Interpreting Seasonal Cycles of Atmospheric Oxygen and Carbon Dioxide Concentrations at American Samoa Observatory

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INTRODUCTION AND METHODOLOGY

Precise atmospheric oxygen (O_2) measurements can be used as a tool for studying the global carbon cycle. *Keeling and Shertz* [1992] calculated global land and ocean carbon sinks from O_2 and CO_2 concentrations measured from flask samples collected at three different locations. From an analysis of the seasonal cycles of O_2 and CO_2 they were also able to provide an estimate of net biological productivity in the oceans. Their work has been updated with more recent data and findings by *Bender et al.* [1996], *Keeling et al.* [1996], and *Battle et al.* [2000]. Atmospheric O_2 measurements can also be used in a variety of other biogeochemical applications such as measuring air-sea gas exchange rates [*Keeling et al.*, 1998a], assessing the performance of ocean carbon cycle models [*Stephens et al.*, 1998], and interpreting and validating satellite ocean color data [*Balkanski et al.*, 1999].

From June 1993 to the present, CMDL staff have collected flask samples from Cape Matatula, American Samoa (SMO) as part of the Scripps global atmospheric oxygen sampling network. These data up to June 2000 are presented in this report. Flask sampling protocols are described in detail in *Keeling et al.* [1998b]. Briefly, ambient air samples are collected approximately biweekly, in triplicate, in 5-L glass flasks equipped with two stopcocks that are sealed with Viton o-rings. Air is drawn through a Dekoron intake line mounted up a tower or mast. A small compressor pump maintains an air flow of approximately 5 STP L min^{-1}, flushing ambient air through each flask. Flushing continues until a minimum of 15 flask volumes has passed through each flask, and then the sample is sealed off at a pressure of about 1 bar. A cryogenic cold trap at about -70°C pre-dries the air to remove water vapor. Flask samples are shipped back to the laboratory in La Jolla, California, for measurements of both O_2 and CO_2 concentrations.

Flask samples are collected by station personnel during what are considered to be "clean, background air" conditions; sample air that has not been contaminated by local or regional anthropogenic or terrestrial processes is required. In this manner seasonal and interannual temporal patterns in O_2 and CO_2 concentrations can be observed. The general criteria used to determine when these conditions are met are a pre-established wind direction and speed and relatively steady, non-fluctuating, in situ atmospheric CO_2 concentrations. At Samoa the criteria used are a wind direction between 330° and 160°, a wind speed greater than 2 ms^{-1}, and 2 consecutive hours of CO_2 concentration agreeing to within 0.25 ppm [*Waterman et al.*, 1989].

In the Scripps laboratory, flask samples are analyzed simultaneously for CO_2 concentration on a Siemens nondispersive infrared analyzer (NDIR) and for O_2/N_2 ratio on our interferometric analyzer [*Keeling*, 1988]. Samples are analyzed relative to a working gas, which in turn is calibrated each day against a pair of secondary reference gases of predetermined O_2/N_2 ratios and CO_2 concentrations. A suite of 12 primary reference gases are analyzed roughly every 6 months as a check on the long-term stability of the secondary reference gases. (See *Keeling et al.* [1998b] for a detailed discussion of reference gases and calibration procedures.)

Measurements of O_2/N_2 ratios are used to report changes in O_2 concentration, relying on the assumption that N_2 concentrations are constant. Based on the results of other studies [*Manning*, 2000], the possibility of O_2 fractionation relative to N_2 in our samples collected at Samoa became a concern. It was discovered that under certain flow, pressure, and temperature conditions, O_2 will fractionate relative to N_2 at "tee" junctions where an incoming air stream divides into two. Room temperature variability and the ratio of the flow rates at the tee junction appear to be the two most crucial parameters [*Manning*, 2000]. At Samoa a tee existed in the intake line because this line is shared with the continuous CO_2 analyzer operated by CMDL personnel. Therefore in May 1999 the intake setup was modified by installing a dedicated line with no tee junctions. At the same time the physical location of the intake line was shifted from the top of a mast at 42 m above sea level to the top of a newly constructed communications tower located approximately 100 m further inland and at a height of 93 m. To assess any potential changes in the O_2/N_2 ratios or CO_2 concentrations of the sampled air created by the removal of the tee or shift in physical location of the inlet, the old setup was left in place, and a schedule was begun alternating the biweekly flask collection between the two intakes. This schedule was started in May 1999 and plans are to continue it for a 2-yr period. There are now 13 months of data from this overlapping collection period, and a preliminary comparison shows no discernible difference between the two intakes. However, further data are needed to validate this conclusion.

