The Holocene
http://hol.sagepub.com/

Speleothem records of changes in tropical hydrology over the Holocene and possible implications for atmospheric methane

Stephen J. Burns

The Holocene published online 21 March 2011
DOI: 10.1177/0959683611400194

The online version of this article can be found at:
http://hol.sagepub.com/content/early/2011/03/12/0959683611400194

Published by:
SAGE
http://www.sagepublications.com

Additional services and information for *The Holocene* can be found at:

Email Alerts: http://hol.sagepub.com/cgi/alerts

Subscriptions: http://hol.sagepub.com/subscriptions

Reprints: http://www.sagepub.com/journalsReprints.nav

Permissions: http://www.sagepub.com/journalsPermissions.nav

Holocene Special Issue

The Holocene
1–7

DOI: 10.1177/0959683611400194
hol.sagepub.com
SAGE

Speleothem records of changes in tropical hydrology over the Holocene and possible implications for atmospheric methane

Stephen J. Burns
University of Massachusetts, USA

Abstract
Recent speleothem records from the tropics of both hemispheres document a gradual decrease in the intensity of the monsoons in the Northern Hemisphere and increase in the Southern Hemisphere monsoons over the Holocene. These changes are a direct response of the monsoons to precession-driven insolation variability. With regard to atmospheric methane, this shift should result in a decrease in Northern Hemisphere tropical methane emissions and increase in Southern Hemisphere emissions. It is plausible that that overall tropical methane production experienced a minimum in the mid-Holocene because of decreased seasonality in rainfall at the margins of the tropics. Changes in tropical methane production alone might, therefore, explain many of the characteristics of Holocene methane concentrations and isotopic chemistry.

Keywords
Holocene, hydrology, methane, oxygen isotopes, speleothems, tropical

Introduction

Over the past several glacial–interglacial cycles atmospheric methane concentrations have varied in concert with the 20 ky precession cycle in Earth's orbit, and in particular with Northern Hemisphere summer insolation (Brook et al., 1996; Chappellaz et al., 1990). This correlation is attributed to a strong influence of the summer monsoons in the Northern Hemisphere on tropical wetland methane emissions (Brook et al., 1996; Chappellaz et al., 1990; Loulergue et al., 2008).

In contrast to most previous interglacials, however, an increase in atmospheric methane concentrations is observed during the latter half of the Holocene. Chappellaz et al. (1997) proposed that changes in tropical wetland emissions were largely responsible for these changes in methane concentrations. They suggested that the broad minimum in methane concentration is the result of decreased tropical emissions (Chappellaz et al., 1997). Ruddiman (2003) offered an alternative explanation for the rise in methane (and CO_2) over the past 5 ky: the 'early anthropogenic hypothesis' proposed that early civilization began affecting atmospheric trace gases as long ago as the mid Holocene. This hypothesis has been the source of considerable lively debate in the recent literature (e.g. Broecker and Stocker, 2006; Masson-Delmotte et al., 2006; Ruddiman, 2005, 2007; this issue). A third explanation of the observed pattern is changes in the sink term for atmospheric methane (Reeburgh, 2004).

As yet, no strong consensus has emerged regarding the validity of the 'early anthropogenic hypothesis' or the alternatives. Because topical wetlands are by far the largest natural source of methane (Aselmann and Crutzen, 1989) even modest changes in the tropical hydrologic cycle may result in large changes in methane concentration. It remains reasonable, therefore, that changes in the hydrology of the tropics alone are responsible for most of the observed changes in methane during the Holocene. Here, I summarize recent results of studies in tropical hydrology over the Holocene, with a focus on the monsoons, which come largely from work done on speleothems (locations shown in Figure 1). Speleothems are a near ideal recorder of changes in monsoon intensity and location over the course of the Holocene. They generally have excellent chronological control and the primary climate proxy in speleothems, the oxygen isotope ratios of speleothem calcite, is directly and strongly influenced by monsoon intensity.

How do speleothems record changes in the monsoon?

The term 'monsoon' was originally used to denote a region of seasonally reversing winds and accompanying large changes in seasonal precipitation with very wet summers and generally dry winters. Use of the word in meteorological literature has evolved to more broadly describe large-scale, seasonal changes in atmospheric circulation and precipitation regardless of whether the wind field reverses (Trenberth et al., 2000). The monsoon regions of the world are roughly coincident with regions classified as having a 'tropical moist climate': most of tropical South America and Africa, Asia and Australia, and Indonesia. In all of these areas,

Received 11 June 2010; revised manuscript accepted 4 November 2010

Corresponding author:
Stephen J. Burns, Department of Geosciences, 611 N. Pleasant Street, University of Massachusetts, Amherst MA 01003, USA
Email: sburns@geo.umass.edu

