

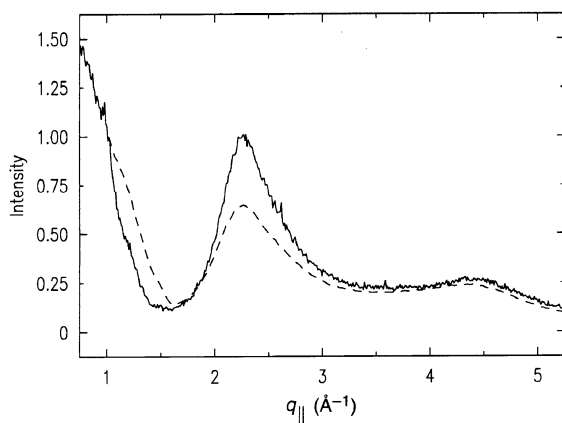


FIG. 4 Grazing-incidence diffraction patterns of a bare (dashed line) and a C_{18} monolayer-covered (bold solid line) mercury surface, measured with an incidence angle $\alpha = 0.2^\circ = 0.6\alpha_c$ (where α_c is the critical angle) and a vertical detector acceptance of $0 \leq q_z \leq 1.1 \text{ \AA}^{-1}$ (intensity given in arbitrary units). Here $q_{\parallel} = 4\pi/\lambda \sin \theta$ is the in-plane momentum transfer and θ is defined in Fig. 1 inset. Only the broad peaks corresponding to the mercury liquid structure factor are found in the monolayer data (in-plane resolution $\Delta(2\theta) = 5 \text{ mrad}$). This data was obtained at the TROIKA undulator beamline of the ESRF¹⁹. GIXD measurements at X22B and X25 at NSLS gave similar results.

in-plane order is usually found. This order results not only from the confinement of the monolayer to the water surface, because such in-plane order also appears in alkanes where crystalline monolayers form at the surface of their own melts at temperatures up to a few degrees above the bulk freezing point¹⁸. In this case the 'monolayer' and 'subphase' molecules are identical, and, of course, fully miscible. Both systems are dominated by the inter-chain interactions and the bonds to the sub-phase ($\sim 10 \text{ kJ mol}^{-1}$ hydrogen bonds in Langmuir monolayers and $\sim 1 \text{ kJ mol}^{-1}$ van der Waals interactions in alkanes) are relatively weak. Thus, we conclude that the inter-chain interactions are responsible for the long-range order in these systems. The interactions with the disordered atoms of the liquid subphase tend, in principle, to disrupt this ordering but are too weak to cause more than slight changes in the structure and the phase diagrams of these films.

For SAMs, spatial variations of the interactions with the substrate (corrugation potential) may either promote or oppose the ordering favoured by the inter-chain interactions, depending on the spatial periodicities of both interactions. For alkanethiols on Au(111) (refs 5–7) this corrugation potential favours well ordered monolayers which may be either commensurate or uniaxial incommensurate with the underlying metal. The small mismatch between the underlying substrate and alkane spacings is compensated by a molecular tilt. The elevated melting temperature of C_n on Au(111) relative to that of the bulk⁵ manifests the strong ordering tendency imposed by the interactions with the substrate.

Thiols on mercury 'feel' a similarly strong subphase interaction ($\sim 200 \text{ kJ mol}^{-1}$), but as the liquid mercury surface has no intrinsic long-range order, there is no underlying corrugation potential to order the thiol monolayer. This should promote formation of the order favoured by the inter-chain interaction. If, on the other hand, the ordered thiol layer were to impose its order on the underlying mercury through the strong subphase interaction, with the same structure as found for alkanethiols formed on gold and silver, then the resultant 5–10% compression of the mercury atoms would carry a great energy cost. In addition, this ordered mercury layer, at a temperature where the bulk is disordered, would represent a large increase in the entropic contribution to the free energy of the mercury and for these two reasons seems unlikely. Instead the (liquid-like) subphase surface structure is imposed on the adsorbate film, resulting in an in-plane-disordered film. □

Received 22 May; accepted 15 October 1996.