LONG-TERM AND SEASONAL TRENDS IN O_2/N_2 RATIOS AND CO_2 CONCENTRATIONS

In Figure 1 the raw O_2/N_2 ratio and CO_2 concentration data collected at Samoa are shown. The differences are expressed in O_2/N_2 ratios in "per meg" units, where

$$\delta(O_2/N_2) \ (\text{per meg}) = \frac{(O_2/N_2)_{\text{sam}} - (O_2/N_2)_{\text{ref}}}{(O_2/N_2)_{\text{ref}}} \times 10^6, \quad (1)$$

where $(O_2/N_2)_{\text{sam}}$ is the ratio of the sample gas and $(O_2/N_2)_{\text{ref}}$ is the ratio in an arbitrary reference gas cylinder. One per meg is equivalent to 0.001 per mil, the unit typically used in stable isotope work. By making the assumption that atmospheric N_2 concentrations are constant, this ratio essentially reports variations in atmospheric O_2 concentrations. In these units, 4.8 per meg are essentially equivalent to 1 ppm (i.e., 1 μmole O_2 per mole of dry air). CO_2 concentrations are expressed in ppm. In this figure the y axes have been scaled in such a way that changes in O_2 and CO_2 are comparable visually on a mole-to-mole basis. The curve fits are computed as a least squares fit to the sum of a four harmonic annual seasonal cycle and a stiff Reinsch spline [*Reinsch*, 1967] to account for the interannual trend and other nonseasonal variability.
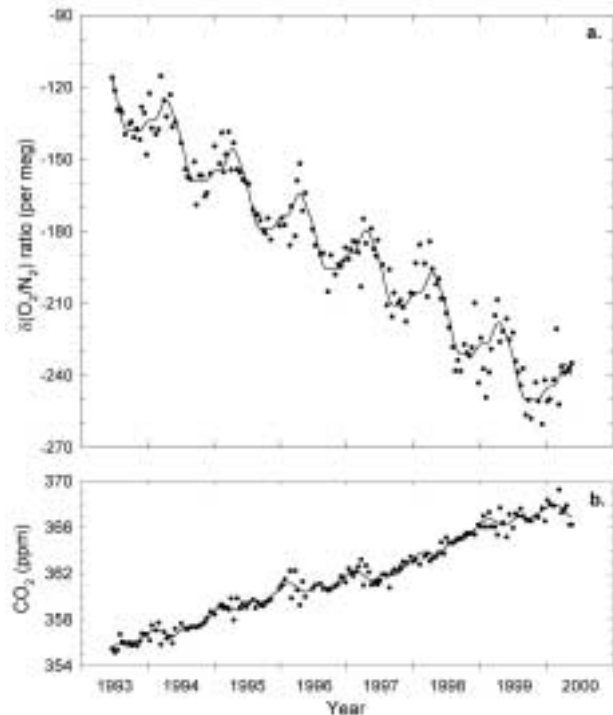
Fig. 1. O_2/N_2 ratios (a) and CO_2 concentrations (b) measured from flask samples collected at Cape Matatula, American Samoa (14°S, 171°W). Plots (a) and (b) were scaled so that changes in O_2 and CO_2 can be compared visually on a mole-to-mole basis. Curve fits are least squares fit to the sum of a four harmonic annual seasonal cycle and a stiff spline. The O_2/N_2 decreasing trend and CO_2 increasing trend are primarily because of fossil fuel combustion.

