The influence of vegetation activity on the Dole effect and its implications for changes in biospheric productivity in the mid-Holocene

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The Dole effect is defined as the difference between the oxygen isotope composition of atmospheric oxygen and seawater (currently 23.5‰) and reflects the balance between processes and fractionations associated with O₂ consumption and production by the terrestrial and marine biospheres. Isotopic records from ice cores and ocean sediments provide a means of assessing variations in the Dole effect during the late Quaternary but the biogeochemical interpretation of these changes is limited because we are currently unable to account adequately for vegetation effects on the global isotopic balance of atmospheric O₂. Here, I show that the previously unquantified influence of canopy transpiration on the isotopic composition of atmospheric water vapour now closes the mass balance budget for the isotopes of atmospheric O₂ under the current climate. Using this new finding, the effects of vegetation on the Dole effect have been assessed at the global scale for the mid-Holocene (6000 years ago). The results indicate that the small reduction in the Dole effect in the mid-Holocene represented a fall in the ratio of terrestrial to marine gross primary production from 1.8 to 1.0. Improved understanding of the environmental and physiological processes controlling the oxygen isotopic composition of plants and their feedback on the isotopes of atmospheric O₂ offers considerable promise in quantitatively accounting for the changes in biospheric productivity associated with the Dole effect over glacial–interglacial cycles. In addition, such work should provide an as yet unexploited basis for testing the results of climate models against the oxygen isotope composition of Quaternary plant fossils.

Keywords: vegetation; photosynthesis; atmospheric oxygen; isotopes; palaeoproductivity

1. INTRODUCTION

Current accounting of the isotopic mass balance of the global O₂ cycle is incomplete (Bender *et al.* 1994; Keeling 1995) and, consequently, we are unable to account fully for the Dole effect (Dole 1935; Dole *et al.* 1954), the difference in isotopic composition of atmospheric O₂ (δ_{ATM}) relative to contemporary seawater (currently 23.5‰; Kroopnick & Craig 1972). The Dole effect reflects the balance between fractionations associated with the consumption and production of O₂ by the terrestrial and marine biospheres. Measurement of the isotopic composition of molecular oxygen trapped in ice sheets, together with isotopic data from foraminifera, has shown that the Dole effect has been remarkably stable over the last glacial–interglacial cycle, although small cyclical variations have been detected which probably reflect the changing ratio of gross production on the land and in the oceans (Bender *et al.* 1985, 1994). However, uncertainties in the current global isotopic O₂ budget feed through to limit our understanding of the biogeochemical implications of the relative stability and the subtle cyclical variations of the Dole effect during the late Quaternary.

Vegetation influences δ_{ATM} because over half the annual O₂ flux is derived from net photosynthesis by terrestrial plants (Berry 1992; Bender *et al.* 1985, 1994).

This O₂ flux carries an isotopic signal reflecting evaporative enrichment in ¹⁸O of leaf water over soil water, due to the slower transpiration of H₂¹⁸O than H₂¹⁶O (Farquhar *et al.* 1993). The enrichment is then passed to the O₂ molecules produced by photosynthetic CO₂ assimilation without further fractionation (Guy *et al.* 1993). Despite this secure theoretical underpinning for terrestrial vegetation, one of the greatest uncertainties in the contemporary global inventory of ¹⁸O isotopes in atmospheric O₂ lies in the estimate of globally averaged vegetation impacts, expressed as a global mean for the isotopic composition of leaf water (δ_{L}). Current estimates of δ_{L} (Farquhar *et al.* 1993; Ciais *et al.* 1997) are approximately half (3.3–4.4‰) the theoretically expected value of 8.8‰ (Dongmann 1974; Bender *et al.* 1985, 1994). δ_{L} is, however, an extremely difficult quantity to estimate since it is equal to the time-averaged isotopic composition of water in the chloroplasts of leaves of all vegetation on the Earth's surface, weighted by O₂ production.

