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Isotope amount effects in hydrologic and climate reconstructions of monsoon climates: Implications of some long-term data sets for precipitation

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ABSTRACT

Many studies of Quaternary climate make use of terrestrial stable isotope records which are interpreted based on seasonal patterns of stable isotopes in modern precipitation. Multi-decade records of isotopes in rainfall allow testing of the assumed behavior of isotope signals used for this interpretation on multi-year to decadal scales. A 32-year record of stable O and H isotopes in precipitation in Tucson, Arizona permits a detailed examination of stable isotope amount effects, at time scales ranging from individual events to decades, in a location with summer monsoonal and winter frontal rainy seasons. Amount effects are weak to non-existent in Tucson at seasonal and longer time scales, and are not useful for discriminating either wetter or drier rainy seasons or wetter or drier decades. Amount effects are also weak to non-existent in published data for annual and multi-year amount-weighted averages for monsoonal precipitation in New Delhi and Hong Kong, but an annual amount effect appears to be present on Guam (U.S. Territory). In addition, site-specific amount effects do not correlate with measures of regional monsoon intensity. This data analysis challenges the general validity of paleoclimate reconstructions based on short-term (sub-annual) relationships observed in precipitation isotope data when applied to long-term records such as speleothem studies.

1. Introduction

Time-series stable isotope data are frequently enlisted as proxies of climate variations during the late Quaternary and on longer time scales. Often, stable isotope ratios in a geological archive are interpreted as somehow related to the isotopic composition of ancient precipitation and that inferred variance in ancient rainfall or surface water is related to changes in the ancient climate at that location. Some examples of this are the use of oxygen isotopes in lacustrine carbonates, mollusk shells, ice cores, speleothems and tree rings among many others. For example, speleothem carbonates hold oxygen isotope records interpreted in terms of changes (qualitative or quantitative) in local temperature or rainfall amounts through time. In ice cores, O or H isotope ratios are related to temperature changes in the record. In each of these approaches, interpretation of a stable isotope record tends to rely on an idealized conception of the behavior of water isotopes in the hydrologic cycle. Most commonly, authors extrapolate a short-term (seasonal or annual) relationship between stable isotopes in precipitation and a climate variable and apply this relationship to time scales of interest in climate research; or authors may take modern regional or spatial relationships and apply them through time (e.g. Fleitman et al., 2003; Paulsen et al. 2003, Cheng et al., 2006; Yadava et al., 2004; Yadava and Ramesh, 2005; Yuan et al., 2004). It is not clear if the use of short term or local relationships is valid in the interpretation of stable isotope records that span thousands of years and record transitions in climate. As longer records of modern isotopes in precipitation become available some of these relatively simplistic relationships can be tested on a multi-year to decadal basis, although questions clearly remain about the validity of extrapolation to millennial climate variability.

In this paper, we present a new data set for Tucson, Arizona (Table 1). The data have few gaps across a span of 32 years, a period including an observed change in local climate. Our aims are: first, to examine the relationships between $\delta^{18}O$ and precipitation amount (the "amount effect") at a single location (Tucson) at seasonal to decadal time scales, using raw data, and amount-weighted and arithmetic means; and second, to discuss the results in the context of hydrologic and paleoclimate reconstructions, particularly those deriving from speleothem isotope data. We focus on the amount effect because: 1. Precipitation data from Tucson have been cited as an example of rainfall isotope data depending in part on seasonal amount (Wright et al., 2001; Wagner et al., 2010); 2. Seasonal amount-effects have been proposed elsewhere in the region (e.g. central Texas, Pape et al., 2010); 3. Explanations of rainfall isotope data in western North America in

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terms of sources and paths of atmospheric water vapor generally apply at short time scales (days, weeks), and do not preclude amount effects at longer time scales (see Section 2); 4. Tucson's warm (mean annual temperature = 21.6 °C) and arid climate, low latitude setting (32°N), and monsoon rainfall pattern are factors usually thought to be associated with the amount effect (e.g. Hoffmann et al., 2005; Cheng et al., 2006); and 5. Determining past changes in precipitation amount from monsoon region isotope data archives is one of the persistent aims of speleothem isotope research. The results for Tucson prompted a re-examination, also presented here, of long-term rain isotope data from New Delhi (India), Hong Kong (China) and Guam (U.S. Territory), data that have been cited in previous paleoclimate studies reviewed below.

2. Modern isotopes in precipitation and paleo-isotope records

The interpretation of oxygen isotope ratios in speleothems (after some assessment of equilibrium behavior in the geochemistry) usually invokes a demonstrable relationship between isotopes in the modern meteoric water at the cave location and the climatic phenomenon of interest (Quade, 2003). In the middle latitudes (35–55°), $\delta^{18}O$ variation in precipitation is often correlated with seasonal (monthly) temperature change (Rozanski et al., 1993). Speleothem studies in this region often use this seasonally-based $\delta^{18}O$ — temperature relationship, summed with the temperature dependent fractionation of oxygen isotopes in calcite, to determine the sense of paleo-temperature change from variation in speleothem $\delta^{18}O$ values (e.g. Hellstrom et al., 1998; Bar-Mathews et al., 1999; see also Quade, 2003). In contrast, low-latitude studies (<35°) commonly make use of the isotope amount effect in precipitation (Dansgaard, 1964). This proxy uses a correlation between the $\delta^{18}O$ of meteoric water and the amount of precipitation and usually assumes the effects of temperature change are small compared to changes in meteoric water $\delta^{18}O$ values (Quade, 2003). Where amount effects exist, the correlation between the amount of precipitation and the weighted mean $\delta^{18}O$ of the precipitation is commonly negative (e.g. Rozanski et al., 1993). Positive correlation is also possible, as in subtropical Brazil (Cruz et al., 2005).

Working with the IAEA Database of Isotopes in Precipitation, Dansgaard (1964) defined the amount effect as a low latitude anticorrelation between the isotopic composition and amount of rain based on monthly means. This has apparently led to a focus on monthly isotope variations in precipitation isotopes, often averaged over multiple years, in much subsequent research. Classic amount effect examples are cited for Guam, New Delhi and Hong Kong (Rozanski et al., 1993). Note that there are at least three mechanisms that can generate amount effects: the evaporation of raindrops falling through dry air (Dansgaard, 1964); progressive rainout at regional scale (Kurita et al., 2009); or change in moisture source between seasons with unequal amounts of rainfall (e.g. Cruz et al., 2005). The amount effect forms the basis for a number of studies of past monsoon intensity in South and East Asia using isotopic time series derived from speleothems (Fleitmann et al., 2003; Paulsen et al., 2003, Cheng et al., 2006; Yadava et al., 2004, Yadava and Ramesh, 2005; Yuan et al., 2004). More recent studies using similar methods include Wagner et al. (2010) in southwestern North America, Lachniet et al. (2012) in central Mexico, and Partin et al. (2012) in Guam. Although the amount effect is clearly present in the monthly isotopic data from New Delhi, Hong Kong, or Guam, it is not at all clear whether a monthly effect can be extrapolated to long term records, or to data with low time resolution, for the following reasons. In speleothem records single samples may represent multiple (up to hundreds) of years, and the isotopic time series generated can span hundreds of thousands of years (Wang et al., 2008; Cruz et al., 2005, Paulsen et al., 2003). Furthermore, isotope studies of cave drip water indicate that cave roof aquifers store water for periods of years to decades (Kaufman et al., 2003; Kluge et al., 2010), resulting in drip water with the isotope signature of local long-term average precipitation (Schwarz et al., 2009; Fuller et al., 2008; Yonge et al., 1985).