The figure shows the well-known increasing trend in CO_2 concentrations owing to fossil fuel combustion and also a corresponding decreasing trend in O_2/N_2 ratios. For the 7-yr period from June 1993 to June 2000 an average increase in CO_2 concentration of 1.9 ppm yr^{-1} and an average decrease in O_2/N_2 ratio of 18.8 per meg yr^{-1} were observed, or in comparable units, CO_2 increased by 3.3×10^{14} mol yr^{-1} and O_2 decreased by 7.0×10^{14} mol yr^{-1}. By contrast, over the same time period, fossil fuel combustion released an average of 5.4×10^{14} mol yr^{-1} of CO_2 into the atmosphere and consumed 7.6×10^{14} mol yr^{-1} of O_2. The O_2 consumption by fossil fuel combustion was offset by net growth in the land biosphere, producing atmospheric O_2 and consuming a portion of atmospheric CO_2. The overall decrease in atmospheric O_2 is greater than the increase in CO_2 because a further portion of the CO_2 emitted by fossil fuels is taken up by the oceans. There is no corresponding flux out of the oceans offsetting the O_2/N_2 decrease because O_2 (and N_2) is much less soluble in seawater than CO_2.

Figure 1 also 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. Because there is relatively little land cover in the temperate and high latitudes of the southern hemisphere apart from the sterile antarctic continent, and because there is little seasonality in the tropics, only a small seasonal cycle in atmospheric CO_2 at Samoa would be expected. This is what was observed, but in fact the contributions to the seasonal cycle at Samoa are also influenced by long-range atmospheric transport as discussed in more detail in the

following section. Seasonality in atmospheric O_2/N_2 is generally caused by seasonality in photosynthesis and respiration of both land and marine biota. There is no corresponding marine biotic seasonal component in the atmospheric CO_2 signal. Biologically induced seasonal variability in pCO_2 in seawater is significantly buffered because of both the inverse correlation with seasonal solubility changes driven by temperature and the geochemical reactions of CO_2 with water to form carbonic acid and carbonate and bicarbonate ions [*Keeling et al.*, 1993]. Oxygen, on the other hand, is chemically neutral in the oceans, and biologically induced changes are in phase with temperature-induced solubility changes and are, therefore, reinforced in the atmospheric O_2/N_2 seasonal imprint.

UNIQUE FEATURES OBSERVED IN ATMOSPHERIC DATA COLLECTED AT SAMOA

When compared to other stations in our flask sampling network, data from Samoa are unusual, exhibiting higher short-term variability and seasonal cycles not in phase with other stations. The unusual seasonality is illustrated in Figure 2, which
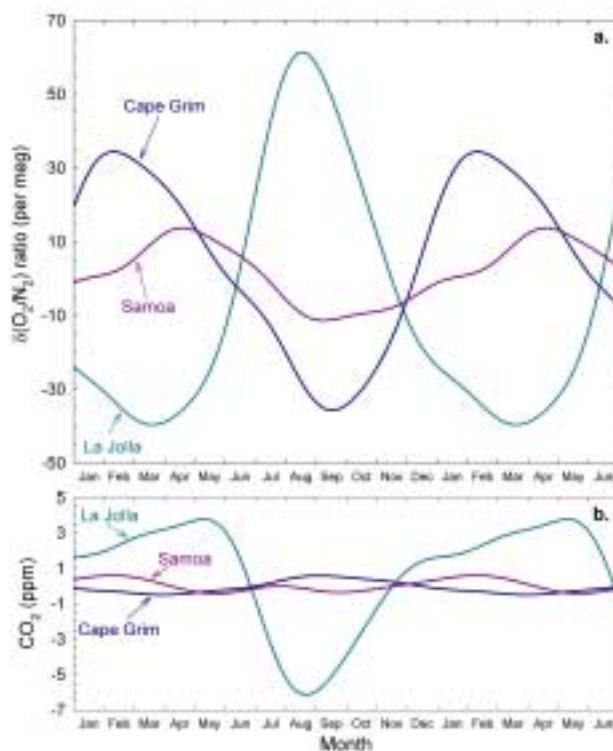

