Table 1 Azeotropes at 1 atm

Boiling temperature (°C)	Mole fractions			
	Acetic acid	Isopropanol	Isopropyl acetate	Water
75.5	0.00	0.1377	0.4737	0.3887
76.6	0.00	0.00	0.5980	0.4020
80.1	0.00	0.6480	0.3520	0.00
80.1	0.00	0.6873	0.00	0.3127

Data reported by Horsley³.

time. Eventually, the amount of liquid residue was small enough to preclude sampling, ending the experiment. Subsequent experiments, beginning at compositions close to the end point of the previous experiment, were necessary in most cases to get a clear measure of each residue curve.

We studied the effect of catalyst concentration by using the same initial composition of the mixture with different amounts of catalyst. Our interest here is in the limiting case approaching phase and reaction equilibrium so we sought to find a large amount of catalyst, a low rate of vapour withdrawal, and the appropriate start-up procedure to approach this condition. With 27.5 g of catalyst (0.135 mol H⁺) in an initial volume of 306 ml liquid, the theoretical residue curve is approached closely. The similarity between the experimental residue curves for 22.0 and 27.5 g of catalyst showed an approach to this limiting case. Based on these results, we used 30.0 g catalyst (0.147 mol H⁺) in an initial volume of 306 ml for all experiments reported here. Using a similar approach, we determined a heating rate low enough to ensure that the results are independent of the rate of mass transfer between liquid and vapour phases. In our experiment, this was achieved in a time of ~6 hours to remove ~75% of the initial liquid or an average vapour removal rate of ~38 ml h⁻¹.

A series of nine experiments with initial conditions in the neighbourhood of the calculated azeotrope were performed in a total of 39 runs; each set in a series was intended to represent one residue curve; successive runs were necessary in most cases to show a significant portion of each curve. The results are shown in Fig. 1a. The open circles indicate the position of the reactive azeotrope as closely as it could be determined; these points are nearly overlapping as predicted. This single run consists of five data points taken over a span ~4 hours, during which time the compositions remained nearly constant and the boiling temperature varied by <0.1 °C. The measured molar liquid composition of the reactive azeotrope was 5.4% acetic acid, 56.5% isopropanol, 21.4% isopropyl acetate and 16.7% water at a temperature of 78.6 °C, with a corresponding vapour composition of 0.0% acetic acid, 49.1% isopropanol, 27.0% isopropyl acetate and 23.9% water. The corresponding transformed compositions are $X_A = 0.268$, $X_B = 0.779$ and $Y_A = 0.270$, $Y_B = 0.761$.

We assessed the reproducibility of the results by repeating two runs and found the data to be highly reproducible, as shown in Fig. 1b.

These results demonstrate the existence of a reactive azeotrope not present in the non-reactive mixture. This confirms the predictions of a model based on classical thermodynamics and provides a basis for predicting the behaviour of other mixtures. For example, we also predict reactive azeotropes in the esterification of acetic acid with *n*-propanol or iso-butanol, as well as a near reactive azeotrope in the reaction of methanol and isobutene to form methyl *t*-butyl ether (MTBE). In the production of MTBE the 'reactive azeotrope' is predicted to contain a substantial amount of MTBE and is responsible for making reactive distillation the preferred process technology⁹. We believe that reactive azeotropes are common and for some systems can determine the optimal choice of process technology. As a further example, the manufacture of methyl acetate uses reactive distillation, because reaction eliminates the azeotrope

between water and methyl acetate that otherwise limits the purity of the product^{8,9}. But our results show that a similar process will not work for isopropyl acetate because of the existence of a reactive azeotrope in the four-component reactant/product mixture. □

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Correspondence should be addressed to M.F.D. (e-mail: mdoherty@ecs.umass.edu).

