Interpreting the seasonal cycles of atmospheric oxygen and carbon dioxide concentrations at American Samoa Observatory

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[1] We present seven years of atmospheric O_2/N_2 ratio and CO_2 concentration data measured from flask samples collected at American Samoa. These data are unusual, exhibiting higher short-term variability, and seasonal cycles not in phase with other sampling stations. The unique nature of atmospheric data from Samoa has been noted previously from measurements of CO_2, methyl chloroform, and ozone. With our O_2 data, we observe greater magnitude in the short-term variability, but, in contrast, no clear seasonal pattern to this variability. This we attribute to significant regional sources and sinks existing for O_2 in both hemispheres, and a dependence on both the latitudinal and altitudinal origins of air masses. We also hypothesize that some samples exhibit a component of ''older'' air, demonstrating recirculation of air within the tropics. Our findings could be used to help constrain atmospheric transport models which are not well characterized in tropical regions. *INDEX TERMS:* 1615 Global Change: Biogeochemical processes (4805); 3319 Meteorology and Atmospheric Dynamics: General circulation; 1610 Global Change: Atmosphere (0315, 0325). **Citation:** Manning, A. C., R. F. Keeling, L. E. Katz, W. J. Paplawsky, and E. M. McEvoy, Interpreting the seasonal cycles of atmospheric oxygen and carbon dioxide concentrations at American Samoa Observatory, *Geophys. Res. Lett.*, *30*(6), 1333, doi:10.1029/2001GL014312, 2003.

1. Introduction

[2] We present O_2/N_2 ratio and CO_2 concentration data from flask samples collected at Cape Matatula, American Samoa (see Figure 1) from June 1993 to January 2001 and discuss unusual features present in these data. The unique climatological conditions at Samoa and their impact on concentrations of atmospheric constituents have been noted previously. Following the wind climatology at Samoa presented by *Bortniak* [1981] and from an analysis of air mass backward trajectories, *Halter et al.* [1988] were able to show that the air arriving at Samoa came from one of three broadly-defined source regions centered on anticyclones named A_{NP}, A_{SP}, and A_{ANZ} (Figure 1), representing the north Pacific tropical anticyclone, the southeast Pacific tropical anticyclone, and the Australia-New Zealand anticyclone respectively.

[3] By analyzing three years of CO_2 data from 1979–1981, *Halter et al.* [1988] demonstrated that the observed Samoa CO_2 seasonal cycle was a superposition of three distinct seasonal cycles originating from each of these three air mass source regions. *Halter et al.* [1988] then showed that the seasonal dependence of the CO_2 variability observed at Samoa arises from an interplay between the seasonally varying interhemispheric gradient in CO_2 concentration, and of the seasonally varying frequency of occurrence of A_{NP} air arriving at Samoa, which is sensitive to the position and strength of the ITCZ and the SPCZ, shown in Figure 1. This interplay results in greater CO_2 variability during austral summer and autumn and accounts for an offset between the timing of the maximum in the interhemispheric gradient and the timing of the maximum variability.

[4] *Prinn et al.* [1992] and *Hartley and Black* [1995] found relatively high short-term variability in methyl chloroform concentrations measured at Samoa during austral summers, but only in non-El Niño years. *Hartley and Black* [1995] showed that these observations could be explained by changes in large-scale atmospheric circulation patterns at Samoa similar to the seasonal changes described by *Halter et al.* [1988] and *Bortniak* [1981]. They demonstrated that the frequency of occurrence of air originating from the A_{NP} anticyclone was significantly reduced during El Niño years, explaining the lack of methyl chloroform variability in these years.

[5] *Harris and Oltmans* [1997] observed variability in tropospheric ozone concentrations at Samoa approximately six months out of phase with the variability in CO_2 described by *Halter et al.* [1988]. They attributed these observations to not to variations in the latitudinal origin of the air masses arriving at Samoa, but to variations in the altitudinal origin which impact the relative strengths of ozone sources and sinks.