Fig. 2. Four-harmonic seasonal components of the curve fits in Figure 1 showing O_2/N_2 ratios (a) and CO_2 concentrations (b). Also shown for comparison are similar seasonal curve fits calculated from our flask sampling programs at Cape Grim, Tasmania (41°S, 145°E), and La Jolla, California (33°N, 117°W), representing the midlatitudes of the southern and northern hemisphere respectively. To show the seasonal characteristics more clearly, the first 6 months of each cycle are repeated. Southern hemisphere and northern hemisphere cycles are roughly 6 months out of phase with each other, whereas Samoa shows a more complicated signal. 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.

shows the four-harmonic seasonal component of the O_2/N_2 and CO_2 curve fits in Figure 1. The curves shown are the average seasonal cycles calculated from all data over the 7-yr record. Also shown are similar curve fits calculated from data collected at our sampling stations at Cape Grim, Tasmania, Australia (CGO) (41°S, 145°E), and La Jolla, California (LJO) (33°N, 117°W), that are assumed to be broadly representative of midlatitudes in the southern and northern hemispheres, respectively. To illustrate the characteristics of the seasonal variability more clearly, the first 6 months of data are repeated in order to generate an 18-month-long record.

As shown in Figure 2a the maximum O_2/N_2 ratio at Samoa occurs in April, approximately 2 months later than the peak at Cape Grim occurring in February. 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 2b 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 as seen in the figure. The La Jolla curves show that Samoa O_2/N_2 ratios and CO_2 concentrations are also not in phase with northern hemisphere trends. In addition at each of the sampling stations at La Jolla and Cape Grim, O_2/N_2 and CO_2 changes are to a good approximation anticorrelated with each other, whereas at Samoa this is clearly not the case.

The unique climatological conditions at Samoa and their impact on concentrations of atmospheric constituents have been noted before. *Halter et al.* [1988] presented 3 years of CO_2 data from 1979-1981. They discussed the seasonal dependence of the variability observed in their CO_2 data and related this to air masses arriving at Samoa from different source regions. 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} representing the north Pacific tropical anticyclone, the southeast Pacific tropical anticyclone, and the Australia-New Zealand anticyclone, respectively.

Halter et al. [1988] further 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. Because the seasonal cycles of CO_2 in the northern and southern hemispheres are out of phase, these cancel out partially, but not completely, at Samoa resulting in the complex seasonal pattern that was also observed as shown in Figure 2b. *Halter et al.* [1988] then showed that the seasonal dependence of the CO_2 variability observed at Samoa is a function of the seasonally varying interhemispheric gradient in CO_2 concentration and also of the seasonally varying frequency of occurrence that air arriving at Samoa originated from the northern hemispheric A_{NP} anticyclone. This frequency of occurrence varies because of seasonal variations in the position and strength of the Intertropical Convergence Zone (ITCZ) and the South Pacific Convergence Zone (SPCZ). These two effects result in greater CO_2 variability during austral summer and autumn.

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]. It was demonstrated that the frequency of occurrence of air originating from the A_{NP} anticyclone during El Niño years was significantly reduced, explaining the lack of methyl chloroform variability in these years. The CO_2 data in Figure 1b support this conclusion where it can be seen that during the strong 1997-1998 El Niño, CO_2 variability during the austral summer is significantly reduced compared to other years.

Harris and Oltmans [1997] observed variability in tropospheric ozone concentrations at Samoa approximately 6 months out of phase with the variability in CO_2 described by *Halter et al.* [1988]. They also attributed these observations to summer-winter changes in atmospheric transport, in this case explaining the high austral winter variability not by variations in the latitudinal origin of the air masses arriving at Samoa, but by variations in the altitudinal origin that impacts the relative strengths of ozone sources and sinks, thus influencing the concentration of arriving air masses.