More recently a number of studies have broadened the definition of the amount effect to relate the stable isotope variation at one location (e.g. the site of the speleothem sample) to interannual changes in regional rainfall intensity, driven by progressive rain-out from air masses upwind of the site (Yuan et al., 2004; Cheng et al., 2006). Climate models with isotope capability (Liu et al., 2014; Le Grande and Schmidt, 2009; Pausata et al., 2011) can reproduce this effect. The models also suggest that speleothem isotope variations at millennial time-scales can be driven by global forcing of climate.

Other studies have raised questions about the validity of using the amount effect to interpret speleothem data. Bowen (2008) suggested that an isotope — climate relationship constructed from data for a particular monitoring station might not apply at a distant study site. Aggarwal et al. (2004) compared mean annual $\delta^{18}O$ values and precipitation amount across a region stretching from South Asia into the central Pacific. From the lack of correlation they argued that there is no amount effect in the region, but their definition of the amount effect is unusual, involving the comparison of average precipitation amounts at widely separated locations, rather than differences of amount over time at a single site. Lechler and Niemi (2011) adopted a similar approach in a study of 206 widely separated stations in the western USA, finding several instances of strong correlation (R^2 near 0.8) between mean annual precipitation and average $\delta^{18}O$. Vimeux et al. (2011), Moerman et al. (2013) and Lekshmy et al. (2014) suggested that an important control on $\delta^{18}O$ in low-latitude rainwater was the intensity of convective activity rather than amount.

Yet other authors have sought to account for isotope variation in precipitation in terms of source regions and trajectories of atmospheric vapor. Aggarwal et al. (2012), using monthly means at twelve sites representing latitudes from the equator to the poles, argued that most of the variation in $\delta^{18}O$ of meteoric water at a particular location is explained by atmospheric vapor residence times. Breitenbach et al. (2010), identified such a relationship on the time scale of individual rain events in northeast India. Dayem et al. (2010) showed that amount effects could account for less than half the amplitude of the long-term $\delta^{18}O$ variation in Chinese speleothems, and modeled changes in source of water vapor, vapor transport pathways, the proportions of different precipitation types, and the interplay of condensation and evaporation in the atmosphere as potential explanations. Large seasonal isotope variations were ascribed to changes in moisture source in East Asia by Xie et al. (2011), Peng et al. (2010), Tang et al. (2015), and Moerman et al. (2013). Friedman et al. (2002) and Strong et al. (2007), examining data for western North America, proposed that isotope variation in precipitation on a time scale of days is related to vapor source region and trajectory. At the monthly to annual time scale, it seems to be related to the strength of the Pacific/North America (PNA) teleconnection pattern (Liu et al., 2011), and to sea-surface temperatures in vapor source region (Wright et al., 2001).

Such correlations do not a priori preclude isotope amount effects at seasonal or longer time scales, for the following reasons. First, the reported correlations leave much of the variance of the isotope data unexplained. Second, short-term variables such as vapor trajectories and residence times with time scales of days tend to average out at longer time scales, potentially leaving wetter and drier seasons or years unexplained. Third, a long-term relationship between precipitation amount and variables like vapor trajectory and PNA index is not precluded by short-term correlations. All of the approaches discussed above leave open the possibility of an isotope amount effect related to year-to-year changes in precipitation amount at a particular location.

Speleothems form from groundwater that represents a combination of rainwater from many individual precipitation events. The wet season dominates the groundwater record in most wet/dry seasonal climates, and our discussion will therefore look mainly at isotope effects at the time-scales of individual wet seasons or longer. For example, we will ask the question: do wet seasons at one location differ in $\delta^{18}O$ signature as a function of the total precipitation amount? And does this relationship apply at even longer time-scales (wet decades vs. dry decades)? Although modern data sets spanning three decades or more are rare, they are becoming increasingly available (e.g. through the GNIP database, International Atomic Energy Agency, 2015) and can begin to answer these questions. In addition, we will offer a preliminary examination of the relationship between wet-season rainfall intensity across three monsoonal regions (southwestern North America, India, and East Asia) and records of seasonal amount-weighted mean $\delta^{18}O$ values.

3. The Tucson data set

3.1 Background and methods

The late Professor Austin Long initiated collection of rainwater (and rarely, snowmelt) samples at the University of Arizona (here termed the UA station) in February 1981, and collection continues to the present. All samples were collected from simple cylindrical rain gauges at locations (see Supplementary Table 1) that lie within 1.5 km of the intersection of Speedway Blvd. and Campbell Ave. in Tucson (Lat. 32.2361 N, Long. 110.9439 W, 753 m above sea level). The precipitation amounts were recorded. Care was taken to avoid evaporation as a result of sampling procedure; samples were bottled as soon as possible after each event, but at times when immediate bottling was not feasible, oil was left in the rain gauge to prevent evaporation. When necessary, long-term storage was in glass bottles with paraffin wax as a sealant. Small precipitation events occurring during a period of 24 h were aggregated into single samples. Only those events yielding >0.5 mm produced sufficient water for measurement. Some data gaps exist between 1981 and 1990; too few data are present to calculate meaningful averages for 9 of the months in that interval.

For all samples collected since 1995 and many of those collected earlier, $\delta^{18}O$ and δD were measured on an automated gas-source isotope ratio mass spectrometer (Finnigan Delta S). For hydrogen, samples were reacted at 750 °C with Cr metal using a Finnigan H/Device coupled to the mass spectrometer. For oxygen, samples were equilibrated with CO_2 gas at approximately 15 °C in an automated equilibration device coupled to the mass spectrometer. Standardization is based on international reference materials VSMOW and SLAP (Coplen, 1995). Analytical precision (1σ) is 0.9 ‰ or better for δD and 0.08 ‰ or better for $\delta^{18}O$ on the basis of repeated internal standards. Prior to 1995, gases for mass spectrometry were prepared manually by reduction of water to H_2 gas using Zn metal for H isotopes, and CO_2 equilibration for O isotopes. Analytical precision (1σ) was poorer, 1.5 to 2‰ for H, and 0.15‰ for O, but accuracy is comparable in the two data sets.

Fig. 1 shows seasonal and annual rainfall statistics for the UA station. The climate in Tucson is semi-arid, with an average annual precipitation of 343 mm at our collection site from 1983 to 2012, in comparison with 294 mm at the official Tucson Airport station, 12.5 km to the south, from 1981 to 2010 (National Weather Service, 2015). Seasonal and annual rainfall totals are highly variable. Precipitation can occur in any month in Tucson, but is largely limited to two wet seasons, a winter season in which Pacific cold fronts bring moisture from the west or southwest, and a summer season in which the North American monsoon deposits moisture originating either from the Pacific Ocean to the southwest, or the Gulf of Mexico to the east (Hu and Dominguez, 2015, and references therein). Winter precipitation is typically regional in distribution, but summer precipitation is localized, at times to areas of a few square kilometers. Tropical depressions originating as Pacific coast hurricanes and tropical storms may bring additional localized precipitation in the fall. For the purposes of this study, “Summer” precipitation is deemed to include any rainfall for the months of June to October, and “Winter” for November to May because these periods encompass summer and winter weather patterns, respectively (Fig. 1, inset); the term “seasonal” will be used here to refer to these periods. On average, seasonal and annual rainfall amounts have decreased at the UA station since 1983, and summer rainfall, formerly about equal to winter rainfall, has predominated since the late 1990s (Fig. 1). Although specific reasons for these changes have not been clearly identified, this change coincided with a transition in global climate indices; values of the Atlantic Multidecadal Oscillation (AMO) index changed from negative to positive while values of the Pacific Decadal Oscillation (PDO) index passed from positive to negative. Under former conditions (AMO−, PDO+) the southwestern USA tends to experience higher than average rainfall, while under the latter conditions, (AMO+, PDO−), the region tends to experience drought (McCabe et al., 2004). The (AMO+, PDO−) state has prevailed from about 1998 to the present (National Oceanic and Atmospheric Administration, 2015a, b).