[6] For our flask samples, collection, analysis, and calibration gas procedures are described in detail in *Keeling et al.* [1998]. The external imprecision of individual flask analyses is estimated to be ±3.3 per meg and ±0.2 ppm for O_2/N_2 ratios and CO_2 concentrations respectively [*Keeling et al.*, 1998]. Flasks are typically collected in triplicate, resulting in a standard error for a given sample date of ±1.9 per meg in O_2/N_2 ratio and ±0.12 ppm in CO_2 concentration.

2. Seasonal Trends in O_2/N_2 Ratios and CO_2 Concentrations

[7] Similarly to methly chloroform data [*Hartley and Black*, 1995] our CO_2 data show significantly reduced

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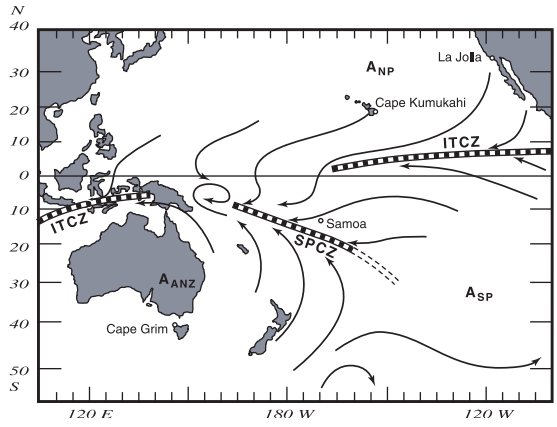

Figure 1. Average surface air circulation patterns in the region of American Samoa (14°S, 171°W), shown for austral summer. This figure is after *Bortniak* [1981] and *Halter et al.* [1988]. Lines labeled ITCZ and SPCZ are the axes of the Intertropical Convergence Zone and the South Pacific Convergence Zone respectively. In austral winter the ITCZ extends further westwards and the SPCZ shifts northwards, resulting in a lower frequency of occurrence of air from the anticyclone, A_{NP}, arriving at Samoa, and a higher frequency of air from anticyclone, A_{ANZ}.

variability during the austral summer of the strong 1997–1998 El Niño, when compared to other years. The figure shows the expected secular increase in CO_2 concentrations and decrease in O_2/N_2 ratios. These trends result from fossil fuel combustion, but are attenuated by net growth of the land biosphere and, in the case of CO_2, oceanic uptake. The CO_2 data in Figure 2b support the conclusion of *Hartley and Black* [1995], showing that during the strong 1997–1998 El Niño, CO_2 variability during the austral summer is significantly reduced compared to other years. Figure 2 shows a small seasonal cycle in CO_2, and a much larger-amplitude cycle in O_2/N_2. Seasonal variability in CO_2 is generally attributed to seasonality in photosynthesis and respiration processes on land. In the case of Samoa the seasonal cycle can also be influenced by long-range atmospheric transport as discussed below. Seasonality in atmospheric O_2/N_2 is generally caused by seasonality in photosynthesis and respiration of both land and marine biota and thus exhibits a much greater amplitude than CO_2 at Samoa.

[8] The unusual seasonality observed at Samoa is illustrated in Figure 3, which shows the four-harmonic seasonal component of the O_2/N_2 and CO_2 curve fits in Figure 2. In Figure 3a the maximum O_2/N_2 ratio at Samoa occurs in April, approximately two months later than the maximum at Cape Grim. The minimum O_2/N_2 ratio at Samoa occurs in late August or early September, a few weeks earlier than Cape Grim. There is some evidence of a weak second maximum in late December at Samoa. CO_2 data in Figure 3b show an even larger contrast to typical southern hemisphere patterns. Maximum CO_2 at Samoa occurs in February in contrast to September for Cape Grim, whereas the minimum occurs in May at Samoa and April at Cape Grim. CO_2 also exhibits a clearer second maxima and minima at Samoa. The La Jolla curves show that Samoa O_2/N_2 ratios and CO_2 concentrations are also not in phase with northern hemisphere cycles.