LAND AND OCEAN PARTITIONING OF AIR MASS INFLUENCES AT SAMOA

With the O_2/N_2 ratio measurements, to a good approximation, Scripps is able to distinguish between land and ocean processes affecting the air masses arriving at Samoa. This is done by defining a tracer, Atmospheric Potential Oxygen (APO), that is conservative with respect to O_2 and CO_2 exchanges in land biota. APO is defined as

$$\text{APO (per meg)} = \delta(O_2/N_2) + \frac{R_{O_2:C}}{X_{O_2}} \delta X_{CO_2}, \qquad (2)$$

where $R_{O_2:C}$ represents the $-O_2$:C exchange ratio for land biotic photosynthesis and respiration, X_{O_2} is the standard mole fraction of O_2 in dry air, and δX_{CO_2} is the difference in the CO_2 mole fraction of the sample from an arbitrary reference gas, in ppm. This definition is a simplified version of the formula presented in *Stephens et al.* [1998] where minor influences from CH_4 and CO oxidation have been neglected. $R_{O_2:C} = 1.1$ based on measurements of *Severinghaus* [1995] and $X_{O_2} = 0.20946$ from *Machta and Hughes* [1970] were used.

To a good approximation APO is not influenced by land biotic exchanges, and variations in APO can only be caused by air-sea exchanges of O_2, N_2, and CO_2 and by combustion of fossil fuels since the $-O_2$:C exchange ratio for fossil fuels is approximately 1.4 higher than the value of 1.1 for land biotic exchanges [*Keeling et al.*, 1998a; *Stephens et al.*, 1998]. In contrast to APO, variations in CO_2 on seasonal and shorter time-scales are mainly caused by land biotic exchanges because of the buffering of CO_2 changes in the ocean as mentioned previously.

Figure 3 shows 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 from June 1993 to June 2000 where all samples have been collapsed into 1 calendar year. The curves shown are the four-harmonic seasonal component of the curve fits to data from Cape Grim and Cape Kumukahi, Hawaii (KUM) (20°N, 155°W), representing the nearest sampling stations from which there are data in the southern and northern hemispheres, respectively.
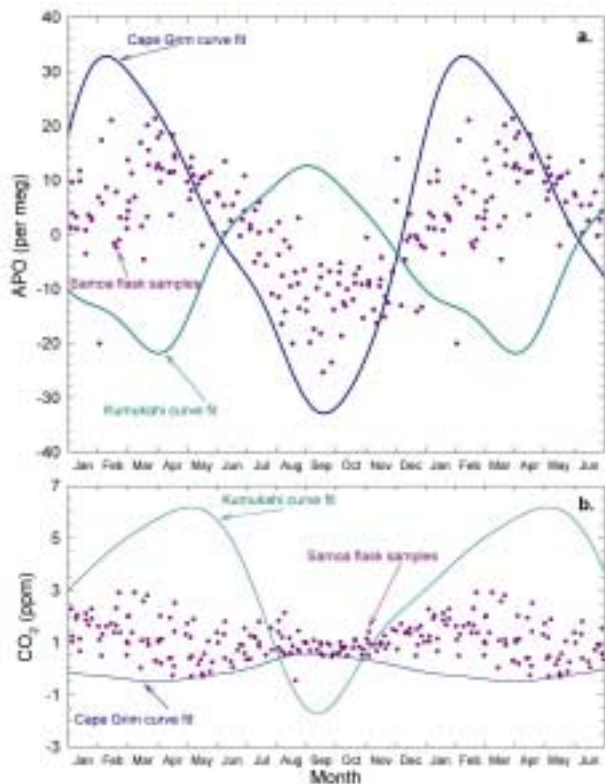
Fig. 3. Oceanic (a) and land biotic (b) influences on the air masses arriving at Samoa are shown. Atmospheric Potential Oxygen (APO), defined in the text, is essentially not influenced by land biotic processes and, therefore, represents oceanic influences. The seasonal component of the Samoa flask samples 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. Data were normalized as described in the text. As for the previous figure, the first 6 months of each cycle are repeated, and the plots were scaled to be able to visually compare mole-to-mole changes in APO and CO_2 concentrations.