The Tucson stable isotope data are available as a supplementary material for this article (Supplementary Table 1). Monthly averages are also available in the Global Network of Isotopes in Precipitation database (International Atomic Energy Agency, 2015).

3.2 Individual rain events

Fig. 2 shows all data collected between 1981 and 2012. The data have these features:

1. Samples are broadly distributed about the global meteoric water line, GMWL, (Craig, 1961). Almost all measurements plot with $-40 < d < 30$ (where d is the deuterium excess: $d = \delta D - 8\delta^{18}O$). Low values of d are most common in summer precipitation with $\delta^{18}O$ values >−4‰.
2. The ranges of δD and $\delta^{18}O$ are very large; for δD the range is −154 to +42‰ (with 98% of data between −110 and +23‰), and for $\delta^{18}O$ −20 to +8‰ (98% between −15 and +6‰).
3. The ranges of summer and winter samples overlap at low values of δD and $\delta^{18}O$, but at high values, summer samples predominate.
4. Local meteoric water lines (LMWL) weighted for precipitation amount (Hughes and Crawford, 2012) are given as slopes and intercepts in Table 1. The LMWL for the entire data set (Fig. 2) is similar to those for winter and for summer data. However, visual inspection of Fig. 2 suggests that two linear trends are present, rather than a single local meteoric water line. Data with $\delta^{18}O$ values <−6‰ yield a line essentially coincident with the GMWL. For the set of data with $\delta^{18}O$ values >−6‰, the line has a slope of consistent with evaporation. Such evaporation is not a result of sample collection procedures.
5. The long-term amount-weighted averages of ($\delta^{18}O$, δD‰) are (−6.0, −42) for summer, (−8.9, −59) for winter, and (−7.3, −49) overall.

The highest $\delta^{18}O$ values correspond to very small rain events, but the converse is not generally true, because many small rain events can have low or average $\delta^{18}O$ values (Supplementary Fig. 1A, B).

Table 1
Local meteoric water lines for Tucson.

Data subset	Slope	Intercept
All data	6.24	−4.33
Winter	6.30	−3.05
Summer	6.30	−4.51
$\delta^{18}O > -6$‰	4.97	−6.96
$\delta^{18}O < -6$‰	7.78	9.92

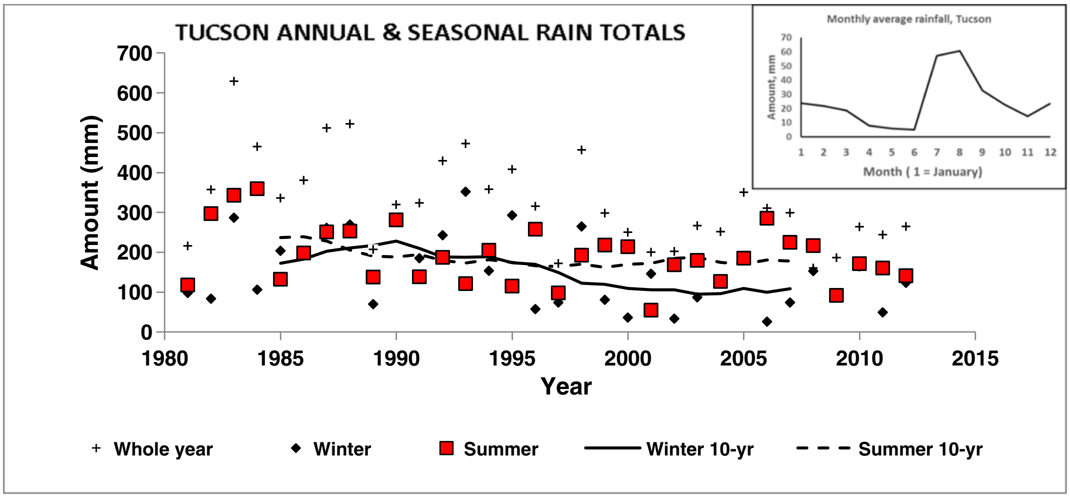

Fig. 1. Annual and seasonal rainfall totals at the UA station, 1981–2012. Inset: Monthly precipitation averages at Tucson Airport (National Weather Service, 2015).

3.3 Seasonal and longer time scales

Seasonal (i.e. winter and summer) amount-weighted mean $\delta^{18}O$ values are shown with seasonal amount data in Fig. 3. Three-year amount-weighted running means are shown as a function of precipitation amount in Fig. 4A and as a time series in Fig. 4B. The overall weighted mean $\delta^{18}O$ values for both summer and winter based on the entire data set are marked by the horizontal lines Fig. 4B. In Fig. 4C 10-year running means are plotted as a time series. Amount-weighted $\delta^{18}O$ and δD data for summer and winter season (June–Oct., Nov.–May) for each year, and three-year and ten-year running means are compared to the GMWL in Supplementary Fig. 2. The regression lines in these and other figures are presented with the statistical parameters R^2 (R being the Pearson correlation coefficient) and p (the p-value being a measure of the significance of the correlation, which is statistically significant if $p \leq 0.05$).

No attempt has been made to correct this data set for the impact of other climate variables on the $\delta^{18}O$ value of rainfall. The most likely climate correlation with isotopic composition in this context is temperature averaged over the time scale of interest. Because we observe no correlation or very weak correlation between seasonal or monthly averages of temperature (calculated from unpublished data of National Weather Service, Tucson) and seasonal amount-weighted $\delta^{18}O$ values in rainfall, we have not adjusted our data for temperature effects (Supplementary Fig. 3). Correlations between seasonal averages of amount and temperature are also weak and insignificant (Supplementary Fig. 3C).

The following generalizations emerge:

1. As time scale increases, the separation of summer and winter precipitation becomes clearer, and the weighted means converge on the amount- weighted means for the entire dataset. Weighted mean values of deuterium excess converge on 12 for winter, and 5 for summer (Supplementary Fig. 2).
2. In the summer data, there is a weak correlation between $\delta^{18}O$ and precipitation amount at seasonal and three-year time scales (Figs. 3 and 4A).
3. For the winter season, a weak correlation between $\delta^{18}O$ value and precipitation amount is observed only at the seasonal time scale, but not in the 3 year running means (Figs. 3 and 4A).
4. Fig. 4C shows how well any data set for 10 sequential years would estimate the 32-year amount-weighted means of $\delta^{18}O$ for summer and winter precipitation. In summer, the long-term mean is −6.0‰, and the estimates vary between −5.4 and −6.4‰. For winter, the long-term mean is −9.1‰, and the estimates vary between −8.2 and −10.0‰. The poorer agreement for winter is due partly to an extreme mean $\delta^{18}O$ value, −13.7‰, for winter 1994–1995 (Fig. 3).

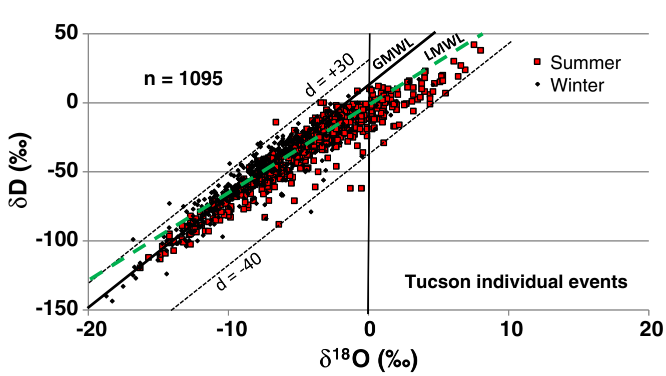

Fig. 2. δD vs. $\delta^{18}O$ for individual rain events at the UA station, central Tucson. GMWL = global meteoric water line (Craig, 1961); LMWL = local meteoric water line for the entire dataset. Deuterium excess (d) contours are also plotted.