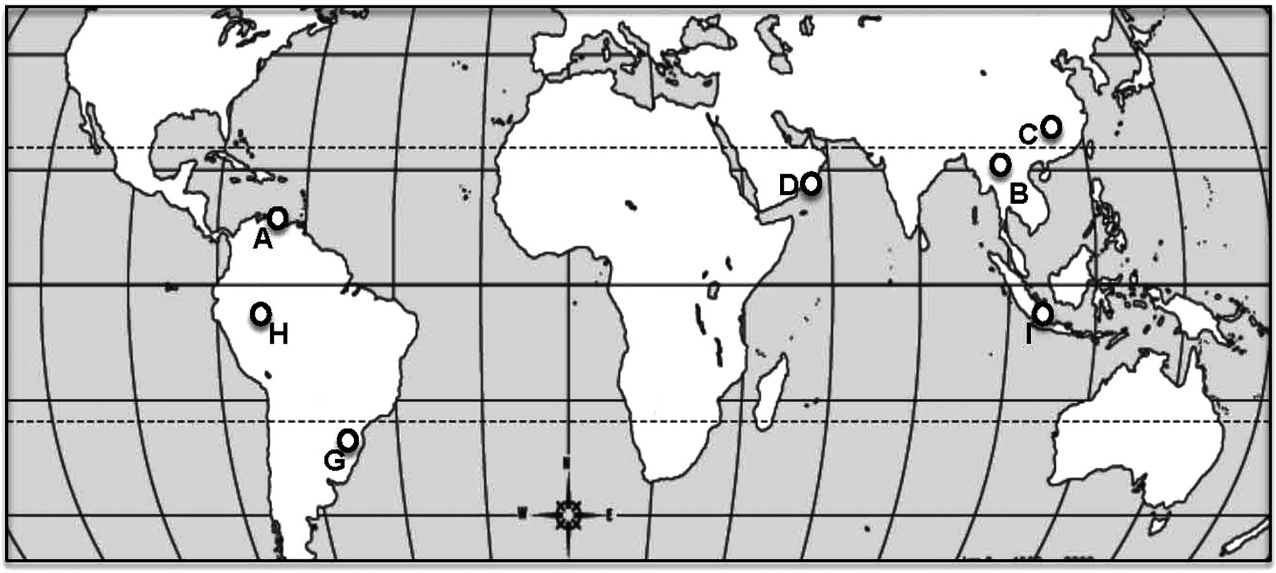

Figure 1. Location map of speleothem sites presented in Figure 2. Letters correspond to sites identified in Figure 2 caption

rainfall is primarily associated with summer heating of a land mass that initiates monsoonal circulation – moisture is drawn inland from adjacent oceans, is warmed and convected high into the atmosphere. Latent heating associated with monsoon rainfall leads to further atmospheric heating and drives deeper convection and yet more intense rainfall (Trenberth et al., 2000).

Because of the association of the amount of rainfall with the intensity of convection and degree of rainout, the stable isotopes of precipitation are excellent potential recorders of the intensity of monsoon rainfall. An empirical relationship between the amount of rainfall and the stable isotope ratios of precipitation, the 'amount effect', has long been recognized (Dansgaard, 1964; Rozanski et al., 1993). Dansgaard proposed that the amount effect results from three processes: (1) intense precipitation results in a high degree of rainout of convecting moisture, leading to a large isotopic depletion of precipitation, (2) isotopic re-equilibration of falling rain with atmospheric moisture below cloud base is less for the large raindrops associated with intense precipitation, and (3) during intense precipitation there is less evaporative enrichment of raindrops falling through the atmosphere below cloud base (Dansgaard, 1964). Rozanski et al. (1993) added an additional process – during prolonged intense precipitation the water vapor below cloud base becomes progressively isotopically depleted because of exchange with falling raindrops that themselves are quite depleted, thereby limiting isotopic enrichment during re-equilibration of falling raindrops (Rozanski et al., 1993). Recent model simulations of the amount effect largely confirm that these processes are important and suggest that the latter two are dominant (Bony et al., 2008; Lee and Fung, 2007; Risi et al., 2008). In addition, Risi et al. (2008) found that as the moisture in the atmosphere below the cloud base becomes more isotopically depleted over the course of prolonged intense rainfall, this now depleted moisture becomes a source of more depleted water vapor feeding the convecting system, resulting in further isotopic depletion of the entire system. Finally, Risi et al. (2008) note that the amount effect is best expressed at timescales of several tens of days or longer, timescales for which the amount effect can explain up to 90% of isotopic variance in their model.

With regard to speleothem studies it is important to note that the above-mentioned modeling studies are one-dimensional models that, at best, would be applicable to interpreting speleothems studies from near-coastal sites (Lee and Swann, 2010). For sites more distant from an oceanic moisture source, the isotopic composition of rainfall may also be affected by moisture source and transport and degree of upstream rainout that can precondition the water vapor advected to particular site (Sturm et al., 2007; Vimeux et al., 2005; Vuille et al., 2003a, b). For example, Vuille et al. (2003b) have shown that in the South American Monsoon System increased precipitation along a moisture transport pathway will result in a more isotopically depleted moisture source for local convection. Thus, the isotopes of local rainfall will reflect not only the intensity of local rainfall, but also be an integrative measure of the intensity of rainfall all along the moisture transport pathway. Thus, while the isotopes of rainfall in monsoon regions distant from the ocean may not be ideal indicators of local rainfall amount, they are probably even better indicators of overall changes in monsoon intensity. And while there certainly are parts of the tropics where additional influences on the isotopic composition of monsoon rainfall beyond an amount effect need to be considered, nearly all studies of the isotopic composition of tropical rainfall have concluded than the amount effect is of primary importance.

For monsoon systems and rainfall associated with deep convection such as the monsoons or ITCZ, the amount effect makes the isotopes of precipitation excellent recorders of changes in monsoon intensity. But can we be sure that speleothems reliably record temporal changes in $\delta^{18}O$ of rainfall? A number of other factors may influence the isotopic composition of speleothems calcite, for example the oxygen isotopic fractionation between water and calcite is temperature dependent. Evaporation of water in the epikarst or within the cave could result in enrichment prior to calcite precipitation and kinetic isotope effects can lead to non-equilibrium precipitation (Hendy, 1971).

For the consideration of speleothem isotopes in tropical regions over the Holocene, temperature is unlikely to be an important influence on speleothem $\delta^{18}O$. Temperature has likely varied by 2°C or less in the tropics over the past 10 ky (Mayewski, 2004), which would at maximum cause about a 0.5‰ variation on speleothem $\delta^{18}O$. Karst areas, almost by definition, usually have rapid infiltration of groundwater into the karst system and evaporation of water in the epikarst is generally minimal (McDermott et al., 1999). Evaporation could also occur in the cave if exchange of cave air with the outside atmosphere is too rapid. But these effects are avoidable by choosing sampling sites of high relative humidity that are distant from cave entrances (McDermott et al., 1999).