3. Land and Ocean Partitioning of Air Mass Influences at Samoa

[9] With our O_2/N_2 ratio measurements, to a good approximation, we are able to distinguish between land and ocean processes affecting the air masses arriving at Samoa. We do this by defining a tracer, Atmospheric Potential Oxygen (APO), defined in *Stephens et al.* [1998]. Variations in APO on seasonal and shorter time-scales can only be caused by air-sea exchanges of O_2, N_2, and CO_2 [*Stephens et al.*, 1998]. In contrast to APO, variations in CO_2 on these time-scales are mainly caused by land biotic exchanges, and not by the oceans owing to chemical buffering of CO_2 changes in the oceans.

[10] In Figure 4 we show plots of APO and CO_2 concentrations representing oceanic and land influences respectively. The symbols on each plot show all flask samples collected at Samoa where all samples have been collapsed into one calendar year. All data and curves in Figure 4 have been interannually detrended by removing the interannual spline component of the Cape Grim curve fit.

[11] Samoa CO_2 data in Figure 4b agree very well with the earlier, shorter record presented by *Halter et al.* [1988], showing greater variability in the austral summer and autumn. An additional feature, however, emerges from

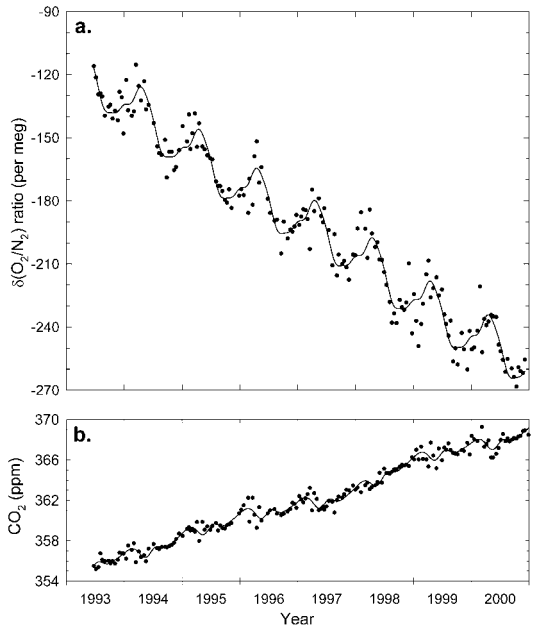

Figure 2. O_2/N_2 ratios (a) and CO_2 concentrations (b) measured from flask samples collected at Cape Matatula, American Samoa. The *y* axes of plots a and b have been scaled so that changes in O_2 and CO_2 can be compared visually on a mole to mole basis (and also for Figures 3, 4, and 5). 1 per meg is equivalent to 0.001 per mil. For comparison purposes, a change in O_2/N_2 ratio of 4.8 per meg corresponds to a change of 1 ppm in CO_2. Curve fits are least squares fits to the sum of a four harmonic seasonal cycle and a stiff spline.

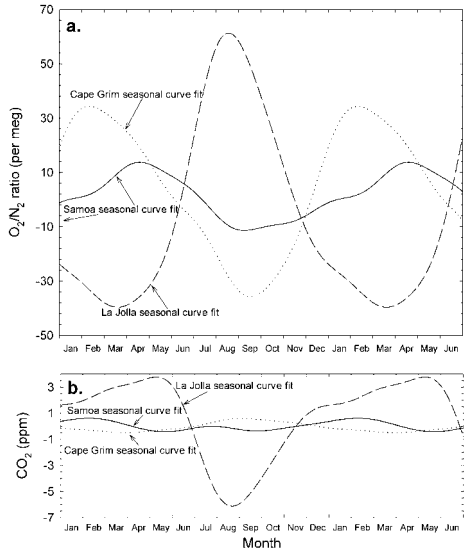

Figure 3. Four-harmonic seasonal components of the curve fits in Figure 2, showing O_2/N_2 ratios (a) and CO_2 concentrations (b). The curves shown are the average seasonal cycles calculated from all data over the 7.5 year record. Also shown for comparison are similar seasonal curve fits calculated from data collected at our sampling stations at Cape Grim, Tasmania, and La Jolla, California (labeled in Figure 1), which we assume are broadly representative of mid-latitudes of the southern and northern hemisphere respectively.