Typically, data that have been interannually detrended are centered on zero and have no absolute frame of reference. Here, in order to compare detrended data across different stations, all data have been normalized to the Cape Grim interannual trend. In other words, the Samoa flask data shown are the raw data points of Figure 1 with the interannual spline component of the Cape Grim curve fit subtracted. Because of slight variability from year to year in the interannual trends, the Kumukahi four-harmonic curve fit is not shown in the same manner. Instead, the average offset between the Kumukahi and Cape Grim spline components was calculated from 1993 to 2000 ($\Delta O_2/N_2$ = -3.6 per meg; ΔCO_2 = 2.8 ppm), and this offset was added to the Kumukahi four-harmonic curve fit resulting in the Kumukahi curves shown in Figures 3a and 3b. The Cape Grim curves shown are simply the Cape Grim four-harmonic components of the Cape Grim curve fits. As with Figure 2, the first 6 months are repeated to generate 18 months of data, and APO and CO_2 changes are comparable visually on a mole-to-mole basis.

There are several prominent features apparent in Figure 3. Samoa CO_2 data in Figure 3b agree very well with the earlier data presented by *Halter et al.* [1988], showing greater

variability in the austral summer and autumn. However, based on additional information from our APO data, a slightly different hypothesis of source air mass origins is suggested to explain this variability. For periods of May, June, and December in the APO signal, and from August to October in the CO_2 signal, Samoa data exhibit persistently higher concentrations than seen in air masses either to the north or to the south. It is believed that these data represent recirculated air, perhaps as a component of the Pacific Walker cell circulation. In other words, this is air not recently originating from the north or the south, but from the tropics at some point in the past.

To further support this hypothesis Figure 4 presents the statistical variability in the data. The residuals of all flask samples shown in Figure 1 were calculated from the curve fits also shown in Figure 1. The standard deviation of these residuals for each month was then calculated where, for example, all January samples from 1993 to 2000 were binned together. These standard deviations for each month are shown in the top plots of Figures 4a and 4b for APO and CO_2, respectively. Thus these plots give a statistical measure of the variability in APO and CO_2 at monthly time intervals. To provide a comparison, Cape Grim data are calculated in the same manner. As for Figures 2 and 3, the first 6 months are repeated. Figure 4b shows what was readily apparent in Figure 3b, a clear seasonal pattern to the variability in the CO_2 signal, and a good correlation of this variability with the north-south interhemispheric gradient, shown in the bottom plot of Figure 4b. In contrast, Figure 4b shows that Cape Grim does not exhibit such seasonal variability, and that during the austral winter and spring, Samoa variability is similar to that at Cape Grim. Figure 4a shows that there may also be a seasonal component to the APO variability. However, such seasonality is much less readily apparent than the CO_2 seasonality, is not of the same phasing as CO_2, and is almost equally apparent in Cape Grim APO as it is in Samoa APO.

Relatively low monthly standard deviations are observed for all of the months described previously in Figure 3 exhibiting APO or CO_2 concentrations higher than present in the northern or southern hemisphere for that month with the exception of APO in December (Figure 4). This lower variability also suggests that this air has had more time to mix and become homogenized and has not been influenced to the same extent by air masses from the north or the south, supporting the hypothesis of recirculated tropical air.

Figures 3 and 4 both show a clear difference in the pattern of variability in the APO signal compared with the CO_2 signal. APO does not show as clear a seasonal distinction in variability as CO_2 and does not show significant differences from Cape Grim variability (Figure 4). The top plots of Figure 4 have been scaled to enable direct comparison of the magnitude of variability of APO with CO_2. Thus it is clear that APO exhibits about twice the magnitude of variability of CO_2. These differences between APO and CO_2 cannot be directly explained either by the seasonally varying interhemispheric gradient or by the seasonally varying frequency of occurrence of the different air masses arriving at Samoa, both of which can be expected to affect APO in a similar manner as CO_2. There is, however, a difference in the southern hemisphere with respect to APO and CO_2. Regional sources and sinks for CO_2 are relatively small, whereas sources and sinks for APO are comparable to those in the northern hemisphere.

