current and future impacts from anthropogenic activities in fragile wetlands systems and predict and respond more effectively to the accelerating impacts of human-induced climate change. This analysis and the new hydrological conceptual models we present will improve our ability to reduce the risk of depleting vulnerable freshwater resources and damaging ecosystems reliant on the delicate balance between modern and pre-modern water inputs and plan human development that avoids the most damaging potential impacts on water quantity and quality. For instance, a particular focus with high potential benefit would be to prioritize the protection of these modern water conduits from disruption or obstruction and/or the removal of existing obstructions. An understanding of connections to modern and past climates will also improve our ability to plan for the effects of future climate changes in these environments.

Data Availability

All data necessary to interpret, replicate, and build upon the findings reported in this article are provided as tables in the supplemental information.

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Acknowledgments

The authors would like to thank Felicity Arengo, Patricia Marconi, and Diego Frau for inviting us to join multiple sampling campaigns that were pivotal to collecting the data that initiated this study on the Puna. We also want to thank Ricki Sheldon, the Consejo de Pueblos Atacameños, Asociación de Agricultores Zapar, Asociación de Agricultores Soncor, Comunidad de Toconao, Comunidad de Catarpe, Comunidad de Coyo, Familia Bautista de Tambillo, and CONAF for graciously volunteering to access and conduct sampling that was pivotal to this study.

Author Contributions

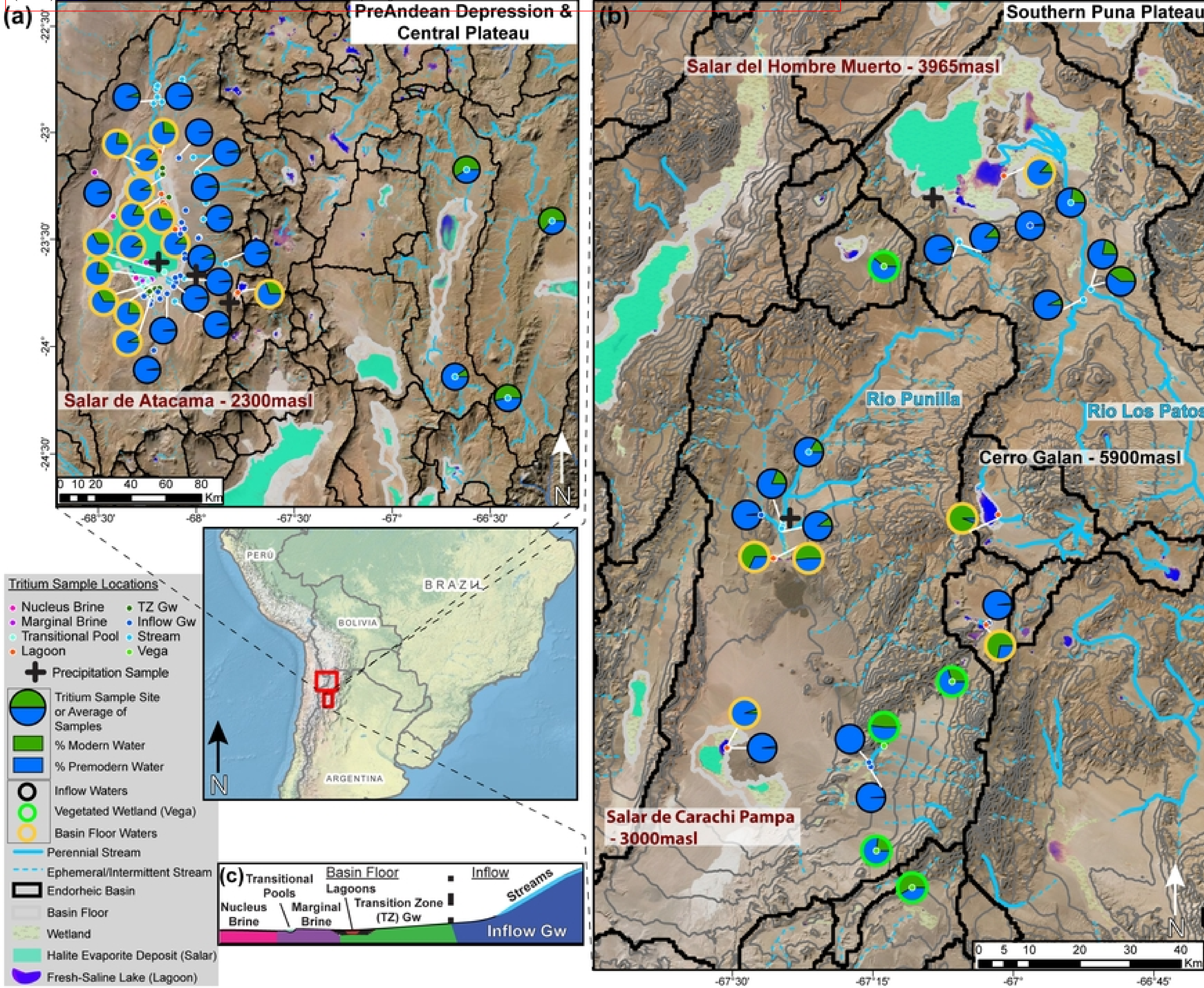
Conceptualization, B.M; Methodology, B.M., D.B; Formal Analysis, B.M.; Investigation, B.M., D.B., L.M.; Resources, D.B., L.M., J.F.; Writing – Original Draft Preparation, B.M.; Writing – Review & Editing, B.M., D.B., L.M., J.F.; Funding Acquisition, B.M., D.B., L.M., J.F.