Figure 4b which was not discussed by *Halter et al.* [1988]. For the period from August to October, Samoa CO_2 data exhibit persistently higher concentrations than present in air masses either to the north or to the south (represented by curve fits to Cape Kumukahi and Cape Grim data respectively). A similar feature is seen in the APO data during May and June. A simple explanation for these features is that the air at Samoa includes a component not recently originating from the north or south, but from the tropics at some point in the past. Simulations of the seasonal cycles in APO with extra-tropical sources in an atmospheric tracer transport model account well for the phasing of the APO seasonal cycle at Samoa, as well as in stations to the north and south, showing that the APO cycle can be simply accounted for based on the finite time scale for transport from higher latitudes into the tropics and the finite residence time of air within the tropics [*Garcia and Keeling*, 2001].

[12] In Figures 5a to 5d we analyze the monthly variability in APO and CO_2 data and compare these monthly values to the monthly values of the absolute north-south interhemispheric gradient in APO and CO_2. Our Samoa CO_2 data (Figures 5c and 5d) show that the minimum variance in CO_2 is roughly synchronous with the time of minimum CO_2 gradient (July–November), whereas the time of maximum CO_2 variance (March–April) is offset from the time of maximum CO_2 gradient (April–May), both features being consistent with the findings of *Halter et al.* [1988], as discussed earlier. Both features can be explained assuming the CO_2 variability is tied to the interhemispheric gradient in CO_2, with the gradient exhibiting greater or lesser influence depending on the frequency of occurrence of the A_{NP} air mass.

[13] A corresponding comparison of variance and gradients in APO is complicated (Figures 5a and 5b), however, because APO variance at Samoa has less clear seasonality. The only pronounced feature is the minimum in variance during May–June, which is roughly synchronous with one (of two) minima in the APO gradient. The other minimum in the APO gradient (November–December) is not aligned with a clear minimum in variance. The difference is most likely explained by seasonal variations in the homogeneity of southern hemisphere air masses. In particular, the southern hemisphere is likely to be less homogenous in APO during the November–December period due to strong sources of atmospheric O_2 associated with marine biological production. These strong sources lead to the steep seasonal rise observed in APO at Cape Grim at this time of year, which can be contrasted with the more gradual decrease later in the season [*Bender et al.*, 1996]. This interpretation is also consistent with the fact that the variability at Cape Grim also shows an apparently clear minimum during the May–June period, as shown also in Figure 5a. The results thus suggest that much of the APO variability at Samoa is tied to inhomogeneities in air masses within the southern hemisphere as opposed to inhomogeneities between the northern and southern hemispheres, as is evidently the case for CO_2.

[14] A further indication of the role played by southern hemisphere air mass inhomogeneities can be seen in the contrasting variability in CO_2 and APO at Cape Grim. Whereas the APO variability at Cape Grim is similar to that at Samoa throughout the year, the CO_2 variability at

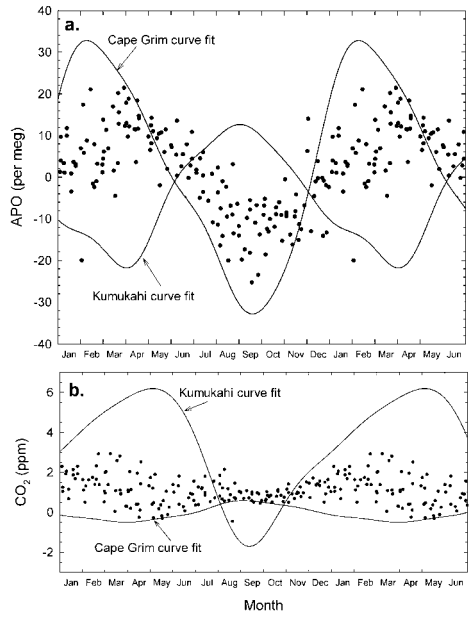

Figure 4. Oceanic (a) and land biotic (b) influences on the air masses arriving at Samoa. The seasonal component of all Samoa flask samples are shown, as well as seasonal curve fits from Cape Grim, Tasmania, and Cape Kumukahi, Hawaii, representing the nearest stations from which we have data in the southern and northern hemisphere respectively.