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ACKNOWLEDGEMENTS. We thank C. Chidsey for providing the C_{22} and C_{30} thiols and D. Mandler, I. Rubinstein, G. Whitesides and P. Fenter for discussions. This work was supported by the Division of Material Sciences, US Department of Energy, the US National Science Foundation, and the US-Israel Binational Science Foundation.

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Prediction of global rainfall probabilities using phases of the Southern Oscillation Index

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THE El Niño/Southern Oscillation (ENSO) is a quasi-periodic interannual variation in global atmospheric and oceanic circulation patterns, known to be correlated with variations in the global pattern of rainfall^{1–3}. Good predictive models for ENSO, if they existed, would allow accurate prediction of global rainfall variations, thus leading to better management of world agricultural production^{4,5}, as well as improving profits and reducing risks for farmers^{6,7}. But our current ability to predict ENSO variation is limited. Here we describe a probabilistic rainfall 'forecasting' system that does not require ENSO predictive ability, but is instead based on the identification of lag-relationships between values of the Southern Oscillation Index, which provides a quantitative measure of the phase of the ENSO cycle, and future rainfall. The system provides rainfall probability distributions three to six months in advance for regions worldwide, and is simple enough to be incorporated into management systems now.

Climate forecast systems offer a means to reduce risks in potentially 'bad' years and maximize profits in potentially 'good' years. The Southern Oscillation Index (SOI) provides a measure that can be used in developing a seasonal forecast system. The SOI is here defined as the difference in atmospheric pressure anomalies between Tahiti and Darwin divided by the standard deviation of the difference (and multiplied by 10)⁸. The SOI is moderately correlated with future seasonal rainfall in some regions^{9,10}, partly due to the strong auto-correlation between SOI values in early austral winter with those three to six months ahead¹¹. This 'phase-locking' of the SOI into the annual cycle permits seasonal forecasting to be attempted once the early stages of various manifestations of the ENSO cycle are underway. In other words,

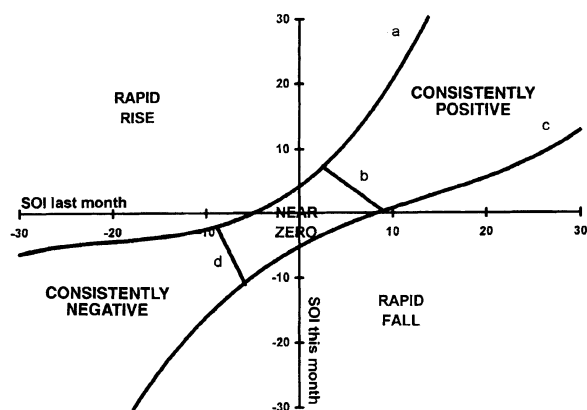


FIG. 1 Categorization of the five SOI phases, depending on SOI values in the current and immediately preceding month. The five SOI phases are: 'consistently negative', 'consistently positive', 'rapid fall', 'rapid rise' and 'consistently near zero'. For these regions, the current and previous month means, averaged over each region, are respectively $(-12.18, -14.52)$, $(+9.49, +11.21)$, $(-9.92, +2.75)$, $(+6.62, -4.38)$ and $(-1.67, -0.36)$ ¹². The boundaries between the regions (phases) in the figure are defined as follows: curve a, $M_2 = 4.2 + 1.07M_1 + 0.048M_1^2 + 0.0008M_1^3$; curve b, $M_2 = 10 - 1.08M_1$; curve c, $M_2 = -5.2 + 0.78M_1 - 0.024M_1^2 + 0.0006M_1^3$; curve d, $M_2 = -27.8 - 2.9M_1$. Here M_1 is the SOI value for the first month, and M_2 is the value for the second month¹⁹. The latest monthly SOI and the current SOI phase are available on <http://www.dpi.qld.gov.au/longpdk>.