4. Implications of the Tucson dataset

4.1 Amount relationships at seasonal and longer timescales

Figs. 3 and 4A show that correlations between weighted average $\delta^{18}O$ and precipitation amount at seasonal and 3-year scales are weak to non-existent for both summer and winter datasets. The correlation is also weak for total annual precipitation (Supplementary Fig. 5). The strongest correlation, with an R^2 value of 0.35, is for summer data in Fig. 3, and indicates that only 35% of the variance in $\delta^{18}O$ is due to precipitation amount. Fig. 3 also shows a simple statistical analysis of these data. Means and standard deviations were calculated for the sets of amount values corresponding to $\delta^{18}O$ ranges of -2 ± 1‰, -4 ± 1‰, etc. The ranges of the amount variable in three of the brackets of data are statistically indistinguishable at 68% and 95% confidence levels, and the fourth bracket, corresponding to $\delta^{18}O = -2 \pm 1$‰, is not conclusively distinguished from the others. In other words, one cannot infer different rainfall amounts from $\delta^{18}O$ values between −1 and −9‰ in this data set, even though it is possible to fit a statistically-significant regression line to the data. Note that our statistical analysis of summer seasonal data differs from that of Wagner et al. (2010, Supplemental information) who used only data for July to September for 20 years of

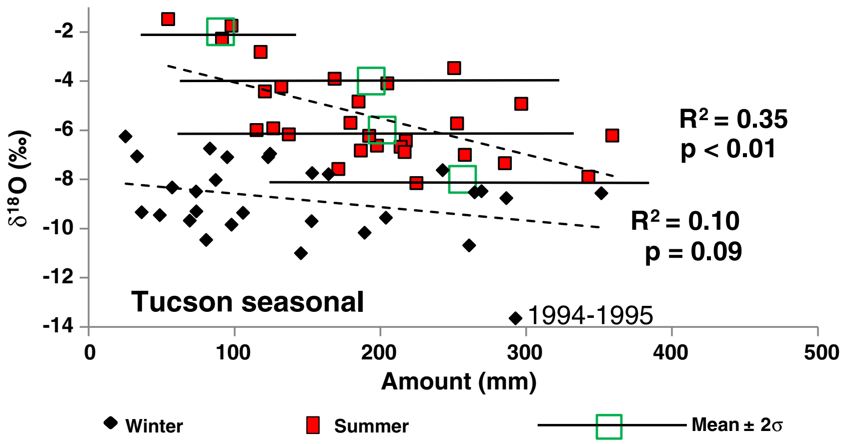

Fig. 3. Seasonal amount-weighted mean δ^{18}O vs. precipitation amount with regression line, UA station. The summer δ^{18}O data have been divided into brackets 2‰ wide, viz. $\delta^{18}O = -2 \pm 1$‰, -4 ± 1‰, etc. The statistics of precipitation amount in each bracket are shown as a mean (large square symbol) and the range mean $\pm 2\sigma$ (solid horizontal lines).

records from our collection. Their R^2 value is 0.50, but interpretation of the data is limited in the same fashion as that in our Fig. 3, again showing that a significant correlation does not necessarily lead to an interpretable amount relationship based on the δ^{18}O of rainfall.

The seasonal data for Tucson can be compared with data for 1999–2007 from Austin, Texas (Pape et al., 2010), where for monthly to bimonthly aggregate rain samples, there is no correlation between amount and δ^{18}O for rainfall. However, when ten of the twelve warmest intervals were selected (monthly temperatures >26.9 °C) there was a strong correlation between amount and isotopic composition. But as in the Tucson data set, it is not possible to identify wetter or drier periods when data is integrated at a seasonal or annual basis.

4.2 Estimating long-term mean δ^{18}O

Fig. 4B, C shows the degree of convergence of seasonal weighted mean δ^{18}O on the long-term (32-year) weighted means with increasing time scale. Fig. 4C shows that if precipitation events were measured over any sequential 10 year interval in Tucson, the difference between the 10-year weighted mean and the long-term weighted mean δ^{18}O might be as much as 0.7‰ in summer and 1.1‰ in winter. Data collection over a period longer than a decade is required for an adequate estimate of the long-term weighted mean. Fig. 4B, C can also be used to compare years prior to and following the change to the (AMO+, PDO−) state, which encompasses a significant drop in the amount of Tucson winter rain (Fig. 1). There is, to date, no convincing isotope response to this observed climate change at three-year and decadal time scales.

4.3 Causes of seasonal isotope variation in Tucson rain

No single and simple cause for isotope variation in Tucson rain at the seasonal time-scale has emerged. Precipitation amount per se is not necessarily a cause of seasonal isotope variation; rather both are likely to be observable effects of the same underlying causes. Factors such as average temperature in Tucson and sea surface temperatures in the Pacific south of Baja California have been observed to correlate with averaged δ^{18}O in Tucson rain (Wright et al., 2001), but at the monthly time scale only and using a more limited data set. When working with the full data set presented here, correlation between monthly or seasonal average temperature and rain δ^{18}O value is either non-existent, or very weak in the case of monthly data for winter (Supplementary Fig. 3A, B). The slope of the winter monthly trend, 0.22‰/°C, is much less than slopes found in other regions (Figs. 18 and 19 of Rozanski et al., 1993). Sources and advection paths of water vapor account for much of the variance of δ^{18}O in precipitation in the western USA (Friedman et al., 2002; Strong et al., 2007), and therefore presumably also in Tucson, but at relatively short time scales (days to months). Hu and Dominguez (2015), using the data set presented here, have demonstrated such a relationship for summer monsoon rain at event timescale; higher values of δ^{18}O correspond with vapor sources in the Gulf of Mexico and the Caribbean, while lower values correspond to sources in the Pacific and the Gulf of California. The dependence of precipitation δ^{18}O values at monthly time scales on vapor source and transit path (Aggarwal et al., 2012) applies globally, and is therefore likely to explain much of the variation in Tucson. Tritium measurements provide independent evidence for the addition of tropopause moisture to the water vapor sampled in Tucson (Eastoe et al., 2011), but the effect is observed at daily to monthly time scales, and is unlikely to result in changes when averaged at seasonal or greater time scales.

This study contributes the following new observations germane to the causes of isotope variability in Tucson precipitation at seasonal time scale. The observed variations in d-parameter suggest that evaporation of falling rain during dry summers contributes to summer seasonal isotope variation in Tucson rain; values of d are lowest in summers with mean δ^{18}O values > −4‰ (Fig. 2 and Supplementary Fig. 2). Relative humidity in vapor source regions, which also affects values of d (Merlivat and Jouzel, 1979), accounts for little of the seasonal variation in other cases, summer or winter. Typical moisture sources for summer and winter rain in Tucson lie to the southwest over the Pacific Ocean, where sea-surface temperatures are known to vary. In Fig. 5, the El Niño Southern Oscillation (ENSO) index (National Oceanic and Atmospheric Administration, 2015c), averaged over the summer and winter seasons as defined in this study, is used as a proxy for sea-surface temperature. There is no simple relationship between mean δ^{18}O values for winters and the ENSO index. The plot suggests that most isotope variation in winter arises in years of neutral ENSO index. For summers, a weak but significant correlation ($R^2 = 0.20$, $p = 0.01$) arises from the limitation of high seasonal average δ^{18}O to years of positive ENSO index. Our findings stand in contrast to conclusions of Moerman et al. (2013) who found a relationship between interannual changes of weighted average δ^{18}O in rain and ENSO indices in a 5-year rain isotope dataset from Borneo. It must be remembered that the various studies report correlations, not necessarily causes, and that none of the correlations emerges as truly dominant (e.g. Friedman et al. 2002; Strong et al., 2007; Wright et al., 2001) One can speculate that a complex combination of all of these factors operates to bring about the observed changes in δ^{18}O from season to season.