Decadal predictability of North Atlantic sea surface temperature and climate

R. T. Sutton*† & M. R. Allen*‡

* *Atmospheric Oceanic and Planetary Physics, Clarendon Laboratory, University of Oxford, Parks Road, Oxford OX1 3PU, UK*

† *Centre for Global Atmospheric Modelling, Department of Meteorology, University of Reading, PO Box 243, Earley Gate, Reading RG6 6BB, UK*

‡ *Space Science Department, Rutherford Appleton Laboratory, Chilton OX11 0QX, UK*

The weather at middle latitudes is largely unpredictable more than a week or so in advance, whereas fluctuations in the ocean may be predictable over much longer timescales. If decadal fluctuations in North Atlantic sea surface temperature^{1–6} could be predicted, it might be possible to exploit their influence on the atmosphere^{7–10} to forecast decadal fluctuations in climate¹¹. Here we report analyses of shipboard observations that indicate significant decadal predictability of North Atlantic sea surface temperature, arising from the advective propagation of sea-surface-temperature anomalies⁴ and the existence of a regular period of 12–14 years in the propagating signals. The same timescale can be identified in a dipole-like pattern of North Atlantic sea-level pressure variability^{1,7,12}. We propose a mechanism which may connect these oceanic and atmospheric fluctuations, possibly as part of a coupled ocean–atmosphere mode of variability⁷. Our results are encouraging for the prospects of forecasting natural fluctuations in the climate of the North Atlantic region several years in advance.

Several authors have suggested that much of the decadal variability in North Atlantic sea surface temperature (SST) can be explained as a local oceanic response to atmospheric variability^{1,3,13},

whereas others have argued that non-local dynamical processes in the ocean must play an important role^{2,4,14}. In the latter group, Hansen and Bezdek⁴ have recently presented evidence of advection of SST anomalies, especially along the path of the North Atlantic Current (NAC), an extension of the Gulf Stream. The importance of this suggestion is that fluctuations in SST that arise from advection may be predictable. We use analyses of monthly mean SST compiled from ship observations for the period 1945–89¹⁵ to investigate the evidence for predictability in North Atlantic SST associated with oceanic advection, and examine whether advection could be an important element in a possible coupled ocean–atmosphere mode of North Atlantic variability⁷.

Figure 1a shows an estimate of the upper-ocean circulation in the North Atlantic¹⁶. Figure 1b shows the correlation between low-frequency fluctuations in local wintertime SST and low-frequency fluctuations in wintertime SST averaged over the region 80–60° W, 31.5–38.5° N (the vicinity of Cape Hatteras) as a function of lag in years. SST anomalies are most likely to express deeper subsurface

anomalies in winter, when the oceanic mixed layer is at its deepest. Coherent SST fluctuations appear to propagate from the coast of North America across the Atlantic to the northwest of Scotland, following the strong SST gradients that are associated with the Gulf Stream and NAC.

In Fig. 2 we show the propagating SST anomalies that give rise to the correlations seen in Fig. 1b. A series of warm and cold anomalies propagates downstream with an average velocity of $\sim 1.7 \text{ cm s}^{-1}$. The along-path length scale of these anomalies is $\sim 2,000 \text{ km}$ and their amplitude generally lies in the range $0.5\text{--}1.0^\circ\text{C}$, reaching a maximum between 5,000 and 6,000 km downstream of the tip of Florida at approximately 35°W , 50°N . As noted by Hansen and Bezdek⁴, this propagation speed is considerably slower than the near-surface currents in the core of the Gulf Stream ($>1 \text{ m s}^{-1}$ close to Cape Hatteras¹⁷). If, as seems likely, these signals are advective their speed must be determined by the weaker currents either to one side of the core or at some depth below the surface. Subsurface observations close to the path of the Gulf Stream/NAC show evidence of decadal

Figure 1 a, The upper-ocean circulation in the North Atlantic according to ref. 16. The lines indicate the mean flow of waters warmer than 7°C , and the circles numbers indicate the transport in sverdrups ($1 \text{ sverdrup} = 10^6 \text{ m}^3 \text{ s}^{-1}$). The main feature is the anticyclonic Subtropical Gyre, shown in solid lines. The cyclonic Subpolar Gyre lies to the north and is shown by dashed lines. The Gulf Stream lies at the western edge of the Subtropical Gyre. It flows polewards along the coast of North America before leaving the coast at Cape Hatteras. In mid-ocean the Gulf Stream splits into a part which recirculates southwards and another part—the North Atlantic Current—which flows northwards, and then north-eastwards towards Scotland. **b**, Correlation between low-frequency fluctuations in local wintertime SST and low-frequency fluctuations in wintertime SST averaged over the region $80\text{--}60^\circ\text{W}$, $31.5\text{--}38.5^\circ\text{N}$ (the vicinity of Cape Hatteras, VCH) as a function of lag. The contours pick out the regions where lag-correlation with VCH is maximized. The numbers next to each contour indicate the lag in years. In all cases VCH SST leads local SST. The contour value is 0.8 for lags of 0–8 years and 0.75 for the lag of 9 years. The contours are superimposed on the SST field averaged over all winters between 1945 and 1989 (colour scale in $^\circ\text{C}$). Monthly mean SST data were obtained from the NOAA SMD94¹⁵ analysis of ship observations for the period 1945–89 on a $1^\circ \times 1^\circ$ grid. The long-term mean annual cycle was removed from all the data. Winter-mean anomalies for each year are then computed by averaging the SST anomalies for the months November–April, and a five-year running mean is applied to the winter-mean anomalies. Correlations are only computed in the latitude band $25\text{--}65^\circ\text{N}$.