There remains, therefore, a need to quantify the impact of vegetation processes on the isotopic composition of atmospheric O₂ to improve our understanding of this aspect of the global O₂ cycle and interpret past variations in the Dole effect (Keeling 1995; Ciais & Meijer 1998). Here, therefore, I report the results from a set of off-line global vegetation–climate modelling

experiments investigating the sensitivity of δ_L to several different methods of calculating the isotopic composition of atmospheric water vapour (δ_V), one of the greatest uncertainties in estimating the impact of vegetation on δ_{ATM} . The impact of plant transpiration on δ_V has been specifically investigated because it is known to reflect a mixture of water vapour transpired from plant canopies and that entrained from air above the canopy (Ciais *et al.* 1997; Ciais & Meijer 1998) and no attempt has yet been made to quantitatively assess its importance for δ_L at the global scale. It emerges from this work that, by including the effects of plant transpiration, the globally averaged value of δ_L increases in line with theoretical expectations (Dongmann 1974) allowing closure of the isotope mass balance budget for oxygen.

Closure of the mass balance budget enables a first interpretation to be made of past variations in the Dole effect by partitioning biospheric gross primary production between the land and the oceans. Here, I focus on explaining the small reduction in the Dole effect recorded for the mid-Holocene (Bender *et al.* 1994) by quantifying the influence of vegetation on the isotopic composition of atmospheric O_2 using a process-based vegetation–biogeochemistry model (Woodward *et al.* 1995) and two general circulation model (GCM) simulations of global climate for the mid-Holocene, each with a different treatment of ocean heat fluxes (Hall & Valdes 1997; Kutzbach *et al.* 1998). By constraining the isotopic mass balance with the predicted globally averaged value of δ_L for six thousand years ago, it then becomes possible to estimate gross oceanic O_2 production. Furthermore, since leaf water enrichment in ^{18}O is passed to CO_2 in the leaf (Sternberg *et al.* 1986), via the action of carbonic anhydrase, mapping the geographical patterns of δ_L represents a new global-scale method of summarizing climate model predictions, particularly humidity, for comparison with measurements of the oxygen isotope composition of well-dated fossil plant remains.

2. MATERIAL AND METHODS

Leaf-water enrichment was predicted on a monthly basis using a modified version of the Craig–Gordon evaporative enrichment model (CGM) (Craig & Gordon 1965):

$$\delta_L = \delta_S + \epsilon_K + \epsilon^* + (\delta_V - \delta_S - \epsilon_K) \times e_a/e_i, \quad (1)$$

where δ_S is the isotopic composition of the source water, δ_V is the isotopic composition of water vapour in the surrounding air, e_a and e_i are the vapour pressures of water in the atmosphere and intercellular spaces, ϵ^* is the proportional depression of equilibrium vapour pressure by ^{18}O (9.2‰ at 25 °C), with a temperature sensitivity given by Bottinga & Craig (1969) and ϵ_K is the kinetic fractionation factor accounting for the weighted diffusion through stomata and the boundary layer (26.5‰) (Farquhar *et al.* 1993). The isotopic composition of source water (soil water, δ_S) is determined from its relationship between annual mean temperature, elevation and precipitation (Farquhar *et al.* 1993). All other fractionations required by the CGM were as reported by Farquhar *et al.* (1993). The use of the CGM to predict ^{18}O enrichment at the evaporative sites of leaves leads to small differences between modelled and observed values due to the turnover time of leaf water, variations on fine

spatial scales within leaves (Yakir *et al.* 1994), differences in boundary layer conductances and the Péclet effect (Farquhar & Lloyd 1993). However, at the global scale the CGM captures the required detail (Farquhar *et al.* 1993) so, for modelling purposes, it is assumed that δ_L (leaf water) is sufficiently close to the isotopic composition of water at the evaporating sites of leaves.

Uncertainties in applying the CGM at the global scale remain over the method of calculating δ_V (Farquhar *et al.* 1993; Ciais *et al.* 1997). Here, δ_L was modelled using three approaches to calculating δ_V , two based on its published relationship with temperature (table 1) and one with δ_V as a constant 10‰ depletion everywhere with respect to precipitation, as suggested by three-dimensional isotopic-specific tracer modelling studies (Ciais *et al.* 1997; Ciais & Meijer 1998). The influence of transpiration on the global average value of δ_L was then examined using these three approaches to estimating δ_V with and without including a monthly weighting by canopy transpiration (table 1). In each simulation, the monthly value of δ_L was weighted by gross O_2 production from vegetation (photosynthesis and photorespiration). Both gross O_2 production and canopy transpiration were estimated on a monthly basis using a process-based vegetation–biogeochemistry model (Woodward *et al.* 1995) which simulates the productivity of terrestrial vegetation independently of any underlying maps of vegetation or soil classification. The modern and six thousand years ago simulations with the vegetation–biogeochemistry were run using 35 Pa and 28 Pa of CO_2 , respectively.