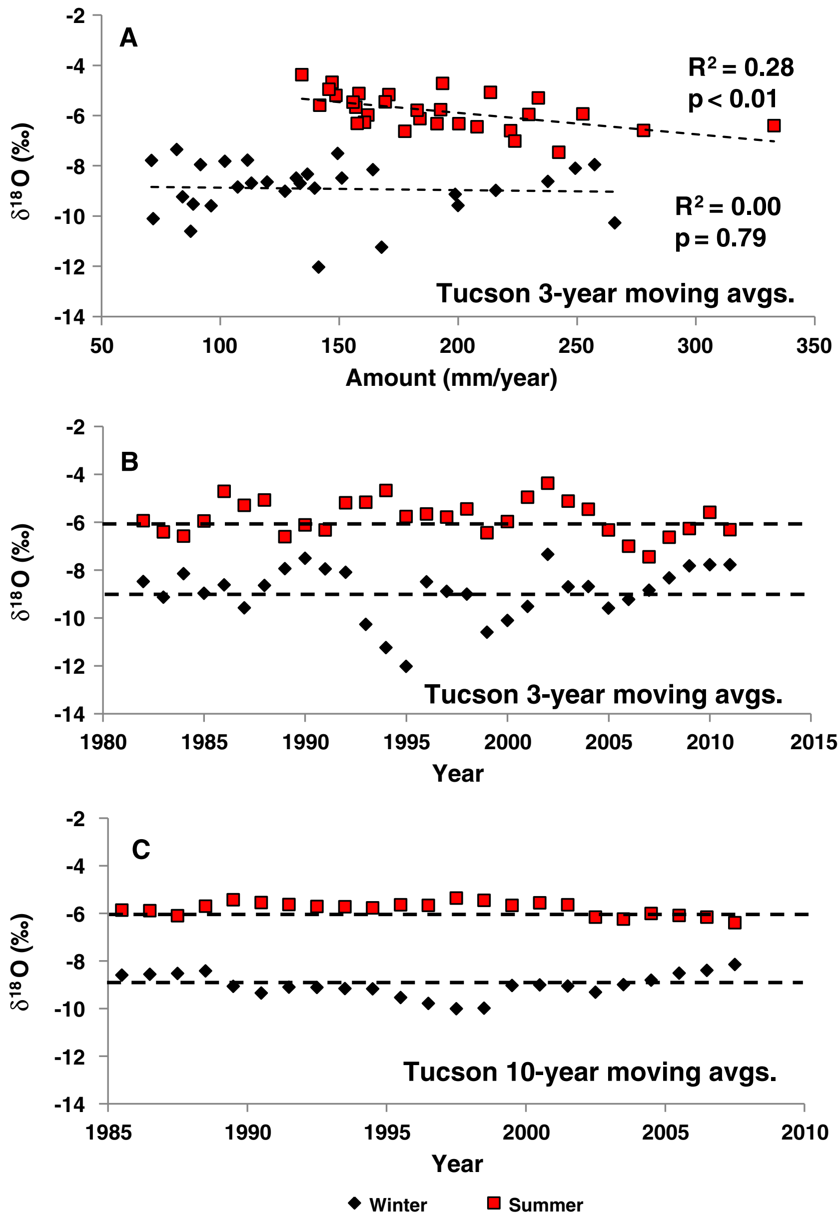

Fig. 4. A. Three-year running mean of amount-weighted $\delta^{18}O$ vs. precipitation amount at the UA station. B. Time series of three-year running mean of amount-weighted $\delta^{18}O$. C. Time series of ten-year running mean of amount-weighted $\delta^{18}O$. Horizontal dashed lines indicate weighted average $\delta^{18}O$ value for summer (upper) and winter (lower) for the entire UA-station data-set.

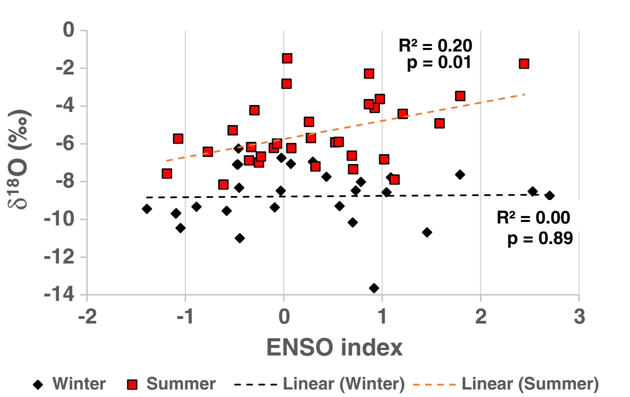

Fig. 5. Seasonal weighted mean $\delta^{18}O$ values for precipitation in Tucson as a function of ENSO index (National Oceanic and Atmospheric Administration, 2015c) averaged over the same months as the precipitation.

5. Modification of precipitation isotope signal in recharge

In the context of paleohydrologic reconstructions tied to sub-surface waters, such as speleothem or groundwater studies, a plausible objection to the approach discussed to this point might be that groundwater recharge does not occur in proportion to precipitation amount. Smaller events give rise to no recharge, especially in summer (a possibility also discussed by Pape et al., 2010), while the amount of recharge from larger events is limited by the rate of infiltration of surface water. How or whether the isotope signals in precipitation are reflected in cave drip water will depend on the mechanisms of recharge and groundwater storage in the catchment of a particular cave.

A useful example is found at the Cave of the Bells, 62 km southeast of Tucson. This cave occurs in a low ridge of Permian limestone on the eastern flank of the Santa Rita Mountains. Local topography indicates a small cave catchment on rocky hillslopes with short drainages, with elevations no more than 200 m higher than the cave entrance, and a lateral extent within 2 km of the entrance on the upslope side. Wagner et al. (2010, Supplementary Fig. 2) collected drip water from four sites in the cave and rainwater from near the cave entrance over 4 years. The variation of $\delta^{18}O$ between rain events was similar in range to that of Tucson rain, but drip water retained a consistent $\delta^{18}O$ value near −10‰, resembling that of average local winter precipitation. There is no evidence of drip water response to single rain events; a single deflection of about 1‰ was recorded at one drip-water collection site after a wet monsoon. In this catchment, summer recharge is all but absent, and winter recharge appears to supply a combination of water from most winter rain events in diffuse fashion (because there are no large drainages on the mountain slope above the cave). Such a recharge mechanism stands in contrast to that associated with large streams in the alluvial flatlands of arid regions, where most recharge is focused in the stream beds and occurs mainly after large flow events (Meredith et al., 2015; Vivoni et al., 2006).

A better match for recharge conditions near the Cave of the Bells may be achieved with this simple model. We assume that small precipitation events, here classed as those of less than 5 mm, lead to no recharge because of evaporation and evapo-transpiration losses, while events of more than 5 mm all contribute similar volumes of recharge, any excess water being lost as runoff. Therefore we compared the arithmetic mean of $\delta^{18}O$ for Tucson precipitation events above 5 mm as a more appropriate measure of contribution to recharge (Fig. 6). Summer data, although not relevant to the Cave of the Bells, are also shown, because summer recharge also is known to occur in other karst terrains of the region (e.g. in the Sacramento Mountains of New Mexico, Newton et al., 2012). The degree of correlation between the variables is very similar to that of the amount-weighted mean $\delta^{18}O$ of the whole seasonal data set (Fig. 3).

6. Comparison with other long-term monsoon precipitation records

The lack of amount-related isotope effects at seasonal to decadal time scales in Tucson precipitation prompted us to examine whether such effects exist at other sites with long isotope records, particularly those that have formed part of the interpretative basis for speleothem paleoclimate studies. Data for New Delhi (28.61°N, 77.21°E), Hong Kong (22.28°N, 114.17°E) and Guam (13.47°N, 114.75°E) were obtained from the WISER database (International Atomic Energy Agency, 2015), and are here represented as weighted means integrating different periods of time: wet season precipitation only for New Delhi and Hong Kong, and total annual rain for Guam. As above, different degrees of averaging are used to capture the water most likely to contribute to soil, surface, and cave waters, and to make up shallow ground water recharge in each region.