temperature fluctuations, possibly extending below the seasonal thermocline^{6,13,18}, and subsurface propagation in the Subpolar Gyre has also been reported^{19,20}. The existence of a deep signal, away from the regions of maximum shear and surface influence, may help to explain the remarkable coherence of the surface signature.

The SST power spectrum averaged along the Gulf Stream/NAC path exhibits a spectral peak at 12–14 years which exceeds the 98th percentile of the red-noise background that is expected if SST fluctuations arise as a local response to atmospheric variability²¹. In addition to this 12–14-year timescale, the prominence of the significant warm event which began in the mid-1940s and the significant cold event which began in the late 1960s suggests that lower-frequency, multidecadal, fluctuations² may also be associated with propagation along the Gulf Stream/NAC. Both timescales contribute to the correlations observed in Fig. 1b, and we stress the difficulty of distinguishing, with a short data record, a multi-decadal timescale from amplitude modulation of the decadal signals.

The 12–14-year timescale which we have identified with advection along the Gulf Stream/NAC agrees with that which previous authors^{1,7} have associated with a hypothetical coupled ocean–atmosphere mode. For any such coupled mode to exist, there must be a consistent atmospheric response to SST anomalies. How the atmosphere responds to mid-latitude SST is poorly under-

stood^{7–10}, but changes in the frequency, intensity or spatial distribution of mid-latitude storms are likely to be important^{8,10}. We may, therefore, expect particular sensitivity to SST anomalies in regions where these storms form. An especially important area is located along the southeastern coast of the USA between Cape Hatteras and Florida²² (which we call the ‘storm-formation region’) where severe wintertime land/sea temperature contrast fuels storm development through baroclinic instability. Figure 2 shows that SST in this region exhibits the decadal-timescale fluctuation, and furthermore that there is a strong correlation between these SSTs and a dipole-like fluctuation in North Atlantic sea-level pressure similar to that discussed in ref. 1. A warming of SST off the US coast, which we would expect to intensify the land/sea contrast and may enhance evaporation, is associated with a strengthening of the mean westerly winds in the mid-Atlantic especially in the region 50–30°W, 30–50°N. Although causality cannot reliably be inferred from correlation alone, this relationship is in line with the theoretical response of the mean flow to an intensified storm track²³ and therefore supports a hypothesis that the sea-level pressure dipole is a response to SST in the storm-formation region.

Increased storminess and/or mean winds will cool SSTs through local mixed layer and Ekman layer processes. Wind and net surface heat flux fields (not shown) indicate that cooling of SSTs in the vicinity of the NAC (40–55°N) and in the tropical North Atlantic

Figure 2 a, SST anomalies (colour scale in °C) as a function of time and distance along the path of the Gulf Stream/North Atlantic Current. Winter (November–April) anomalies only are used, smoothed with a three-year running mean. The path along which the plot is computed (shown in **b** as a solid black line) was taken from ref. 16 (Fig. 1a). The horizontal axis gives distance in thousands of kilometres measured along the path from the start point at 78.5°W, 24.5°N near the tip of Florida. **b**, The fraction of the low-frequency variability (root-mean-squared anomalies) in winter-mean sea-level pressure that can be accounted for by a linear response to SST in the storm-formation region (SFR; 82–69°W, 25–35°N, marked with a letter A). Positive (negative) values indicate fluctuations (anti-) correlated with SFR SST. In **c**, the solid line is a time series of winter-mean SST in region SFR, and the vertical scale is in °C. The dashed line shows winter-mean