The vegetation–biogeochemistry model was driven using the global near-surface 1988 data sets of the International Satellite Land Surface Climatology Project (ISLSCP) (monthly temperature, precipitation and relative humidity and elevation) (Meeson *et al.* 1995) to provide a typical ‘modern’ climate. The mid-Holocene simulations were made using the ten-year integration output from the UK Universities Global Atmospheric Modelling Programme (UGAMP) GCM with interactive sea ice and prescribed sea-surface temperatures (Hall & Valdes 1997). A second set of simulations were made using the National Center for Atmospheric Research (NCAR) GCM, which differs from the UGAMP model by having a lower spatial resolution but an interactive sea–surface scheme via a mixed-layer (slab) ocean model (Kutzbach *et al.* 1998). Both simulations included differences in elevation six thousand years ago due to post-glacial isostatic rebound from ice sheet loading during the last glaciation. To remove climate model bias, the palaeoclimates simulated by both GCMs were subtracted from the corresponding control runs for present-day conditions and the monthly climate anomalies added to the 1988 data sets. The global mean annual temperatures and precipitation over land for each of the three data sets were 11.3 °C and 2.1 mm day^{−1} (ISLSCP, 1988), 11.5 °C and 2.3 mm day^{−1} (UGAMP, adjusted) and 11.3 °C and 2.0 mm day^{−1} (NCAR, adjusted).

3. RESULTS AND DISCUSSION

The globally averaged values of δ_L , weighted by gross O_2 production (i.e. total O_2 produced by photosynthesis and photorespiration), are quite sensitive to each of the methods of calculating δ_V and exclusion of any effects of canopy transpiration effects gave values close to those published previously (table 1) (Farquhar *et al.* 1993; Ciais *et al.* 1997). In all three cases, however, δ_L increased when the isotopic composition of water vapour was weighted by canopy transpiration (table 1). The globally averaged δ_L

Table 1. Modelled globally averaged leaf-water enrichment in ^{18}O and gross O_2 fluxes for terrestrial vegetation activity in a 1988 climate and two global palaeoclimatic simulations of the mid-Holocene (six thousand years ago)

simulation	globally averaged leaf water enrichment ^a (δ_{L})		gross photosynthetic O_2 production (Pmol year^{-1}) ^b	
	1	2	1	2
method for estimating isotopic composition of water vapour for 1988 climate (δ_{V}) ^c				
(i) $-0.014 \times t^2 + 0.67 \times t - 23.5$	3.2	4.0	—	—
(ii) $0.6 \times t - 25.0$	4.5	5.5	—	—
(iii) constant -10‰ depletion	6.9	8.3	—	—
1988 global climate	—	—	12.7	17.3(34%)
mid-Holocene (6 ka)				
UGAMP	—	9.2	9.7	14.2(46%)
NCAR CCM-1	—	9.6	10.5	15.2(45%)
mean	—	9.4	10.1	14.3(45%)

^aWeighted by O_2 production from photosynthesis and photorespiration. Column 1 excludes the effects of weighting of the isotopic composition of water vapour by canopy transpiration and column 2 includes the effects of weighting by transpiration.

^bColumn 1 gives the area-weighted gross photosynthetic O_2 production and column 2 includes O_2 production by photorespiration. The figures in parentheses are the proportions of O_2 produced by photorespiration.

^cTemperature relations from Jacob & Sonntag (1991) where t is the mean monthly temperature.

values obtained without accounting for the effects of canopy transpiration are too low to satisfy the isotope mass balance constraints (Bender *et al.* 1985, 1994). The approach yielding a δ_{L} value closest to the theoretical value of 8.8‰ (Dongmann 1974) was that calculated with a 10‰ depletion everywhere but weighted by monthly canopy transpiration (table 1). Global gross primary O_2 production by terrestrial vegetation for the present-day climate (table 1) was estimated to be lower than used in an earlier analysis of the Dole effect (Bender *et al.* 1994) which excluded the effects of soil nutrient status and soil water availability on vegetation productivity.