Competing Interests

The authors declare no competing interests.

Supplementary Information

Included in a separate document with this submission.



(a)
PreAndean Depression & Central Plateau
Salar de Atacama - 2300masl
(b)
Southern Puna Plateau
Salar del Hombre Muerto - 3965masl
Rio Punilla
Rio Los Patos
Cerro Galan - 5900masl
Salar de Carachi Pampa - 3000masl
PERÚ
BRAZIL
BOLIVIA
ARGENTINA
Tritium Sample Locations
Nucleus Brine
Marginal Brine
Transitional Pool
Lagoon
TZ Gw
Inflow Gw
Stream
Vega
Precipitation Sample
Tritium Sample Site or Average of Samples
% Modern Water
% Premodern Water
Inflow Waters
Vegetated Wetland (Vega)
Basin Floor Waters
Perennial Stream
Ephemeral/Intermittent Stream
Endorheic Basin
Basin Floor
Wetland
Halite Evaporite Deposit (Salar)
Fresh-Saline Lake (Lagoon)
(c)
Transitional Pools
Basin Floor
Lagoons
Inflow
Streams
Nucleus Brine
Marginal Brine
Transition Zone (TZ) Gw
Inflow Gw

Figure 1

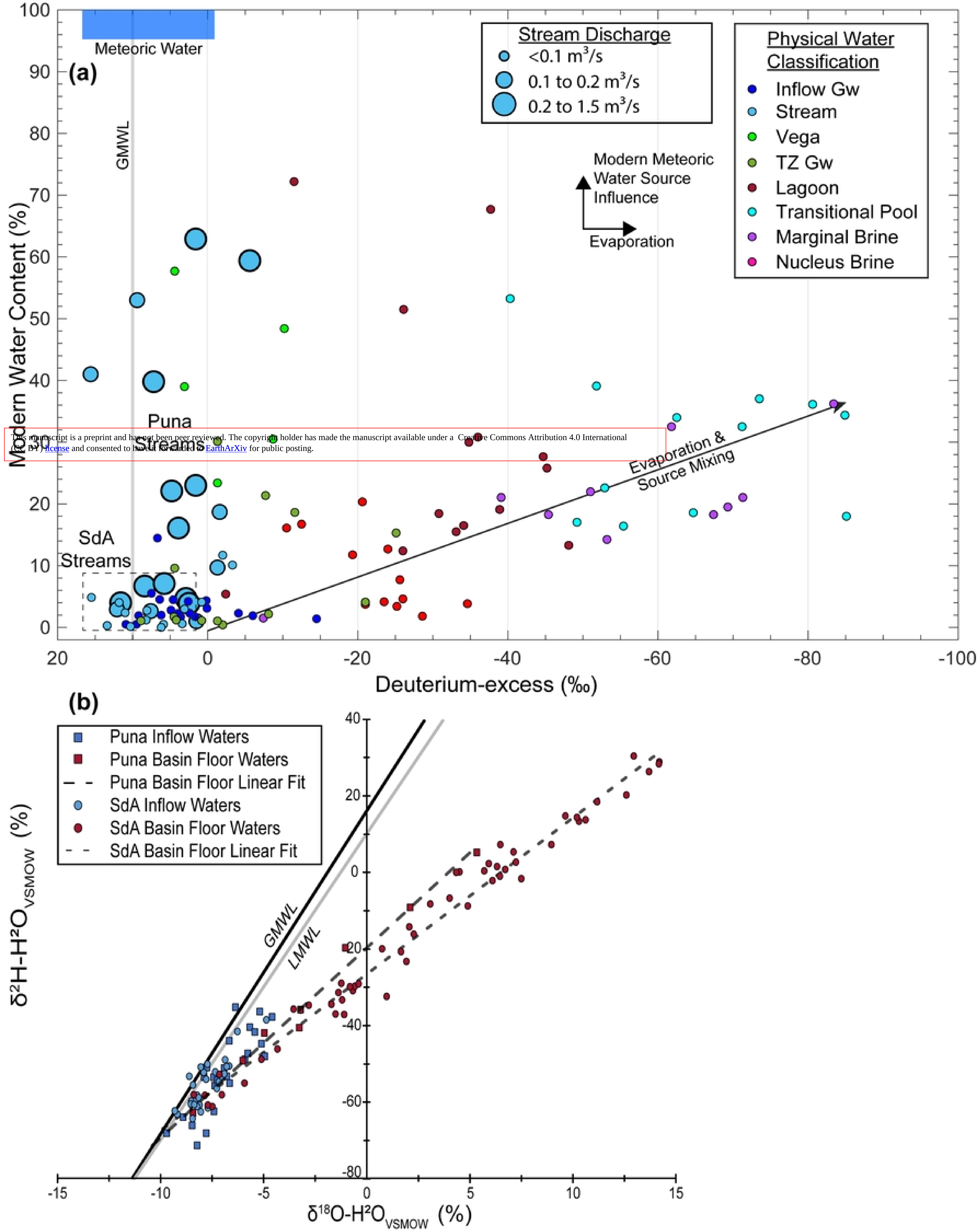

(a)
Meteoric Water
GMWL
Stream Discharge
<0.1 m³/s
0.1 to 0.2 m³/s
0.2 to 1.5 m³/s
Physical Water Classification
Inflow Gw
Stream
Vega
TZ Gw
Lagoon
Transitional Pool
Marginal Brine
Nucleus Brine
Modern Meteoric Water Source Influence
Evaporation
Puna Streams
SdA Streams
Evaporation & Source Mixing
Modern Water Content (%)
Deuterium-excess (‰)
(b)
Puna Inflow Waters
Puna Basin Floor Waters
Puna Basin Floor Linear Fit
SdA Inflow Waters
SdA Basin Floor Waters
SdA Basin Floor Linear Fit
GMWL
LMWL
δ²H-H²O_VSMOW (%)
δ¹⁸O-H²O_VSMOW (%)