Kinetic isotope effects, caused by rapid CO_2 degassing of cave drip waters, are the most likely source of non-equilibrium precipitation, and they have been noted in several studies of modern speleothems (Mickler et al., 2004). Recent work using the 'clumped isotope' technique, in fact, suggests that most or all speleothems are precipitated under non-equilibrium conditions (Affek et al., 2008; Daëron et al., 2011). While this result might seem to preclude using speleothems in paleoclimate studies, such is not the case. For one, the magnitude of the kinetic isotope effect for speleothem calcite growing under natural conditions near the growth axis is in nearly all cases less than 1‰ (McDermott et al., 1999; Spötl and Mangini, 2002). Furthermore, by taking samples for oxygen isotope time series within a centimeter of the vertical growth axis under drips with a relatively fast drip rate (< 50 s), the kinetic effect can be limited to less than a few tenths of a per mille (Dreybrodt, 2008; Wiedner et al., 2008) . In comparison, variability in $\delta^{18}O$ in speleothems is often 4 or 5‰ or more, most of this variability must then be driven by changes in $\delta^{18}O$ of rainfall and be climatic in origin.

Perhaps the ultimate test of whether any of the processes mentioned could systematically prevent speleothem $\delta^{18}O$ from recording changes in $\delta^{18}O$ of precipitation is reproducibility of the isotopic time series of speleothem $\delta^{18}O$. In any number of studies this type of test has been done. For example, Dykoski et al. (2005) show a remarkable coherence of the deglacial isotopic records from speleothems from Hulu and Dongge Caves. The composite record of speleothems from Sanbao Cave contains several samples that overlap for most of the Holocene with excellent reproducibility (Dong et al., 2010). In Botuvera Cave Holocene records from and Cruz et al. (2005) and Wang et al. (2006) also show excellent reproducibility. It seems highly unlikely that the kinetic or evaporative effects on speleothems growing in different sites within a cave or even from different caves would serendipitously yield nearly identical isotopic records. The excellent reproducibility of isotopic time series from speleothem to speleothem within a particular region is a strong indicator that temporal changes in the isotopic composition of rainfall are faithfully recorded in speleothem calcite.

Holocene speleothem records from the Northern and Southern Hemisphere tropics

Figure 2 presents four time series of data that have been interpreted as proxies for monsoon intensity and mean ITCZ location in the Northern Hemisphere: (A) sediment Ti concentrations from the Cariaco Basin (Haug et al., 2001), and speleothem $\delta^{18}O$ records from (B) Sanbao Cave (Dong et al., 2010) in east-central China, (C) Dongge Cave in southeast China (Dykoski et al., 2005; Wang et al., 2005), and (D) Qunf Cave in southern Oman (Fleitmann et al., 2003). These records are thus representative of changes in tropical hydrology for the Northern Hemisphere portion of the South American Summer Monsoon (SASM), the Indian Summer Monsoon (ISM) and the East Asian Summer Monsoon (EASM). Plotted just below these records (Figure 2E) is the July insolation curve for 10°N.

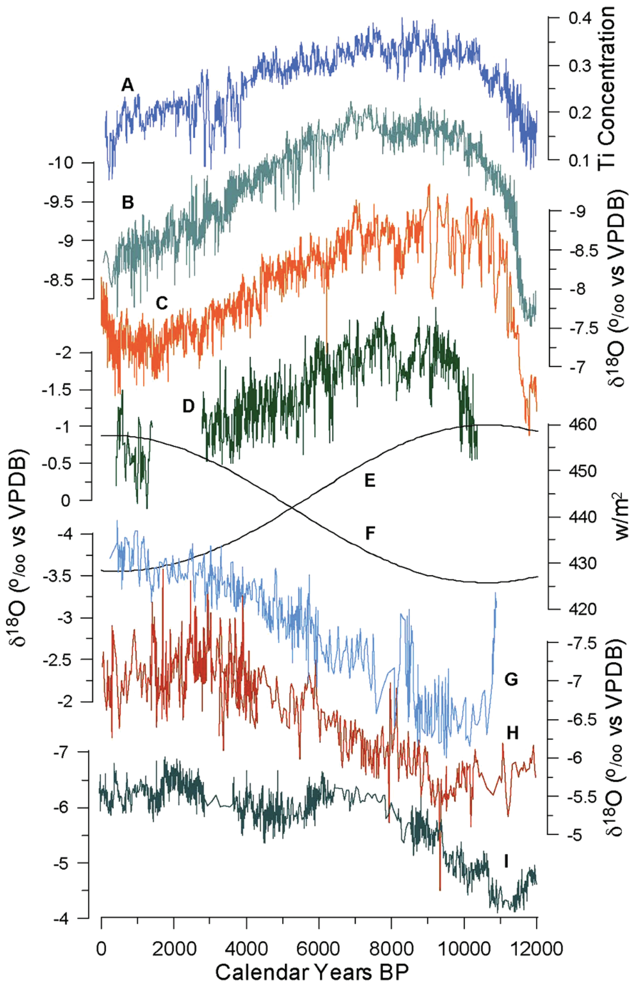

Figure 2. Paleoclimate records of changes in tropical hydrology over the Holocene and summer insolation. With the exception of (A), all are speleothem $\delta^{18}O$ records. (A) Cariaco Basin Ti (Haug et al., 2001); (B) Sanbao Cave, southern China (Dong et al., 2010); (C) Dongge Cave, central China (Dykoski et al., 2005; Wang et al., 2005); (D) Qunf Cave, southern Oman (Fleitmann et al., 2003); (E) and (F) insolation curves for July at 10°N and January at 10°S, respectively; (G) Botuvera Cave, southeastern Brazil (Wang et al., 2006); (H) Cueva del Tigre Perdido, eastern Peruvian lowlands (van Breukelen et al., 2008); (I) Liang Luar Cave, Indonesia (Griffiths et al., 2009)