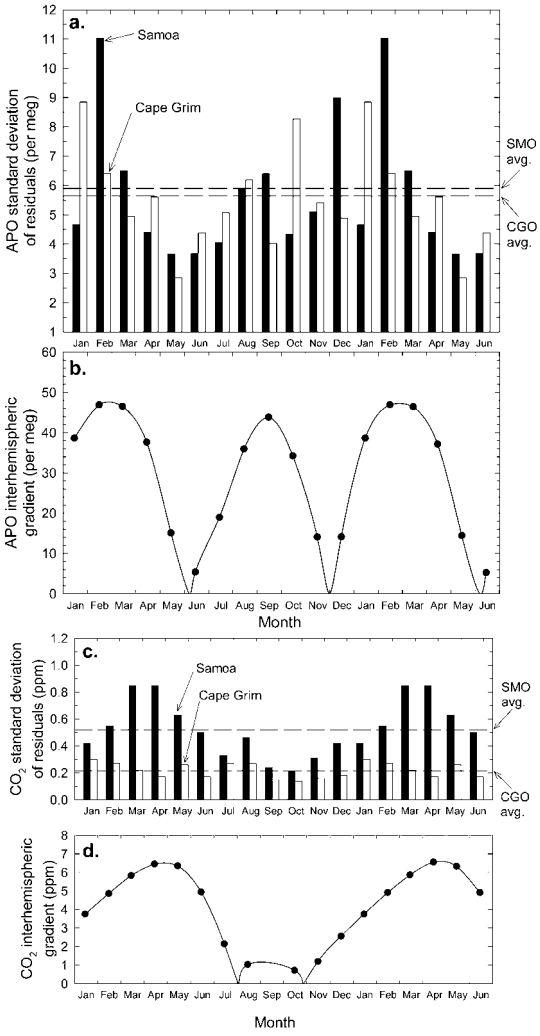

Figure 5. APO (a) and CO_2 (c) monthly standard deviations of the residuals of flask data from curve fits for Samoa and Cape Grim. The annual average residual at each station is shown by horizontal dashed lines. To provide a comparison with Samoa, Cape Grim monthly variabilities are also calculated. (b) and (d) show the absolute magnitude of the north-south interhemispheric gradient for APO and CO_2 respectively, calculated each month, and using Cape Grim and Cape Kumukahi data as representative of the southern and northern hemisphere respectively.

Cape Grim is consistently less than that at Samoa, and does not shown the seasonality observed at Samoa. The lack of strong sources of CO_2 at higher southern latitudes allows CO_2 to become homogenized so that variations in air mass origin within the southern hemisphere have much less impact on CO_2 variability than APO variability. In addition, the backward wind trajectory analyses of *Harris and Oltmans* [1997] showed that air masses originating from the southern hemispheric A_{ANZ} anticyclone arriving at Samoa were more variable in their originating altitude than air masses arriving from A_{NP} or A_{SP}. Because the source and sink mechanisms for APO occur via air-sea gas exchange at the sea surface, this altitudinal variability in air mass origin will contribute further to the variability observed in the APO signal.

[15] In summary, APO seasonal variability at Samoa is a function of the interhemispheric gradient, the frequency of occurrence of air masses originating from the northern hemisphere, and of the strength of O_2 exchange and mixing within the southern hemisphere. Of these three effects it is the latter which accounts for the difference in the patterns of variability in APO versus CO_2. These contrasting findings of APO and CO_2 could be used to better constrain atmospheric transport models which are not well characterized in tropical regions.

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