In New Delhi, the South Asian monsoon generates a summer wet season limited to July, August and September. Seasonal mean data mostly plot closely along the GMWL (Supplementary Fig. 6), indicating that evaporation has little effect on the seasonal means in most years. The correlation between $\delta^{18}O$ and amount is very weak at seasonal time scale, and weak but significant at three-year time scale (Fig. 7). A statistical analysis like that in Fig. 3 shows that seasonal weighted mean $\delta^{18}O$ values cannot be used to discriminate different rainfall amounts for the total monsoon at the seasonal time scale (Fig. 7A).

In Hong Kong, the summer wet season is longer, more variable in duration, and strongly influenced by tropical cyclones. In this case, the seasonal average data represent the interval from the first (March, April or May) to the last month (September or October) in which rainfall exceeded 100 mm. Only $\delta^{18}O$ data are available. There is no correlation between $\delta^{18}O$ and amount at seasonal and three-year time scales (Fig. 8).

Guam has a continuously wet climate. Weighted mean $\delta^{18}O$ values were calculated for the entire year. The data points are few, but appear to indicate the best correlation of all the data sets reviewed (Fig. 9). Similar correlations were reported on other tropical Pacific islands by Conroy et al. (2013), who noted that only part of the variance in the isotope data was related to precipitation amount.

7. Rain isotopes and regional monsoon precipitation

In response to suggestions that precipitation isotopes at a particular site reflect interannual changes of rainfall intensity at regional scale (Yuan et al., 2004; Cheng et al., 2006), we have also compared the isotopic composition of seasonal mean rainfall $\delta^{18}O$ values with regional indices of monsoon rain amount. We have constructed a simple index for the North American southwest monsoon based on rainfall records. In Asia monsoon intensity at the regional scale has been quantified using differences in high-altitude wind shear for the East Asian monsoons (Wang et al., 2001; School of Ocean and Earth Science and Technology, 2014), or using regional rainfall records, as in the case of the All India Rain (AIR) index (Goswami et al., 2006). For the North American Monsoon in the southwestern USA, we have calculated an index like the AIR index from selected Arizona and New Mexico precipitation records from 1982 to 2012, June to October (National Oceanic and Atmospheric Administration, 2015d). The index (Arizona New Mexico Monsoon Rain Index, ANMMRI) is calculated thus: for each of ten stations (Tucson, Payson, Flagstaff, Douglas and Nogales in Arizona, and Albuquerque, Gallup, Tularosa, Cliff and Las Cruces in New Mexico), the precipitation in June to October (JJASO) for a particular year is normalized

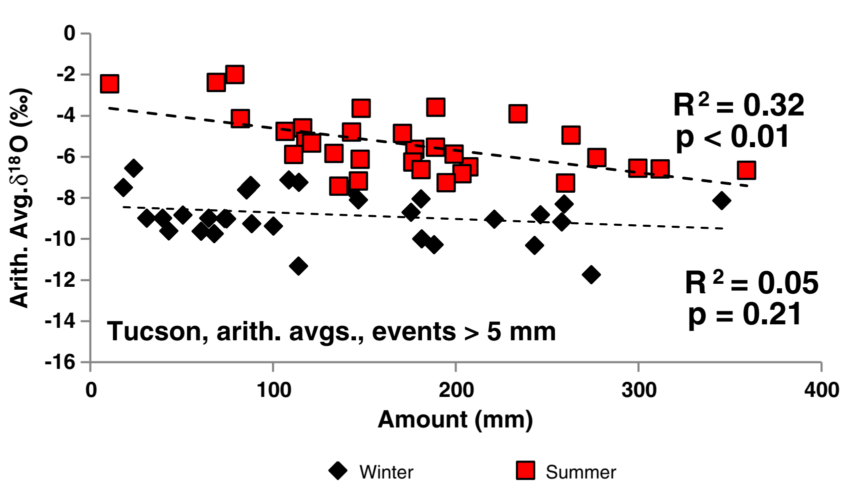

Fig. 6. Arithmetic mean of $\delta^{18}O$ vs. precipitation amount at the UA station, excluding events of <5 mm.

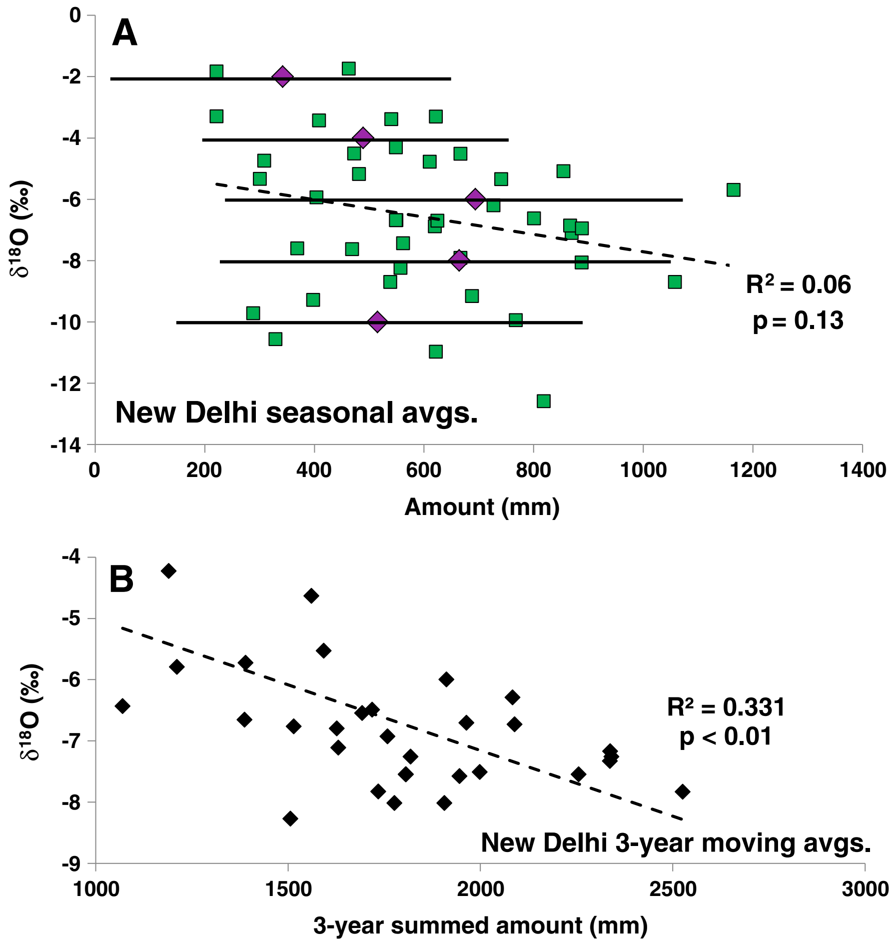

Fig. 7. Average $\delta^{18}O$ vs. amount (squares) for monsoon seasons (July + August + September) in New Delhi. A. Seasonal averages. The $\delta^{18}O$ data have been divided into brackets 2‰ wide, viz. $\delta^{18}O = -2 \pm 1$‰, -4 ± 1‰, etc. The statistics of precipitation amount in each bracket are shown as a mean (large diamond symbol) and the range and the range mean $\pm 2\sigma$ (solid horizontal lines). B. Three-year running means. Data from International Atomic Energy Agency (2015).

to the mean JJASO precipitation amount for 1982–2012. For each year, the sum S of the normalized data for all ten stations is calculated.