Table 1. Location of sites discussed in the text

Location	Latitude	Longitude	Reference
Cariaco Basin	9.5°N	65°W	Haug et al. (2001)
Sanbao Cave	31.4°N	110.3°E	Dong et al. (2010)
Dongge Cave	25.2°N	108.5°E	Wang et al. (2005); Dykoski et al. (2005)
Qunf Cave	17.1°N	58.2°E	Fleitmann et al. (2003)
Botuvera Cave	27.1°S	49.1°W	Wang et al. (2006)
Cueva del Tigre Perdido	6.9°S	78.3°W	van Breukelen et al. (2008)
Liang Luar Cave	8.3°S	120.3°E	Griffiths et al. (2009)

For the Cariaco record, Ti concentration is interpreted as a proxy for continental runoff and therefore rainfall in the Northern Hemisphere part of South America (Haug et al., 2001). As discussed above, the $\delta^{18}O$ records from the speleothems are also proxies for rainfall, with $\delta^{18}O$ being inversely related to amount. All of these records show a very similar overall pattern. Once full interglacial conditions are reached, there is a maximum in monsoon intensity during the early Holocene, from ~10 to ~ 6 ky BP, with a gradual decrease in monsoon strength thereafter. Each of the proxy data sets parallels the summer insolation quite well.

For all of these data, a similar interpretation was made: As summer insolation decreases in response to the precession cycle of the Earth's orbit, the sensible heat component of the monsoons decreases, driving a decrease in overall monsoon intensity and rainfall. Several additional speleothem studies confirm this general interpretation for the ISM and EASM regions, including work from Hoti Cave in northern Oman (Burns et al., 2001; Fleitmann et al., 2007; Neff et al., 2001), Hulu Cave in China (Wang et al., 2001) and Heshang Cave in China (Hu et al., 2008).

The only monsoon region not represented by the data in Figure 2 is the African monsoon. To date, no speleothem studies from tropical Africa cover the Holocene. The Lateglacial to early-Holocene North African Humid Period, however, has long been recognized from lake studies (Gasse, 2000 and references therein). While there is evidence of an abrupt drying of parts of north equatorial Africa (deMenocal et al., 2000), recent sediment geochemical studies of Lake Yoa in Chad (Kröpelin et al., 2008) Jikariya Lake in Nigeria (Waller et al., 2007; Wang et al., 2008), marine Ba/Ca records of runoff of the Niger river (Weldeab et al., 2007) and geochemical studies, including δD of leaf waxes, of continental margin sediments off of Senegal (Niedermeyer et al., 2010) suggest a gradual reduction in available moisture that, as with the records from the ISM and EASM, parallels decreasing summer insolation in the Northern Hemisphere over the Holocene. Thus, a gradual decrease in the Northern Hemisphere part of the African Monsoon over the Holocene is well supported by paleoclimate records.

Figure 2 also shows data from three speleothem records from the Southern Hemisphere: (G) Botuvera Cave, southeastern Brazil (Wang et al., 2006), (H) Cueva del Tigre Perdido in the eastern Peruvian lowlands of the Amazon Basin (van Breukelen et al., 2008), and (I) Liang Luar Cave, Indonesia (Griffiths et al., 2009). Just above these records is the January insolation curve for 10°S (Figure 2). The pattern of change in the isotopic ratios of these three speleothem records is very similar, with more enriched values in the early Holocene and gradually decreasing values into the middle and late Holocene. The records from South America are interpreted as indicating a gradual strengthening of the SASM in the Southern Hemisphere over the Holocene in response to increasing summer insolation. The record from Indonesia is complicated somewhat by the effects of sea level rise inundating the shallow Sunda shelf, which provides a moisture source for much of the Indonesian and Australian monsoon (Griffiths et al., 2009). Nevertheless, the record indicates an increase in monsoon intensity over the Holocene.

Again, there is ample supporting evidence for this interpretation from other archives. In South America isotopic studies of the Huascaran and Sajama ice cores from the Andes (Thompson et al., 1995, 1998), additional speleothem work from Botuvera cave (Cruz et al., 2005), oxygen isotopic data from carbonate sediments in Lake Junin on the Altiplano of Peru (Seltzer et al., 2000), and lakes in the southern Amazon Basin (Mayle et al., 2000) all show increasing monsoon precipitation over the course of the Holocene as the SASM strengthens.

More limited data from the Southern Hemisphere tropics in Africa suggest a similar pattern. The Kilimanjaro ice core record, though not well dated, covers most of the Holocene (Thompson et al., 2002). Measurements of $\delta^{18}O$ of the ice show a decrease of several per mille in the mid Holocene, suggesting an increase in precipitation (Thompson et al., 2002). Similarly, Holocene sediment records from Lake Challa (Verschuren et al., 2009), Lake Rukwi (Thevenon et al., 2002) and Lake Malawi (Castañeda et al., 2007) all show a relatively dry early Holocene in comparison with a wetter late Holocene. At Lake Malawi, this change is attributed to southward migration of the ITCZ and an increase in summer monsoon rainfall (Castañeda et al., 2007). At the more equatorial sites of Challa and Rukwi, which both have two rainy seasons per year, the change from a drier early Holocene to a wetter late Holocene cannot be simply attributed to strengthening of a single summer wet season in response to increased summer insolation (Verschuren et al., 2009). Nevertheless the Holocene climatic pattern is similar to that from Lake Malawi, with, for example relative drought at Challa from 8.5 to 4.5 ky BP and moist conditions since 4.5 ky BP (Verschuren et al., 2009).