The consequences of this new value of land productivity and the higher δ_{L} value require a re-evaluation of vegetation impacts on the Dole effect. This has been examined using the oxygen isotope mass balance analysis of Bender *et al.* (1994), which has a terrestrial and marine component and a stratigraphic diminution term. All three are related to define the Dole effect as

$$\begin{aligned} \text{Dole effect} = & (\text{fraction of } \text{O}_2 \text{ production on land} \\ & \times \text{land Dole effect}) \\ & + (\text{fraction of oceanic } \text{O}_2 \text{ production} \\ & \times \text{marine Dole effect}) \\ & - \text{stratigraphic diminution.} \end{aligned} \quad (2)$$

The terrestrial Dole effect is defined by

$$F_{\text{TGPP}} \times \delta_{\text{L}} = F_{\text{TR}} \times (\delta_{\text{ATM}} - \delta_{\text{TR}}), \quad (3)$$

where F_{TGPP} is the annual total O_2 flux produced by terrestrial vegetation and F_{TR} is the annual total of O_2 consumed by terrestrial respiration processes and δ_{TR} is the net isotopic fractionation associated with these processes. The estimate of δ_{TR} is important since it has a large fractionation and is sensitive to the climate in which the plants are growing. For the current climate, δ_{TR} is estimated to be 18.0‰, taken as a composite flux-weighted

value representing the three main biochemical pathways involved in terrestrial plant respiration (dark respiration, Mehler reaction and photorespiration) (Guy *et al.* 1993; Badger 1985). For the mid-Holocene, the photorespiratory O_2 flux increased under the lower partial pressure of atmospheric CO_2 (table 1) with a corresponding increase in δ_{TR} to 18.4‰.

The oceanic Dole effect can be defined as

$$\begin{aligned} F_{\text{MGPP}} \times \delta_{\text{ML}} = & F_{\text{SOR}} \times (\delta_{\text{ATM}} + \delta_{\text{SE}} - \delta_{\text{SOR}}) \\ & + F_{\text{DOR}} \times (\delta_{\text{ATM}} + \delta_{\text{SE}} - \delta_{\text{DOR}}), \end{aligned} \quad (4)$$

where F_{MGPP} is the total annual flux of O_2 produced by the oceans, δ_{ML} is the isotopic fractionation during this O_2 production (0.0‰), δ_{SE} is the fractionation which occurs when O_2 is dissolved in seawater (0.7‰), F_{SOR} is the total annual flux of O_2 consumed by respiration in the surface ocean ($= F_{\text{MGPP}} \times 0.95$), and δ_{SOR} its fractionation (20‰) and F_{DOR} is the total annual flux of O_2 consumed by the deep ocean ($= F_{\text{MGPP}} \times 0.05$) and δ_{DOR} its net fractionation (12.0‰) (Bender *et al.* 1994).

Finally, a stratospheric diminution term is required, which, expressed on an annual basis, is equal to 0.4‰ (Bender *et al.* 1994). The mass of O_2 involved in this exchange is $660 \times 10^{15} \text{ mol year}^{-1}$. Under steady-state conditions, $F_{\text{TGPP}} = F_{\text{TR}}$ and $F_{\text{MGPP}} = F_{\text{SOR}} + F_{\text{DOR}}$ and, since ocean GPP fractionation is zero (δ_{ML}), equations (2)–(4) can be combined, simplified and solved to predict either δ_{ATM} or, when δ_{ATM} is known from ice core studies, solved for F_{MGPP} (i.e. gross marine productivity).

By taking an isotope mass balance approach and constraining the side of the equation dealing with fractionations and fluxes associated with terrestrial vegetation, the approach can be used to calculate global ocean gross primary production. This value is extremely difficult to measure directly, because it requires information on O_2 production and consumption by phytoplankton and bacterial communities integrated over a wide range of spatial and temporal scales (Falkowski & Raven 1997).

Figure 1. Global patterns of leaf ^{18}O enrichment for terrestrial vegetation modelled for (a) a typical 'modern' (1988) climate, and (b) the mid-Holocene climate simulation by the UK UGAMP GCM. The scale bar is in units of per mil (‰). All of the values are weighted by gross O_2 production (photosynthetic plus photorespiratory O_2 production).