ANMMRI $= 3\left(\frac{S}{10} - 1\right)$.

An average monsoon has ANMMRI = 0 and the arbitrary factor 3 is used to expand the numerical range of the index. Although values of our precipitation-based ANMMRI show little relationship to a broader regional index based on high-altitude parameters (Li, 2015), we prefer our simple index because it is tied directly to regional rainfall amounts. In all three monsoon indices, positive values correspond to more intense monsoons, i.e. higher-than-average precipitation over a broad region, a value of 0 is an average monsoon and negative values denote weak monsoons.

A comparison of the amount-averaged seasonal $\delta^{18}O$ at a particular site (New Delhi, Hong Kong and Tucson) to the monsoon indices in each region reveals a similar and unexpected pattern (Fig. 10). Extreme values of $\delta^{18}O$ are limited to monsoon indices <0. Ranges of $\delta^{18}O$ are narrow for monsoon indices >0, converging on a long-term mean between -6 and -8 ‰.

The relationship between monsoon intensity and seasonal mean $\delta^{18}O$ in rain at a particular site appears to be more complicated than the rain-out effect proposed by Liu et al. (2014). Monsoon seasons of greater or lesser intensity cannot be reliably distinguished according to the relationships shown in Fig. 10. The generation of low mean $\delta^{18}O$ by a large relative fraction of rain-out may indeed be one factor governing the mean $\delta^{18}O$ of rain at seasonal time-scale, *but in low-intensity rather than high-intensity monsoons*. Thus a large isotope effect resulting from rain-out in monsoon air masses (as indicated by more negative $\delta^{18}O$ values in that year's rains) may only occur when the air masses carry less water than occurs in average or unusually wet monsoons, those with indices near 0 or ≥0. Other factors, including evaporation of falling rain, also operate, so that low intensity monsoons may in some circumstances yield high seasonal mean $\delta^{18}O$ values.

8. Implications for hydrologic and climate reconstructions

Isotope data for precipitation at the four sites examined have large variances. Statistical treatments of the data can give different results according to the chosen time scale. So, while *monthly* amount effects, in the sense of Rozanski et al. (1993), are indeed present in the data from New Delhi and Hong Kong, this result does not extend to seasonal or multi-year time scales. In Tucson, for either winter or summer seasons, an amount effect is essentially absent at time scales from seasonal to decadal. Only at the Guam station (among the stations studied here) is there a defensible isotope-amount relationship, in this instance at the annual time scale.

A more complicated formulation of the amount effect involves a proposed relationship between site-specific seasonal $\delta^{18}O$ means (e.g. a cave location) and regional-scale isotope fractionation due to rain-out upwind of the site. This kind of amount effect was tested in preliminary fashion here using indices of monsoon intensity (based on integrated amounts of precipitation across broad monsoon regions in two cases, and monsoon circulation wind strength in a third). In all three regions

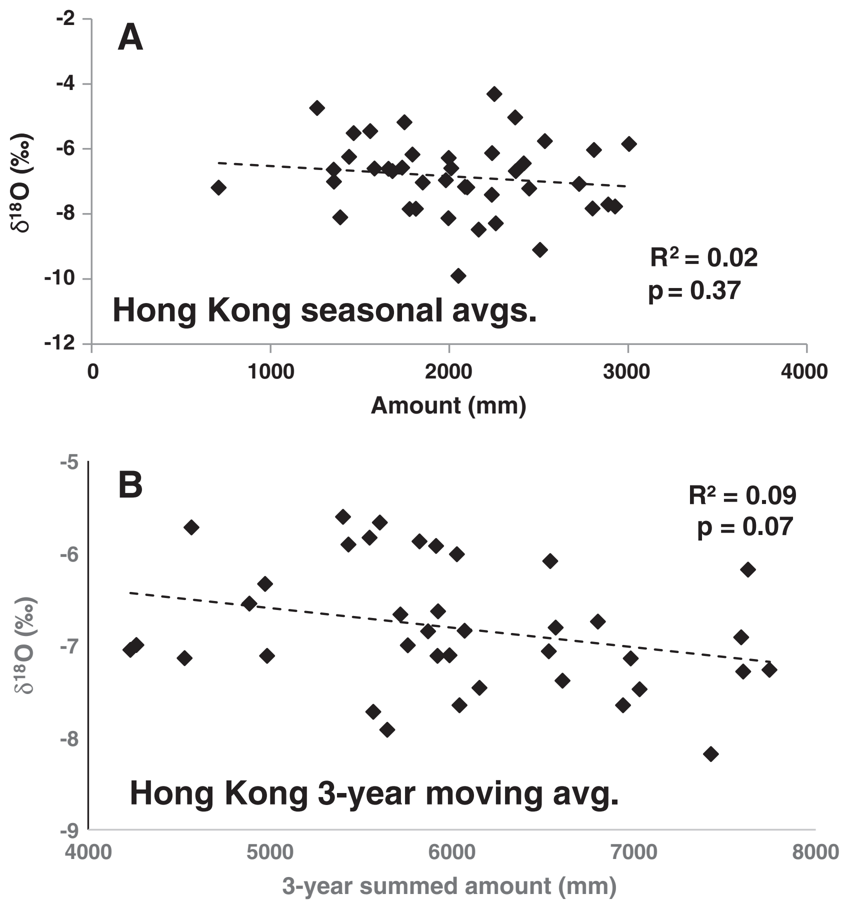

Fig. 8. Amount-weighted mean $\delta^{18}O$ for wet seasons (averaged between the first and last months with >100 mm of rain) vs. precipitation amount in Hong Kong. A. Seasonal means. B. Three-year running means. Data from International Atomic Energy Agency (2015).

the results suggest no interpretable relationship between monsoon intensity and the local isotope record (Fig. 10); further study is warranted as new long-term isotope data sets become available for other monsoon localities.

At the very least, the use of paleohydrologic proxies such as O isotopes in speleothem calcite requires an unambiguous answer to the question: is it possible to use stable isotopes to distinguish wetter and drier rainy seasons in a given location or region on an annual time scale? In most cases, it is even more useful to pose that question at decadal or longer time scales. Isotope records in precipitation are now long enough at several stations to permit a statistical analysis at the time scale of complete wet seasons or annual totals. Because data sets with poor correlation between isotopes and amount can still generate a

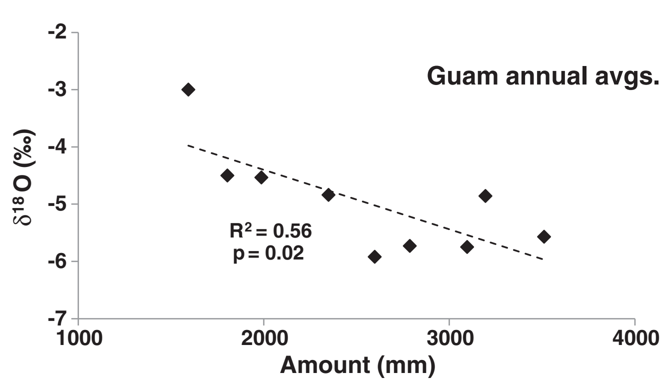

Fig. 9. Amount-weighted mean $\delta^{18}O$ vs. precipitation amount for individual years in Guam. Data from International Atomic Energy Agency (2015).

trend line, it would be much more useful to calculate confidence intervals for the relationships on which interpretations are based (e.g. Figs. 3 and 7).

Much rarer, commonly because of data gaps, are data sets that permit analysis on a decadal time scale. Variations at even longer time scales, which would be of most interest in paleohydrologic reconstruction, cannot be addressed at present, because no suitable data sets exist. Because of this, the importance of maintaining isotope observations in precipitation at a time of increasing climate change cannot be over-emphasized.