To summarize, Holocene speleothem records from the monsoon regions of the tropics, supported by an array of other paleoclimate records, demonstrate a southward migration of the belt of tropical precipitation over the Holocene. The Northern Hemisphere monsoons, particularly at the margins of the tropical rainfall belt have become progressively weaker, while the Southern Hemisphere monsoons, again particularly along their southern margins, have intensified. These changes are a response to the southward shift in maximum summer insolation driven by changes in the precessional component of Earth's orbit.

Possible implications for Holocene methane record

What might be the implications of the southward migration of the belt of tropical precipitation for atmospheric methane concentrations over the Holocene? Methane emissions from natural wetlands primarily depend on three factors: soil temperature, water-table depth and ecosystem productivity (Cao et al., 1996; Kaplan et al., 2006; Walter and Heimann, 2000; Whiting and Chanton, 1993). In tropical wetlands, emissions are highly seasonal, maximizing during summer in both hemispheres (Aselmann and Crutzen, 1989). A recent comparison of satellite-based measurements of atmospheric CH_4, temperature and gravity anomalies (a proxy for water-table depth) show that for the tropics water-table depth is the most important factor in controlling methane emissions (Bloom et al., 2010). Between 40 and 80% of the observed variability in CH_4 measurements over the tropics could be explained by water-table variations alone, and generally higher correlations between methane emissions and water-table depth were found in areas with distinctly seasonal rainfall (Bloom et al., 2010). For tropical wetlands over the course of the Holocene temperature change was minimal and temperature likely played a subordinate role to changes in water-table depth.

The southward shift in mean ITCZ location, weakening of the monsoons in the Northern Hemisphere and strengthening of the monsoons in the Southern Hemisphere, as outlined above, should lead to a decrease in Northern Hemisphere methane emissions and concomitant increase in emissions from the Southern Hemisphere tropics. An increase in late-Holocene, Southern Hemisphere tropical methane emissions is supported by two other pieces of evidence: the decrease in the interpolar gradient in methane from the mid to late Holocene (Brook et al., 1996; Chappellaz, 1997) and the increase in the hydrogen isotope ratio of methane (Sowers, 2009) over the same time period (Sowers, 2009). But a southward shift in the locus of tropical methane production need not lead to the U-shaped curve in methane concentrations observed over the Holocene.

Two other factors, however, suggest mechanisms by which the changes in tropical hydrology indicated by speleothem and other paleoclimate records might have impacted the temporal trend in atmospheric methane. First, recent studies of methane emissions in the tropics show that emissions are higher in wetland that have a strong seasonal cycle in precipitation than in wetland that are continually wet (Mitsch et al., 2009). In wetlands in Costa Rica, those with a strong seasonal cycle of rainfall had annual methane emission rates up to four times higher than continually flooded wetlands (Mitsch et al., 2009; Nahlik and Mitsch, 2010). The higher rates of methane emissions in seasonally flooded areas were observed in spite of lower annual precipitation than continually flooded wetlands.

One way that the precession-driven changes in the relative strengths of the monsoons might impact methane is by changing the degree of seasonality in precipitation, particularly at the margins of the tropics. During the mid Holocene, the maximum in summer solar insolation was approximately equal in both hemispheres and was lower than the maximum in the Northern Hemisphere in the early Holocene and than the maximum in the Southern Hemisphere today (Berger and Loutre, 1991). Thus, it might be expected that the margins of the tropics experienced the lowest seasonality in rainfall during the mid Holocene resulting in reduced tropical methane emissions. At 10 ky BP and today, the Northern Hemisphere and Southern Hemisphere tropics would have seen higher annual variability in insolation and, given the near linear response of the monsoons to insolation, a correspondingly higher degree of seasonality of rainfall. These changes in seasonality might lead to a minimum in tropical methane emissions in the mid Holocene and maxima during the early and late Holocene.

A southward shift in the monsoons might also help explain the Holocene methane record if the latitudinal distribution of tropical wetlands is not symmetrical about the equator, but is weighted toward the Southern Hemisphere. Most estimates of the global distribution of wetland area today suggest a somewhat greater extent of wetlands in the Southern Hemisphere tropics than in the Northern Hemisphere (Lehner and Döll, 2004 and references therein). Wetland location algorithms that estimate wetland area by applying thresholds for soil moisture and temperature on a monthly basis also suggest that wetland area and methane emissions are slightly greater for the pre-industrial Holocene Southern Hemisphere tropics than Northern Hemisphere (Weber et al., 2010). These results are perhaps to be expected given the present-day maximum of insolation and monsoon intensity is in the Southern Hemisphere. A more pertinent comparison would be between the extent of Northern Hemisphere tropics in the early Holocene (necessarily model based) and the Southern Hemisphere tropics today. But considering that there is still no general agreement on even the modern distribution of wetlands and methane emissions, it is questionable whether such a comparison could ever be quantitative enough to confidently address whether the southward shift in the monsoons also resulted in a net increase in tropical methane emissions.

An argument against the hypothesis outlined above is that if it were valid, then methane concentrations during previous interglacial periods should display a temporal trend similar to the Holocene. And, in fact, during most prior interglacial periods methane concentrations peak and then steadily decrease in marked contrast to the Holocene (Loulergue et al., 2008; Spahni et al., 2005). During the long MIS 11 interglacial, however, which is often considered an analog to the Holocene, methane concentrations do show a second maximum after a decrease from an initial maximum (Loulergue et al., 2008), a pattern quite similar to the Holocene. A somewhat similar pattern is also present during MIS 19 (Loulergue et al., 2008; Tzedzakis, 2010). Thus, while most previous interglacial periods do not show a second maximum in methane concentrations, the two that are perhaps the most similar to the Holocene do.