Figure 3

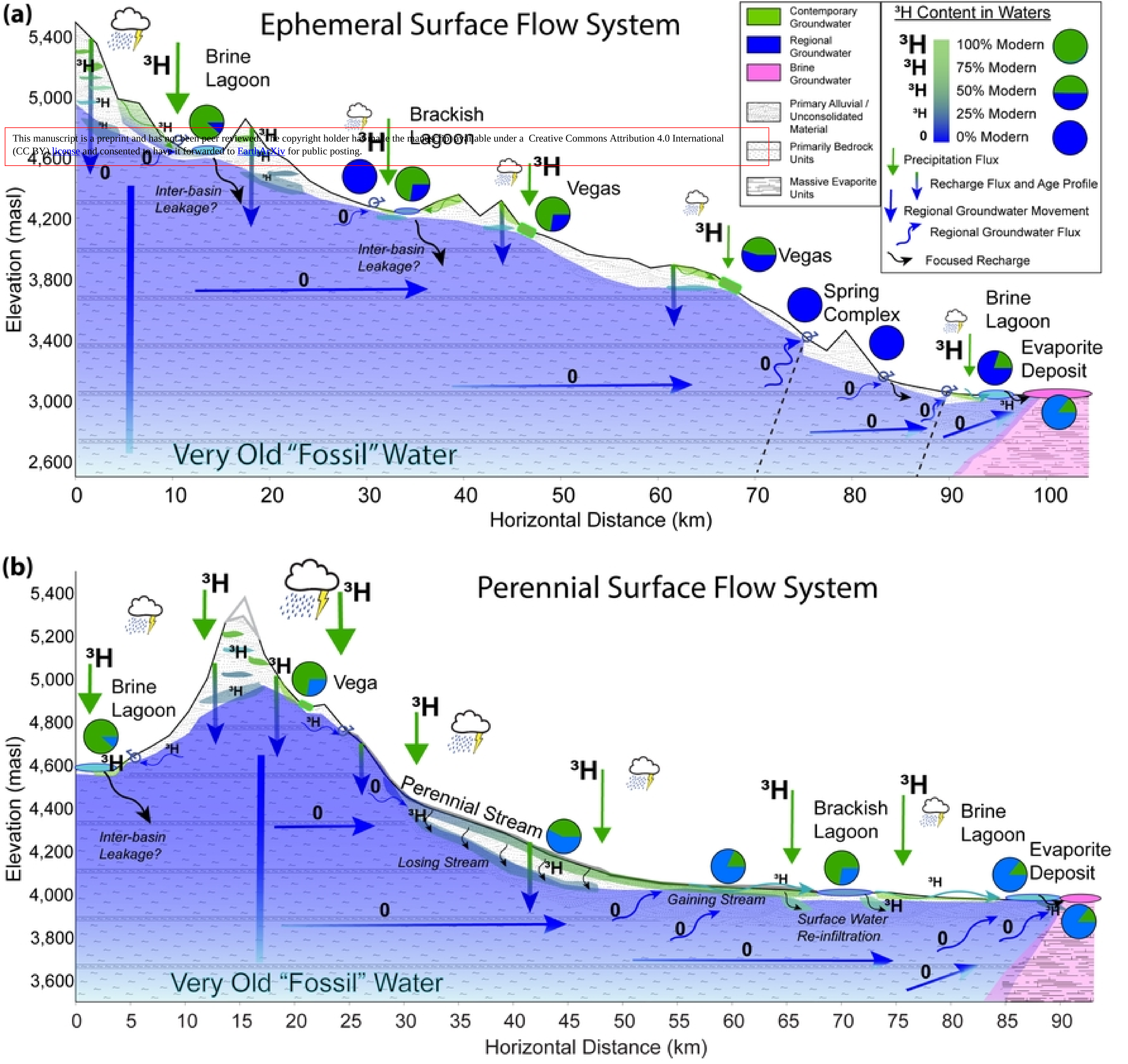