sea-level pressure in the region 50–30°W, 50–60°N (letter B in panel **b**), multiplied by –1. The dotted line shows winter-mean sea-level pressure in the region 60–40°W, 15–25°N (letter C in panel **b**). Both the sea-level pressure time series are renormalized to have approximately the same variance as the time series of SST, and all three time series are detrended and smoothed with a three-year running mean. Before performing the regression for panel **b** both the SST and sea-level pressure time series are binned into 2-year winter means. The SFR SST time series only is further smoothed with a 3-point running mean. Sea-level pressure at any given location is then regressed on SFR SST, a constant term, and a trend, with the residual modelled as an AR(1) (‘red noise’) process²⁶. Values not significant at the 1.5 standard deviation level are not plotted.

(5–20° N) is associated with warm SST in the storm-formation region. Thus fluctuations in SST off the southeastern coast of the USA may affect remote regions of the Atlantic both quasi-instantaneously, via this atmospheric teleconnection, and after a delay of some years via advective propagation through the ocean.

We examine how oceanic advection and atmospheric teleconnections may combine to determine the decadal cycle in SST by regressing SST and sea-level pressure at various lags onto SST in the storm-formation region (Fig. 3). The analysis is designed (see Fig. 3 legend) to focus on the decadal timescale. The regression map at lag zero shows that warm SST in the storm formation region is associated with cold SST in the NAC region and in the tropical North Atlantic. These cold SSTs arise largely as the local SST response to heat-flux anomalies¹. We suggest that these heat flux anomalies arise as part of the atmospheric response to SST in the storm-formation region. At lags of 2 and 4 years, consistent with the reduced amplitude of SST anomalies in this region, the sea-level pressure dipole is much weaker than at lag 0. The SST regression map evolves in a manner broadly consistent with our expectations of advection (Fig. 1a). The warm anomaly in the storm-formation region moves eastwards and then appears to split into two branches over the Mid-Atlantic Ridge, in good agreement with the bifurcation of the Gulf Stream indicated in Fig. 1a. The cold anomaly in the North Atlantic moves eastwards along the path of the NAC. At a lag of 4 years we see the development of cold anomalies in the Gulf of Mexico which, at a lag of 6 years, spread into the storm-formation region. The development of cold anomalies in the latter region stimulates, according to our hypothesis, an atmospheric response of

the opposite sign to that with which we began. This atmospheric response forces warm anomalies in the NAC region and in the tropical North Atlantic, developing a pattern which is 180° out of phase with that seen at lag zero.

The explanation for a preferred timescale is likely to involve feedbacks to SST in the storm-formation region, mediated by the quasi-instantaneous atmospheric response and by subsequent oceanic processes that introduce a lag. The effects of the atmospheric fluctuations on the oceanic mixed layer in the tropical Atlantic, and in the vicinity of the Gulf Stream front (where ventilation may be affected), could be fed back to the storm-formation region by advection. Alternatively, fluctuations in the wind-stress curl over the Subtropical Gyre could generate fluctuations in the strength of the gyre circulation²⁴. These fluctuations could also influence SST in the storm-formation region, but in this case the dominant timescale is associated with the propagation of baroclinic Rossby waves. The fact that anomalies arise in the Gulf of Mexico before their arrival in the storm-formation region is consistent with both mechanisms. In reality it is likely that both advection and wave propagation influence the timescale²; external forcing might also play a role²⁵.

In the NAC region and in the tropical North Atlantic, interference between the instantaneous atmospheric influence and the delayed advective influence of SST in the storm-formation region could also favour the emergence of a preferred timescale³¹, tending to suppress (amplify) variability on timescales that are odd (even) multiples of the ~6-year (Fig. 1b) advection time from the storm-formation region to these regions. Both the instantaneous and delayed signals will have contributed to the correlations seen in Fig. 1b. We note

Figure 3 The fraction of low-frequency local SST variability (grey-scale) and low-frequency local sea-level pressure variability (contours) accounted for by a lagged version of the low-frequency SST variability in the storm-formation region, SFR; see Fig. 2 legend. SST in region SFR leads local SST, and local sea-level pressure, by the number of years indicated on each panel. The regression analysis is identical to that described in Fig. 2 legend but with winter-mean SST

replacing winter-mean sea-level pressure for the grey-scale maps, and with varying lag. The contour levels shown for the sea-level pressure regression are ± 0.5 (thin lines) and ± 0.65 (thick lines). Dashed lines indicate negative correlations. In **c**, the fraction of sea-level pressure variability accounted for fails to reach the 0.5 level, so no contours appear.

that our account of the decadal variability in tropical North Atlantic SST²⁶ is an alternative to the hypothesis that this region is under the control of processes local to the tropical Atlantic^{27,28}.