To conclude, recent speleothem data from the tropics of both hemispheres document a gradual decrease in the intensity of the monsoons in the Northern Hemisphere and increase in the Southern Hemisphere monsoons over the Holocene. These changes are a direct response of the monsoons to precession-driven insolation variability. With regard to atmospheric methane, this shift should result in a decrease in Northern Hemisphere tropical methane emissions and increase in Southern Hemisphere emissions. It is plausible that that overall tropical methane production experienced a minimum in the mid Holocene because of decreased seasonality in rainfall at the margins of the tropics. Changes in tropical methane production alone might, therefore, explain many of the characteristics of Holocene methane concentrations and isotopic chemistry.

References

Affek H, Bar-Mathews M, Ayalon A, Mathews A and Eiler J (2008) Glacial/interglacial temperature variations in Soreq cave speleothems as recorded by 'clumped isotope' thermometry. *Geochimica et Cosmochimica Acta* 72: 5351–5360.

Aselmann I and Crutzen PJ (1989) Global distribution of natural freshwater wetlands and rice paddies, their net primary productivity, seasonality and possible methane emissions. *Journal of Atmospheric Chemistry* 8: 307–358.

Berger A and Loutre MF (1991) Insolation values for the climate of the last 10 million years. *Quaternary Science Reviews* 10: 297–317.

Bloom AA, Palmer PI, Fraser A, Reay D and Frankenberg C (2010) Large-scale controls of methanogenesis inferred from methane and gravity spaceborne data. *Science* 327: 322–325.

Bony S, Risi C and Vimeux F (2008) Influence of convective processes on the isotopic composition ($d^{18}O$ and dD) of precipitation and water vapor in the tropics: 1. Radiative-convective equilibrium and Tropical Ocean–Global Atmosphere–Coupled Ocean–Atmosphere Response Experiment (TOGA-COARE) simulations. *Journal of Geophysical Research* 113: D19305, doi:10.1029/2008JD009942.

Broecker WS and Stocker TF (2006) The Holocene CO_2 rise: anthropogenic or natural? *EOS Transactions* 87: 27 (doi:10.1029/2006EO030002).

Brook E, Sowers T and Orchardo J (1996) Rapid variations in atmospheric methane concentration during the past 110,000 years. *Science* 273: 1087–1091.

Burns SJ, Fleitmann D, Matter A, Neff U and Mangini A (2001) Speleothem evidence from Oman for continental pluvial events during interglacial periods. *Geology* 29: 623–626.

Cao M, Marshall S and Gregson K (1996) Global carbon exchange and methane emissions from natural wetlands: Application of a process-based model. *Journal of Geophysical Research* 101: 14 399–14 414.

Castañeda IS, Werne JP and Johnson TC (2007) Wet/arid phases in the southeast African tropics since the Last Glacial Maximum. *Geology* 35: 823–826.

Chappellaz J, Barnola J-M, Raynaud D, Korotkevich YS and Lorius C (1990) Atmospheric CH_4 record over the last climatic cycle revealed by the Vostok ice core. *Nature* 345: 127–131.

Chappellaz J, Blunier T, Kints S, Dallenbach A, Barnola J-M, Schwander J et al. (1997) Changes in the atmospheric CH_4 gradient between Greenland and Antarctica during the Holocene. *Journal of Geophysical Research* 102: 15 987–15 998.

Cruz FW, Jr, Burns BJ, Karmann I, Sharp WD, Vuille M, Cardoso AO et al. (2005) Insolation-driven changes in atmospheric circulation over the past 116 000 years in subtropical Brazil. *Nature* 434: 63–66.

Daëron M, Guo W, Eiler J, Genty D, Blamart D, Boch R et al. (2011) $^{13}C^{18}O$ clumping in speleothems: Observations from natural caves and precipitation experiments. *Geochimica et Cosmochimica Acta*, in press.

Dansgaard W (1964) Stable isotopes in precipitation. *Tellus* 16: 436–468.

deMenocal PB, Ortiz J, Guilderson T, Adkins J, Sarnthein M, Baker L et al. (2000) Abrupt onset and termination of the African Humid Period: Rapid climate response to gradual insolation forcing. *Quaternary Science Reviews* 19: 347–361.

Dong J, Wang Y, Cheng H, Hardt B, Edwards RL, Kong X et al. (2010) A high-resolution stalagmite record of the Holocene East Asian monsoon from Mt Shennongjia, central China Jinguo. *The Holocene* 20: 257–264 DOI: 10.1177/0959683609350393.

Dreybrodt W (2008) Evolution of the isotopic composition of carbon and oxygen in a calcite precipitating $H_2O–CO_2–CaCO_3$ solution and the related isotopic composition of calcite in stalagmites. *Geochimica et Cosmochimica Acta* 72: 4712–4724.

Dykoski CA, Edwards RL, Cheng H, Yuan DX, Cai YJ, Zhang ML et al. (2005) A high-resolution, absolute-dated Holocene and deglacial Asian monsoon records from Dongge cave, China. *Earth Planetary Science Letters* 233: 71–86.

Fleitmann D, Burns SJ, Mangini A, Mudelsee M, Kramers J, Villa I et al. (2007) Holocene ITCZ and Indian monsoon dynamics recorded in stalagmites from Oman and Yemen (Socotra). *Quaternary Science Reviews* 26: 170–188.

Fleitmann D, Burns SJ, Mudelsee M, Neff U, Kramers J, Mangini A et al. (2003) Holocene forcing of the Indian monsoon recorded on a stalagmite from southern Oman. *Science* 300: 1737–1739.

Gasse F (2000) Hydrological changes in the African tropics since the Last Glacial Maximum. *Quaternary Science Reviews* 19: 189–211.

Griffiths ML, Drysdale RN, Gagan MK, Zhao J-X, Ayliffe LK, Hellstrom JC et al. (2009) Increasing Australian–Indonesian monsoon rainfall linked to early Holocene sea-level rise. *Nature Geoscience* 2: 636–639.