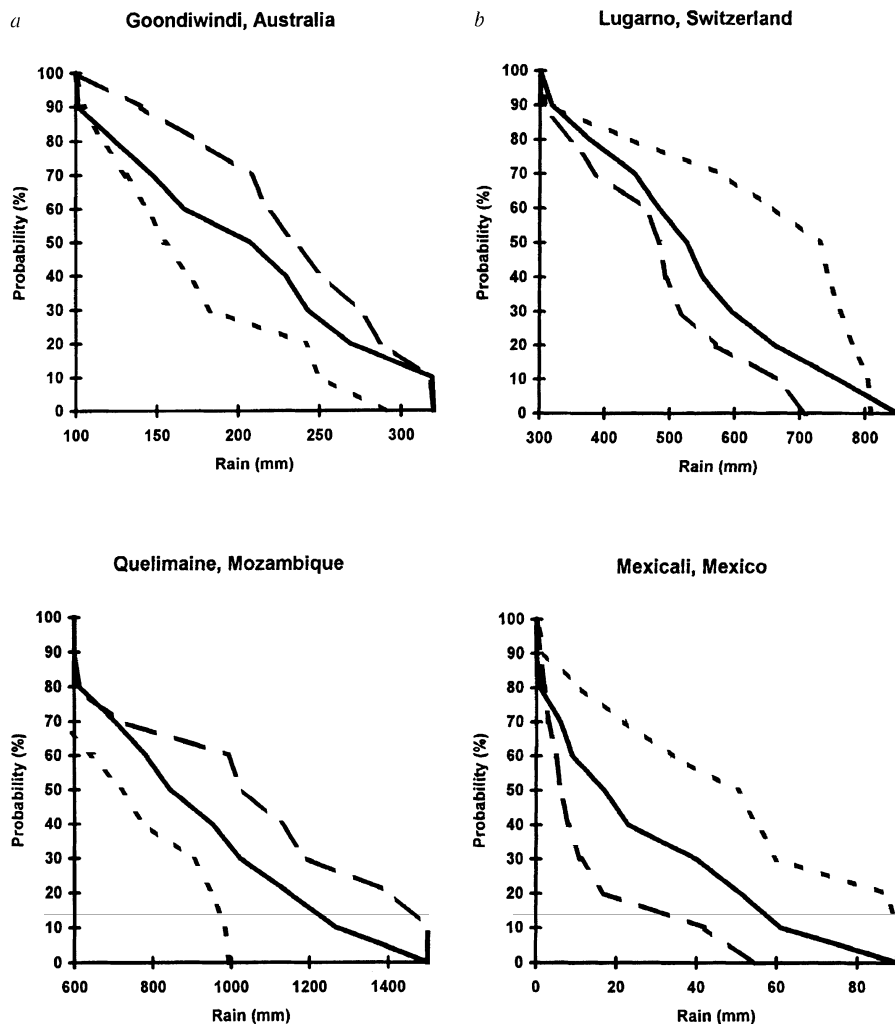
a forecast system based on 'phase-locking' of the SOI does not depend on a precise forecast of an El Niño event. Here we categorize current SOI patterns and relate these patterns to future rainfall probabilities based on lag-relationships derived from historical SOI patterns and rainfall over the past 120 years.

Determining the most appropriate SOI pattern to relate to rainfall is made possible through classification (using principal-components analysis and cluster analysis) of SOI behaviour¹². Every month of the past 120 years has been categorized into one of five SOI types or 'phases' that takes into account both the value and change in SOI. Earlier work demonstrated surprisingly little contamination or noise in monthly SOI data due to the intra-

seasonal oscillation¹³ in monthly SOI data. This point is reinforced by the fact that there is little difference in the effect of the intra-seasonal oscillation on correlations between the SOI and tropospheric variables if either monthly or seasonal data are used¹⁴. Further, the approach of using monthly SOI data has the advantage that the structure of the troposphere in relation to the Southern Oscillation is better identified. The coordinates of the boundaries of the five phases (together with a detailed description of the SOI phases) are depicted in Fig. 1. Further explanation of the SOI phase method may be found in a recent application to frost 'forecasting'¹⁵ and in an estimation of peanut yields¹⁶.