By exploiting the memory inherent in the decadal fluctuations, our results suggest it may be possible to predict a significant fraction of the low-frequency variability in North Atlantic SST and sea-level pressure several years in advance. Although further work will be needed before a serious attempt at forecasting can be made, particularly investigation with models of the mechanisms we have discussed, we consider briefly the outlook for the decadal fluctuations. We have examined the most recent evolution of North Atlantic SST in the NOAA NCEP analyses²⁹ and of North Atlantic sea-level pressure in the NCEP reanalyses³⁰. SST in the storm-formation region reached a maximum in the late 1980s and has since been falling. In line with our expectations of the atmospheric response, sea-level pressure in the region marked C in Fig. 2b peaked at the end of the 1980s and has since been falling, whereas sea-level pressure in the region marked B reached a minimum at the same time and has since been rising. Also consistent with our understanding, SST in the mid-Atlantic at ~50° N reached a minimum in the late 1980s and has since been rising. Similar, if somewhat less clear, behaviour is seen in tropical North Atlantic SST. Based on the apparent period of 12–14 years, and to the extent that other influences (for example, El Niño and multidecadal fluctuations) allow, we expect all these trends to continue into the next century before reversing. □

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Correspondence should be addressed to R.T.S. (e-mail: atmrtm@atm.ox.ac.uk).

Orbitally paced climate oscillations across the Oligocene/Miocene boundary

James C. Zachos*, Benjamin P. Flower†‡ & Hilary Paul*

* Earth Science Department, † Institute of Marine Sciences, University of California, Santa Cruz, California 95064, USA

The late Oligocene and early Miocene periods, some 21 to 27 million years ago, have generally been viewed as times of moderate global warmth and ice-free conditions. Yet several lines of evidence suggest that this interval was punctuated by at least one, and possibly several, episodes of high-latitude cooling and continental glaciation^{1–3}. Here, we present stable-isotope and per cent coarse-fraction data from an equatorial, western Atlantic deep-sea-sediment core that provide high-resolution records of the climate variability across the Oligocene/Miocene transition (22.5–25.7 million years ago). A strong 40-kyr periodicity in the oxygen isotope record is consistent with a high-latitude orbital (obliquity) control on ice-volume and temperature. Orbital influences are also apparent at precession and eccentricity frequencies, including a series of ~400-kyr oscillations that culminate in distinct maxima at the Oligocene/Miocene boundary, about 23.7 million years ago. Covariance between the carbon and oxygen isotope records suggests that the oceanic carbon cycle may have contributed to global cooling during the ~400-kyr cycles, particularly at the Oligocene/Miocene boundary.

The Oligocene/Miocene boundary represents a significant climate transition in Cenozoic Earth history; ocean temperatures were slowly increasing and continental ice-volume was apparently decreasing from the large accumulations of the middle–late Oligocene^{2–4}. Oxygen isotope records indicate that this trend may have been interrupted by a series of brief glaciations that began in the earliest Miocene and continued up to the time of significant middle Miocene cooling². The first and largest of these events, Mi-1, occurred at the Oligocene/Miocene boundary.

As with most other pre-Pliocene intervals, previous isotope records that span the Oligocene/Miocene boundary lack the sampling density needed to resolve palaeoenvironmental changes occurring on timescales of <10⁵ years. Attempts to construct higher resolution records have been hampered either by the lack of continuous, undisturbed sedimentary sections, or by diagenetic overprinting. These deficiencies were recently resolved with the successful recovery of an expanded and hiatus-free section of upper Oligocene and lower Miocene nannofossil chalk in Hole 929A, on Ceara rise in the western equatorial Atlantic Ocean (ref. 5) (4360 m water depth). This section is characterized by prominent decimetre-scale oscillations in sediment colour and magnetic susceptibility with periods similar to those associated with orbital forcing⁶.

‡ Present address: Department of Marine Science, University of South Florida, St Petersburg, Florida 33701, USA.