The poor expression of the isotope-amount effect at three observation sites, two of which have been cited as the basis of paleoclimate reconstructions (via the citation of Rozanski et al., 1993), is a serious issue for the interpretation of speleothem isotope data sets in south and east Asia and in southwestern North America. There is no doubt that speleothems preserve measurable signals of environmental change; however, the confidence with which an amount effect can be invoked when interpreting the data needs to be examined carefully. Multi-proxy approaches on longer time scales (e.g. Buckley et al., 2010) are more likely to yield robust results than studies relying exclusively on speleothem isotopes.

It is incumbent upon researchers who wish to interpret the O-isotope records of speleothems to demonstrate an effective climate – stable isotope relationship in the study area *at the appropriate time scale*. Although we have examined only four locations, this study raises concerns about amount effects at seasonal to decadal time scales in monsoon regions (Figs. 3, 7, and 8). Note, however, that this does not preclude the retrieval of useful information at, for instance, millennial time scales where global forcing phenomena may be reflected in speleothem records (Meyer et al., 2011; Liu et al., 2014; Pausata et al., 2011). As more records of isotopes in precipitation become available

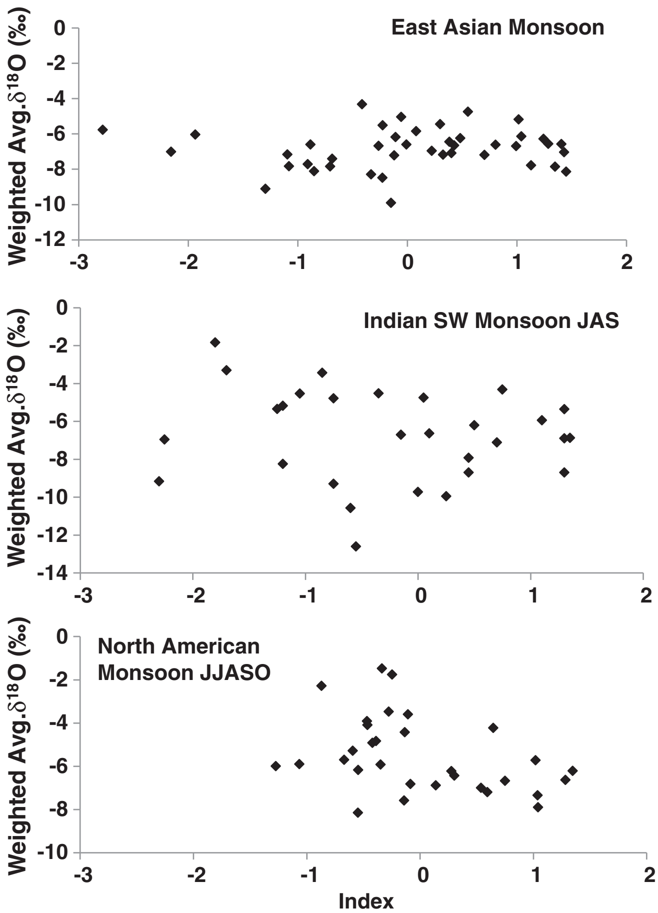

Fig. 10. Site-specific amount-weighted seasonal mean $\delta^{18}O$ vs. monsoon intensity index for East Asia (Hong Kong means vs. JJAS index of Wang et al., 2001 and School of Ocean and Earth Science and Technology, 2014), Indian SW Monsoon (New Delhi means vs. All India Rain index of Goswami et al., 2006) and North America (Tucson means vs. ANMMRI index described in text).

at decadal or longer time scales, these relationships can be tested across well quantified changes in climate. Alternatively, models of atmospheric responses to climate variation that incorporate stable isotope tracers can be used to test long term isotopic responses to climate change, although models have their own associated uncertainties. The latter approach is necessary when examining century scale or longer shifts in climate patterns that may be reflected in speleothem records. Whichever method is used to test isotopic responses to climate changes, the relationship must be significant in the contexts of natural variance and analytical statistics. While useful amount effects do not exist at some locations for which they have been claimed (Hong Kong, New Delhi and Tucson), there are other stations where useful relationships do in fact exist (e.g. Cruz et al., 2005). In the case of Guam (Kurita et al., 2009, Partin et al., 2012), published interpretations are based on short-term isotope and amount data with considerable scatter, but the annual averages presented here (Fig. 9) suggest that a relationship exists at an annual time scale.

To conclude this discussion, we return to the Cave of the Bells speleothem record, close to Tucson. An oxygen isotope data-set spanning 12,000 years reveals $\delta^{18}O$ variation with an amplitude of 3‰ (Wagner et al., 2010). What might explain the changes in $\delta^{18}O$ if they are not due to a correlation between $\delta^{18}O$ and precipitation amount at seasonal or longer time scales? The $\delta^{18}O$ shifts include a stepwise change of about 2.5‰ between 15 and 14 Ka, and a cyclic pattern with an amplitude of about 1.5‰ between 14 and 11 Ka. The stepwise shift could represent the change in $\delta^{18}O$ observed globally in precipitation (preserved as groundwater that has been dated) at the end of the Pleistocene (Clark and Fritz, 1997, pp. 198–200). Possibilities for explaining the later cyclic variations include:

1. Changes in the ratio of summer to winter precipitation. Local climate alternated between the present state (about equal summer and winter precipitation, but recharge dominated by winter) and one with mostly summer rain. The source of drip water in the latter state would shift toward summer recharge, even if only a little of the summer precipitation was able to infiltrate.
2. Changes in the amount of precipitation from tropical cyclonic weather systems, which at present deliver low – $\delta^{18}O$ rainwater in the fall in southern Arizona (Eastoe et al., 2015).
3. Increasing frequency of extreme precipitation events. Our data for individual events (Supplementary Fig. 1) show that large events, both in winter and in summer, tend toward average $\delta^{18}O$ values. Assuming the past to resemble the present in this respect, this possibility cannot explain the cyclic speleothem data. However, an increased frequency of outlier winter seasons with very low average $\delta^{18}O$, like that in 1994–1995 (Fig. 3), could contribute to such a signal. With only one example, we cannot predict whether such seasons are generally associated with high precipitation amount.

Similar explanations may apply in other regions.

9. Conclusions

a. Isotope amount effects are weak to non-existent at time-scales ranging from seasons to decades in a 32-year dataset for precipitation in Tucson, Arizona. Such weak effects as exist could not be used to discriminate between wet and dry time intervals.
b. Although a significant correlation between rainfall amount and the $\delta^{18}O$ of rainfall exists for summer rains on an annual basis in Tucson, variance in the data prevents the use of $\delta^{18}O$ values to calculate rainfall amounts or to reliably classify seasons as wetter or drier than average.
c. At New Delhi and Hong Kong, stations commonly cited as good examples of isotope amount effects, these effects are weak to non-existent at the time scales of individual wet seasons.
d. Guam precipitation appears to give a useful amount effect at an annual time scale.
e. Isotope amount effects exist and are useful for paleoclimate reconstruction in certain regions (Cruz et al., 2005; Partin et al., 2012), but our data show that they cannot be assumed in all warm monsoon settings. Our observations suggest pitfalls in extrapolating long-term "isotope effects" from short-term precipitation datasets. In particular, our analysis poses serious questions for paleoclimate studies in which precipitation amount is inferred from speleothem isotope data, e.g. in East and South Asia and Southwestern North America.
f. A preliminary investigation of the relationship between regional precipitation amounts in monsoonal rain regimes, i.e. "monsoon intensity", and site-specific isotope records shows little promise of effective relationships. Notably, extreme $\delta^{18}O$ values (both high and low) are limited to weaker-than-average monsoon years.
g. Continued acquisition of long-term stable isotope data in precipitation from sites undergoing climate change will be important for evaluation of the relationship between isotopes and climatic phenomena.

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