For every month of the year, rainfall probability distributions

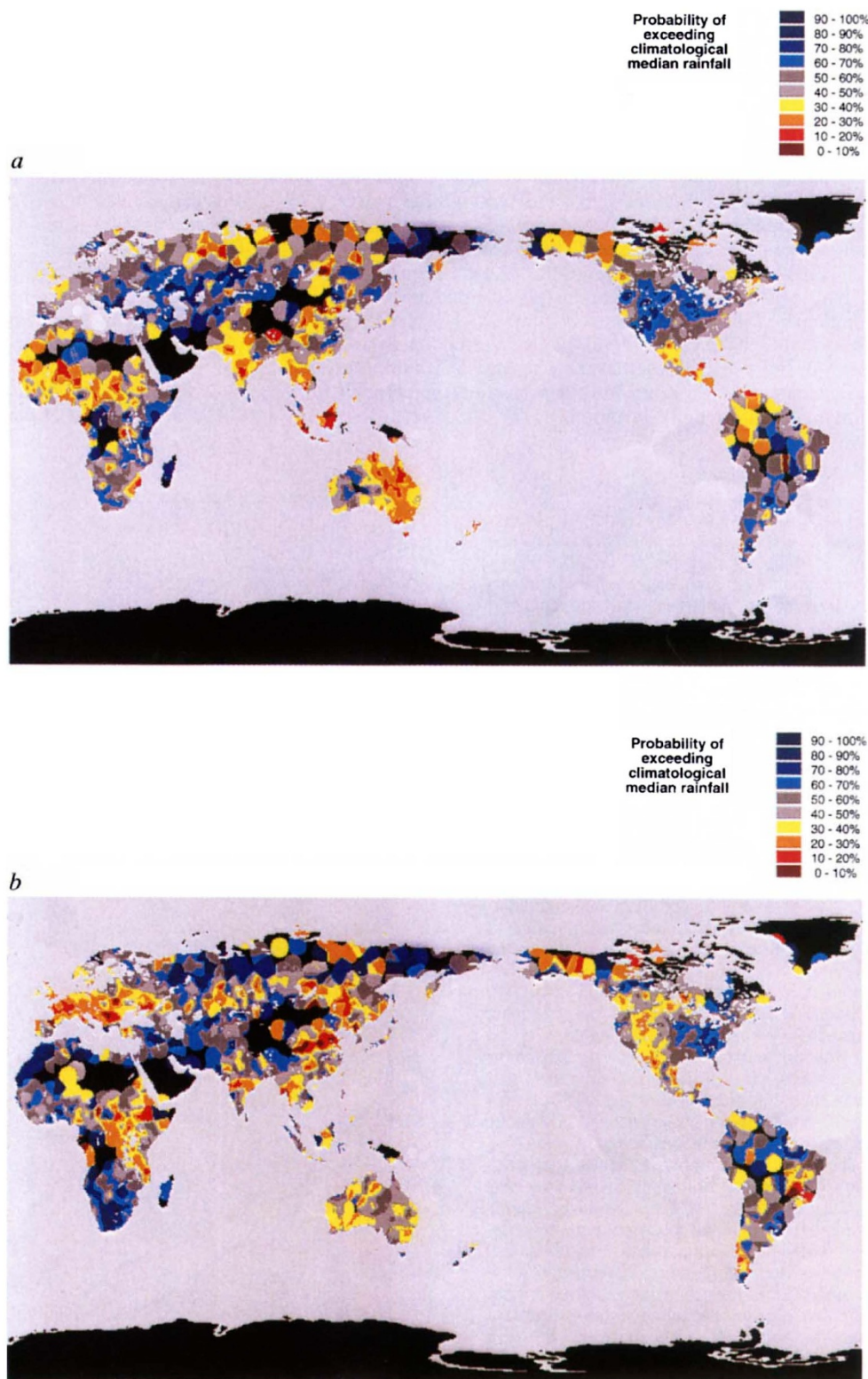
FIG. 2 Cumulative probability distributions of subsequent rainfall associated with SOI phases at the four locations mentioned in the text. The figures show probability of exceeding any particular rainfall amount. At most locations the data set includes at least the past 70 years, although this criterion could not be met in every instance. Broken lines represent years associated with each of two SOI phases; the solid line shows the 'all-years' distribution (climatology). At Goondiwindi, rainfall is for the period June–October. The short-dashed line depicts the cumulative distribution associated with SOI phase 'rapid fall' in the preceding April/May; the long-dashed line shows the distribution following SOI phase 'rapid rise'. The diagram shows that the probability of obtaining 200 mm at rainfall at Goondiwindi is 25% following SOI phase 'rapid fall' and 70% following SOI phase 'rapid rise', and that there is a difference in median rainfall between distributions of 80 mm. At Quelimaine, rainfall is for the period December–February. The short-dashed line shows the distribution associated with SOI phase 'consistently negative' in the preceding October/November, while the long-dashed line represents the distribution following SOI phase 'consistently positive'. The diagram shows that there is a 0% probability of rainfall exceeding 1,000 mm following SOI phase 'consistently negative', but a 65% probability of exceeding that amount following phase 'consistently positive'. At Lugarno, for rainfall in the May–July period, the short-dashed line shows higher rainfall as more likely following phase 'consistently negative' in March/April compared to phase 'rapid fall' (long-dashed line). At Mexicali, for rainfall in the October–December period, higher rainfall is more probable following phase 'consistently negative' (short-dashed line) in July/August than following phase 'consistently positive' (long-dashed line).