Haug GH, Hughen KA, Sigman DM, Peterson LC and Rohl U (2001) Southward migration of the intertropical convergence zone through the Holocene. *Science* 293: 1304–1308.

Hendy CH (1971) The isotopic geochemistry of speleothems-I. The calculation of the effects of different modes of formation on the isotopic composition of speleothems and their applicability as palaeoclimatic indicators. *Geochimica et Cosmochimica Acta* 35: 801–824.

Hu CY, Henderson GM, Huang JH, Xie SC, Sun Y and Johnson KR (2008) Quantification of Holocene Asian monsoon rainfall from spatially separated cave records. *Earth and Planetary Science Letters* 266: 221–232.

Kaplan JO, Folberth G and Hauglustaine DA (2006) Role of methane and biogenic volatile organic compound sources in late glacial and Holocene fluctuations of atmospheric methane concentrations. *Global Biogeochemical Cycles* 20: GB2016, doi:10.1029/2005GB002590.

Kröpelin S, Verschuren D, Lézine A-M, Eggermont H, Cocquyt C, Francus P et al. (2008) Climate-driven ecosystem succession in the Sahara: The past 6000 years. *Science* 320: 765–768.

Lee J-E and Fung I (2007) 'Amount effect' of water isotopes and quantitative analysis of post-condensation processes. *Hydrological Processes* DOI: 10.1002/hyp.6637.

Lee J-E and Swann AL (2010) Evaluation of the 'amount effect' at speleothem sites in the Asian monsoon region. *IOP Conference Series: Earth and Environmental Science* 9: 012023 doi:10.1088/1755-1315/9/1/012023.

Lehner B and Döll P (2004) Development and validation of a global database of lakes, reservoirs and wetlands. *Journal of Hydrology* 296: 1–22, doi:10.1016/j.jhydrol.2004.03.028.

Loulergue L, Schilt A, Spahni R, Masson-Delmotte V, Blu-nier T, Lemieux B et al. (2008) Orbital and millennial-scale features of atmospheric CH_4 over the past 800 000 years. *Nature* 435: 383–386.

Masson-Delmotte V, Dreyfus G, Braconnot P, Johnsen S, Jouzel J, Kageyama M et al. (2006) Past temperature reconstructions from deep ice cores: relevance for future climate change. *Climates of the Past* 2: 145–165, http://www.clim-past.net/2/145/2006/.

Mayewski PA (2004) Holocene climate variability. *Quaternary Research* 62: 243–255.

Mayle FE, Burbridge R and Killeen TJ (2000) Millennial-scale dynamics of Southern Amazonian rain forests. *Science* 290: 2291–2294.

McDermott F, Frisia S, Huang Y, Longinelli A, Spiro B, Heaton THE et al. (1999) Holocene climate variability in Europe: evidence from $\delta^{18}O$, textural and extension-rate variations in three speleothems. *Quaternary Science Reviews* 18: 1021–1038.

Mickler PJ, Banner JL, Stern L, Asmerom Y, Edwards RL and Ito E (2004) Stable isotope variations in modern tropical speleothems: Evaluating equilibrium vs. kinetic isotope effects. *Geochimica et Cosmochimica Acta* 68: 4381–4393.

Mitsch WJ, Nahlik A, Wolski P, Bernal B, Zhang L and Ramberg L (2009) Tropical wetlands: Seasonal hydrologic pulsing, carbon sequestration, and methane emissions. *Wetlands Ecology and Management* DOI 10.1007/s11273-009-9164-4.

Nahlik A and Mitsch WJ (2010) Methane emissions from tropical freshwater wetlands located in different climatic zones of Costa Rica. *Global Change Biology* doi: 10.1111/j.1365-2486.2010.02190.x.

Neff U, Burns SJ, Mangini A, Mudelsee M, Fleitmann D and Matter A (2001) Strong coherence between solar variability and the monsoon in Oman between 9 and 6 ka ago. *Nature* 411: 290–293.

Niedermeyer EM, Schefuss E, Sessions AL, Mulitzaa S, Mollenhauera G, Schulz M et al. (2010) Orbital- and millennial-scale changes in the hydrologic cycle and vegetation in the western African Sahel: Insights from individual plant wax δD and $\delta^{13}C$. *Quaternary Science Reviews* doi:10.1016/j.quascirev.2010.06.039.

Reeburgh WS (2004) Global methane biogeochemistry. In: Keeling RF (ed.) *The Atmosphere. Treatise on Geochemistry*. Oxford: Elsevier-Pergamon, 65–90.

Risi C, Bony S and Vimeux F (2008) Influence of convective processes on the isotopic composition ($\delta^{18}O$ and δD) of precipitation and water vapor in the tropics: 2. Physical interpretation of the amount effect. *Journal of Geophysical Research* 113: D19306, doi:10.1029/2008JD009943.

Rozanski K, Araguas-Araguas L and Gonfiantini R (1993) Isotopic patterns in modern global precipitation. *Climate change in Continental Isotopic Records*. American Geophysical Union, Geophysical Monograph 78: 1–36.

Ruddiman WF (2003) The anthropogenic greenhouse era began thousands of years ago. *Climatic Change* 61: 261–293.

Ruddiman WF (2005) Cold climate during the closest stage 11 analog to recent millennia. *Quaternary Science Reviews* 24: 1111–1121.

Ruddiman WF (2007) The early anthropogenic hypothesis: Challenges and responses. *Reviews in Geophysics* 45: RG4001, doi:10.1029/2006RG000207.

Seltzer G, Rodbell D and Burns SJ (2000) Isotopic evidence for Late Glacial and Holocene hydrologic change in tropical South America. *Geology* 28: 35–38.

Sowers T (2009) Atmospheric methane isotope records covering the Holocene period. *Quaternary Science Reviews* 29: 213–221.