Using the new data on gross O_2 production by terrestrial vegetation under the present climate and taking $\delta_{\text{L}} = 8.3$ (table 1), δ_{ATM} is estimated from mass balance analysis at $+23.2\text{‰}$, much closer to the observed value of 23.5‰ (Kroopnick & Craig 1972) than before (Bender *et al.* 1994). The small 0.3‰ difference implies a lower global gross oceanic primary production than assumed previously (9.4 versus $12.0 \text{ Pmol O}_2 \text{ year}^{-1}$) and compares with estimates of global net annual phytoplankton carbon fixation based on satellite data equivalent to $3.0\text{--}3.8 \text{ Pmol O}_2 \text{ yr}^{-1}$ (Antoine *et al.* 1996; Behrenfeld & Falkowski 1997).

Inclusion of canopy transpiration is a logical development in the analysis of vegetation impacts on the isotopic composition of atmospheric O_2 and leads to a more realistic estimate of δ_{L} . Consequently, this strategy has been used in the mid-Holocene simulations to quantify the role of terrestrial vegetation in mediating the observed reduction ($0.3\text{--}0.4\text{‰}$) in the Dole effect at this time (Bender *et al.* 1985, 1994). In this case, the global mid-Holocene climates simulated by both the UGAMP and NCAR GCMs increased the globally averaged value

of leaf-water enrichment (δ_{L}) relative to the modern situation. Gross primary production was also lower than the present (table 1) as a consequence of the lower CO_2 partial pressure of the mid-Holocene increasing photorespiration. A mass balance analysis using these results and the observed mid-Holocene value for the Dole effect (Bender *et al.* 1994) (23.1‰) predicts that the reduction in terrestrial productivity during the mid-Holocene was accompanied by a 42% increase in oceanic primary productivity to $14.3 \text{ Pmol O}_2 \text{ year}^{-1}$, in line with sedimentary records of marine palaeoproductivity (Berger & Herguera 1991) and predictions from a simple two-box ocean model (Herguera & Berger 1994). Overall, therefore, the reduction in the Dole effect observed for the mid-Holocene implies a reduction in the ratio of global terrestrial to marine primary production from 1.8 ($17.3/9.4 \text{ Pmol O}_2 \text{ yr}^{-1}$) to 1.0 ($14.3/13.4 \text{ Pmol O}_2 \text{ yr}^{-1}$). Application of this global-scale approach further back in time (e.g. to the last glaciation) will require quantifying the relative importance of the different biochemical pathways of respiration, since the roles of cyanide-sensitive and

cyanide-insensitive pathways could also be different (Gonzalez-Meler *et al.* 1996) under the arid, cool, low CO₂ environment of ice ages.

Leaf-water enrichment in ¹⁸O during transpiration is passed to atmospheric CO₂ diffusing into leaves via the action of the enzyme carbonic anhydrase (Sternberg *et al.* 1986; Farquhar *et al.* 1993). Some of this CO₂ is fixed in the leaf by photosynthesis and subsequently becomes incorporated into the cellulose δ¹⁸O signature with a biochemical fractionation of +27.5‰, but with a damped signal due to post-photosynthetic isotope exchanges that occur during cellulose synthesis (Saurer *et al.* 1997; Farquhar *et al.* 1998). A first attempt at this approach has been to produce global maps of δ_L predicted for modern and mid-Holocene climates (figure 1) which represent a set of predictions testable against measurements of cellulose δ¹⁸O from fossil plant materials. Such data sets are limited, but studies of late Quaternary variations in cellulose δ¹⁸O from tropical peat bogs in Burundi, Central Africa (Aucour *et al.* 1996) offer a test of the mid-Holocene predictions in this region. For the mid-Holocene, δ_L was predicted to be higher over large regions of the northern hemisphere but lower in parts of Africa, compared to the current situation (figure 1). In fact, δ¹⁸O measurements of fossil C₃ plant cellulose recovered from peat cores in Burundi show climatically driven, down-core reductions consistent with this prediction, with mid-Holocene values (ca. +24.0‰) lower than modern values (+26.1 to +36.2‰), a response unrelated to diagenesis (Aucour *et al.* 1996). Although limited, this first test shows promise in developing techniques for testing humidity fields from GCMs based on our understanding of the controls on the isotopic composition of leaves.

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