(for the subsequent three-month period), have been produced from the subsets of years corresponding to each of the five SOI phases; this has been done for locations with sufficient monthly rainfall record (>70 years)¹⁷. Figure 2 shows examples of such lagged cumulative rainfall probability distributions associated with two representative SOI phases for four globally dispersed locations: Goondiwindi, Australia; Quelimaine, Mozambique; Lugarno, Switzerland; and Mexicali, Mexico. At each of these locations there is a significant shift in a large part of the distribution associated with the SOI phases. Non-parametric statistical

'tests' (for example, Kruskal–Wallis and Kolmogorov–Smirnov) can be applied to determine whether the rainfall probability distributions (not just the rainfall medians) differ significantly. Applying these tests to the locations in Fig. 2 indicated that the cumulative probability distributions differed significantly at the 95–99% probability level. When such tests are applied at many locations there is, of course, a possibility that significant differences identified at some locations are there by chance; it is also the case that non-significant differences suggested at some other stations may, in fact, be real.

FIG. 3 *a*, Probability of exceeding climatological median rainfall for the August–October period associated with SOI phase 'consistently negative' in June/July. Based on individual analysis of 5,000 locations with >70 years of monthly data. Regions shaded dark brown to red represent the lowest probabilities of exceeding climatological median rainfall (0–20%), those shaded light orange to yellow represent probabilities between 20 and 40%, and so on. Black areas represent regions with insufficient data to perform this analysis. *b*, As *a* but depicting probability of exceeding climatological median rainfall for the September–November period following SOI phase 'rapid fall' in the preceding July/August.



Although the associations vary, there is generally a higher probability of receiving any given 'future' rainfall amount following the 'consistently positive' SOI phase than there is following the 'consistently negative' SOI phase at locations such as Goondiwindi and Qelimaïne. There is also, generally, a higher probability of receiving any given rainfall amount following SOI phase 'rapid rise' in the austral autumn (which may be associated with some breakdown of an El Niño event) than there is following SOI phase 'rapid fall'. Rainfall distributions following SOI phase 'consistently near zero' are usually (but not always) close to the 'all-years climatology' rainfall distribution. Although there is a significant shift in the cumulative probability distributions of subsequent rainfall associated with SOI phases at these locations, the rainfall range may be little altered.

Cumulative rainfall probability distributions for Lugarno and Mexicali demonstrate dissimilar associations with the SOI phases to those represented for locations such as Goondiwindi and Qelimaïne (Fig. 2). At Lugarno and Mexicali, the probability of obtaining any future given amount of rainfall for the May–July and October–December periods, respectively, is highest following the 'consistently negative' SOI phase. This type of relationship for Europe has been hinted at by others¹⁸.

A spatial representation of this analysis was developed by considering the probability of exceeding the climatological median for any season following each SOI phase. Figure 3a shows an example of a map depicting the probability of exceeding the climatological median rainfall for August–October associated with 'consistently negative' SOI phase in June/July. Figure 3b shows (as an example) the probability of exceeding the climatological median rainfall for September–November associated with the 'rapid fall' SOI phase in July/August. These are just two examples from the 60 maps produced using this method. The maps provide a 'snapshot' of the lag-relationships between SOI phase and rainfall. A simple least-squares contouring algorithm was applied to produce the spatial patterning following analysis of global rainfall data, although where data were scarce this resulted in an occasional circular pattern.