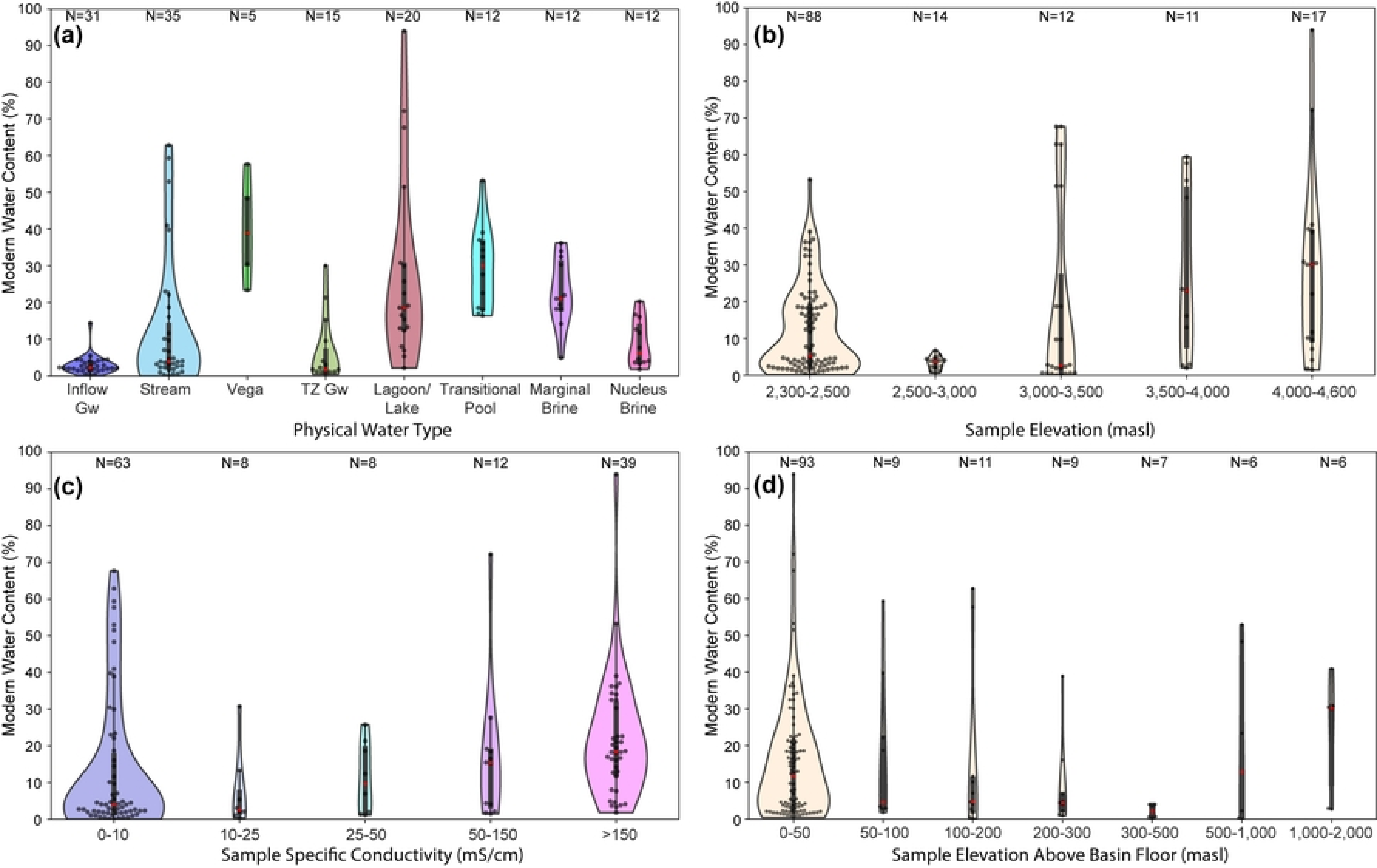