Spahni R, Chappellaz J, Stocker TF, Loulergue L, Hausammann G, Kawamura K et al. (2005) Atmospheric methane and nitrous oxide of the Late Pleistocene from Antarctic ice cores. *Science* 310: 1317–1321.

Spötl C and Mangini A (2002) Stalagmite from the Austrian Alps reveals Dansgaard–Oeschger events during isotope stage 3: Implications for the absolute chronology of Greenland ice cores. *Earth and Planetary Science Letters* 203: 507–518.

Sturm K, Hoffmann G and Langmann B (2007) Climatology of stable water isotopes in South America: Comparing general to regional circulation models. *Journal of Climatology* 20: 3730–3750, doi:10.1175/JCLI4194.1.

Thevenon F, Williamson D and Taieb M (2002) A 22-kyr BP sedimentological record of Lake Rukwa (8°S, SW Tanzania): Environmental, chronostratigraphic and climatic implications. *Palaeogeography Palaeoclimatology Palaeoecology* 187: 285–294.

Thompson LG, Davis ME, Mosley-Thompson E, Sowers TA, Henderson KA, Zagorodnov VS et al. (1998) A 25,000-year tropical climate history from Bolivian ice cores. *Science* 282: 1858–1864.

Thompson LG, Mosley-Thompson E, Davis ME, Henderson KA, Brecher HH, Zagorodnov VS et al. (2002) Kilimanjaro ice core records: Evidence of Holocene climate change in tropical Africa. *Science* 298: 589–593.

Thompson LG, Mosley-Thompson E, Davis ME, Lin P-N, Henderson KA, Cole-Dai J et al. (1995) Late glacial stage and Holocene tropical ice core records from Huascarán, Peru. *Science* 269: 46–50.

Trenberth KE, Stepaniak DP and Caron JM (2000) The global monsoon as seen through the divergent atmospheric circulation. *Journal of Climate* 13: 3969–3993.

Tzedakis PC (2010) The MIS 11 – MIS 1 analogy, southern European vegetation, atmospheric methane and the 'early anthropogenic hypothesis'. *Climate of the Past* 6: 131–144.

van Breukelen MR, Vonhof HB, Hellstrom JC, Wester WCG and Kroon D (2008) Fossil dripwater in stalagmites reveals Holocene temperature and rainfall variation in Amazonia. *Earth Planetary Science Letters* 275: 54–60.

Verschuren D, Sinninghe Damsté JS, Moernaut J, Kristen I, Blaauw M, Fagot M et al. (2009) Half-precessional dynamics of monsoon rainfall near the East African Equator. *Nature* 462: 637–641.

Vimeux F, Gallaire R, Bony S, Hoffman G and Chiang JHC (2005) What are the climate controls on isotopic composition (δD) of precipitation in Zongo Valley (Bolivia)? Implications for the Illimani ice core interpretation. *Earth and Planetary Science Letters* 240: 205–220.

Vuille M, Bradley RS, Healy R, Werner M, Hardy DR, Thompson LG et al. (2003b) Modeling $\delta^{18}O$ in precipitation over the tropical Americas, Part II, Simulation of the stable isotope signal in Andean ice cores. *Journal of Geophysical Research* 108: 4175. doi:10.1029/2001JD002039.

Vuille M, Bradley RS, Werner M, Healy R and Keimig F (2003a) Modeling $\delta^{2}O$ in precipitation over the tropical Americas: Part I. Interannual variability and climatic controls. *Journal of Geophysical Research* 108: 4174. doi:10.1029/2001JD002038.

Waller M, Street-Perrott FA and Wang H (2007) Holocene vegetation history of the Sahel: Pollen, sedimentological and geochemical data from Jikariya Lake, north-eastern Nigeria. *Journal of Biogeography* 34: 1575–1590.

Walter BP and Heimann M (2000) A process-based, climate-sensitive model to derive methane emissions from natural wetlands: Application to five wetland sites, sensitivity to model parameters, and climate. *Global Biogeochemical Cycles* 14: 745–765.

Wang H, Holmes JA, Street-Perrott FA, Waller MP and Perrott RA (2008) Holocene environmental change in the West African Sahel: Sedimentological and mineral-magnetic analyses of lake sediments from Jikariya Lake, northeastern Nigeria. *Journal of Quaternary Science* 23: 449–460.

Wang YJ, Cheng H, Edwards RL, An ZS, Wu JY, Shen CC et al. (2001) A high-resolution absolute-dated late Pleistocene monsoon record from Hulu Cave, China. *Science* 294: 2345–2348.

Wang YJ, Cheng H, Edwards RL, He YQ, Kong XG, An ZS et al. (2005) The Holocene Asian monsoon: Links to solar changes and North Atlantic climate. *Science* 308: 854–857.

Wang X, Auler AS, Edwards RL, Cheng H, Ito E and Solheid M (2006) Interhemispheric anti-phasing of rainfall during the last glacial period. *Quaternary Science Reviews* 25: 3391–3403.

Weber SL, Drury AJ, Toonen WHJ and van Weele M (2010) Wetland methane emissions during the Last Glacial Maximum estimated from PMIP2 simulations: Climate, vegetation, and geographic controls. *Journal of Geophysical Research* 115: D06111, doi:10.1029/2009JD012110.

Weldeab S, Lea DW, Schneider RR and Andersen N (2007) 155,000 years of West African monsoon and ocean thermal evolution. *Science* 316: 1303–1307.

Whiting GJ and Chanton JP (1993) Primary production control of methane emission from wetlands. *Nature* 364: 794–795.

Wiedner E, Scholz D, Mangini A, Polag D, Mulinghaus C and Segl M (2008) Investigation of the stable isotope fractionation in speleothems with laboratory experiments. *Quaternary International* 187: 15–24.