The maps show some remarkable features. In Fig. 3a, the 'consistently negative' SOI phase in June/July is associated with a 'low' probability of exceeding the climatological median rainfall for the subsequent three months in many world regions including much of eastern Australia, Indonesia, West Indies, Alaska, central India, Vietnam, northern parts of the former Soviet Union and sections of western Africa. Conversely, many world regions such as southwestern and north-central United States, Iran, central Asia and parts of South America have relatively high probabilities of exceeding their respective climatological median rainfalls. In Fig. 3b, the 'rapid fall' SOI phase is associated with a relatively low probability (0–40%) of exceeding climatological median rainfall for the subsequent three months over much of central Europe and central China. Conversely, much of South Africa, Namibia, north-west Africa, Iran and the eastern United States have a reasonably high probability (60–90%) of exceeding the climatological median rainfall for the following three months. Note that areas of 'no skill' (that is, close to 50% chance of exceeding the climatological median) are depicted as 'grey areas'. We were

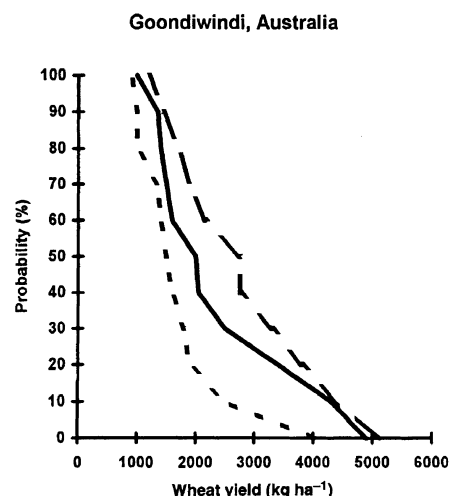


FIG. 4 Cumulative probability distribution of simulated wheat yield at Goondiwindi, Australia. The solid line represents the 'all-years' (100 years) distribution. The short-dashed line represents the probability of exceeding a given simulated yield following SOI phase 'rapid fall' in April/May, while the long-dashed line represents probability of exceeding a given simulated yield following SOI phase 'rapid rise'. The figure shows, for example, that the probability of exceeding 2,000 kg ha⁻¹ following SOI phase 'rapid fall' is 18%, while the probability of exceeding that amount following SOI phase 'rapid rise' is 64%.

surprised that a significant relationship between SOI phase and subsequent rainfall existed in northern parts of the former Soviet Union as this region had hitherto not been regarded as being strongly influenced by ENSO teleconnections (although maps in some references hint that this may be so¹⁸). Closer examination of our data revealed a significant difference at the 95% level in the cumulative distributions for rainfall in the July–September period, for example, associated with the SOI phases in May/June for locations in the former USSR such as Volochanka (lat. 70.95°, long. 94.50°) and Dudinka (lat. 69.40°, long. 86.17°).

These simple 'forecast' maps may have direct relevance to many aspects of human endeavour such as food production and commodity marketing; they may be readily applied to agriculture. Use of the SOI phase system has been found to lead to improved profitability and risk management in Australian wheat cropping. By using daily data from the analogue years associated with each of the SOI phases (for example, phases in April/May) with crop simulation models, a considerable shift in potential yield could be identified. Figure 4 shows cumulative probability distributions of potential wheat yield and the large shift in yield likelihood (shift in median yield of 1,500 kg ha⁻¹) for a simulated crop grown at Goondiwindi, Australia (southern Queensland) depending on whether the SOI phase the previous austral autumn represented 'rapid fall' or 'rapid rise' patterns. Incorporation of global sea surface temperature data may further improve this simple, statistically based rainfall probability system. □

Received 27 December 1995; accepted 11 October 1996.

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ACKNOWLEDGEMENTS. We thank S. Chapman for assistance with access to the climate data bases, and N. Flood for assistance with the forecast maps. This work was supported by the Australian Grains Research and Development Corporation.

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