(a)
Ephemeral Surface Flow System
Contemporary Groundwater
Regional Groundwater
Brine Groundwater
Primary Alluvial / Unconsolidated Material
Primarily Bedrock Units
Massive Evaporite Units
³H Content in Waters
100% Modern
75% Modern
50% Modern
25% Modern
0% Modern
Precipitation Flux
Recharge Flux and Age Profile
Regional Groundwater Movement
Regional Groundwater Flux
Focused Recharge
Brine Lagoon
Brackish Lagoon
Vegas
Vegas
Spring Complex
Brine Lagoon
Evaporite Deposit
Inter-basin Leakage?
Inter-basin Leakage?
Very Old "Fossil" Water
Elevation (masl)
Horizontal Distance (km)
(b)
Perennial Surface Flow System
Brine Lagoon
Vega
Perennial Stream
Losing Stream
Gaining Stream
Surface Water Re-infiltration
Brackish Lagoon
Brine Lagoon
Evaporite Deposit
Inter-basin Leakage?
Very Old "Fossil" Water
Elevation (masl)
Horizontal Distance (km)

Figure 4


(a)
N=31
N=35
N=5
N=15
N=20
N=12
N=12
N=12
Modern Water Content (%)
Inflow Gw
Stream
Vega
TZ Gw
Lagoon/ Lake
Transitional Pool
Marginal Brine
Nucleus Brine
Physical Water Type
(b)
N=88
N=14
N=12
N=11
N=17
Modern Water Content (%)
2,300-2,500
2,500-3,000
3,000-3,500
3,500-4,000
4,000-4,600
Sample Elevation (masl)
(c)
N=63
N=8
N=8
N=12
N=39
Modern Water Content (%)
0-10
10-25
25-50
50-150
>150
Sample Specific Conductivity (mS/cm)
(d)
N=93
N=9
N=11
N=9
N=7
N=6
N=6
Modern Water Content (%)
0-50
50-100
100-200
200-300
300-500
500-1,000
1,000-2,000
Sample Elevation Above Basin Floor (masl)