Therefore, from July to November CO_2 variability is lowest both because of a smaller interhemispheric gradient (Figure 4b, bottom plot) and because of a lower frequency of occurrence of
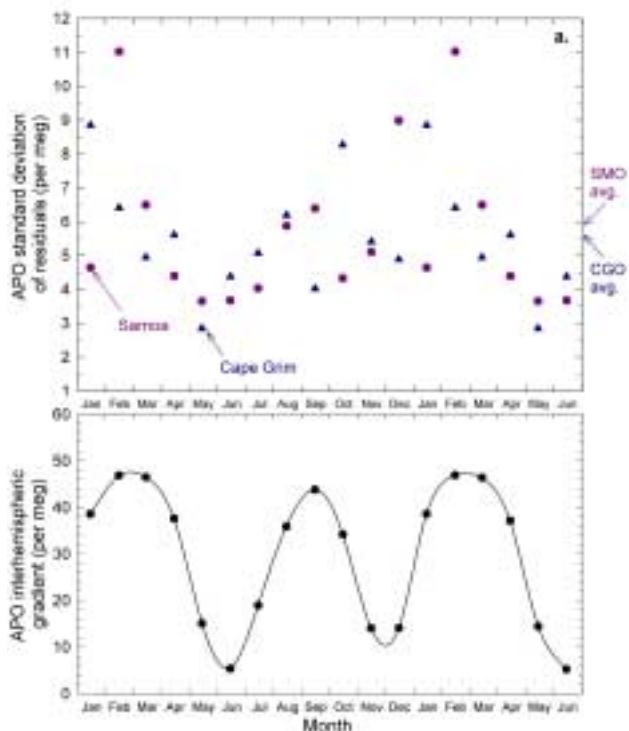
Fig. 4a. (Top) APO monthly standard deviations of the residuals of the flask data from the curve fits. Results are shown for both Samoa and Cape Grim, and the first 6 months are repeated. The annual average residual at each station is indicated on the right. There is little to distinguish Samoa and Cape Grim, and there is only weak evidence of a seasonal trend in the residuals at both stations. (Bottom) The absolute magnitude of the north-south interhemispheric gradient, calculated each month, and using Cape Grim and Cape Kumukahi data as representative of the southern and northern hemisphere, respectively.
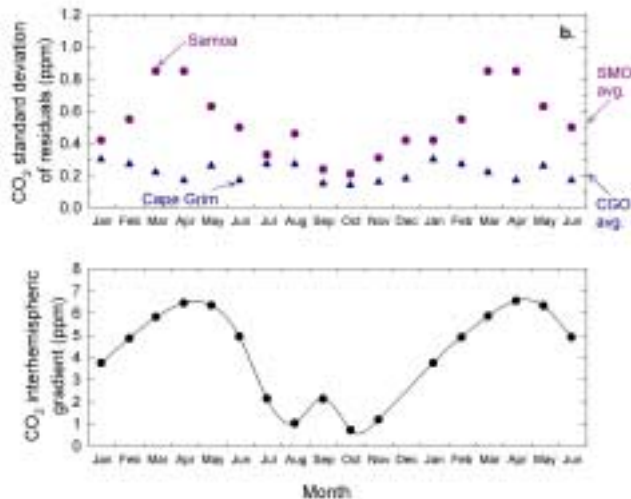

Fig. 4b. Top and bottom plots as for Figure 4a. As for Figures 2 and 3, APO and CO_2 changes are visually comparable between Figures 4a and 4b. In contrast to APO, CO_2 shows a clear seasonal pattern in variability at Samoa, indicated here with higher standard deviations, whereas Cape Grim does not appear to show any seasonality. The pattern at Samoa appears to correlate well with the north-south interhemispheric gradient. Contrasting the magnitude of APO variability with CO_2, it can be seen that the APO signal is much "noisier", reflecting the presence of larger sources and sinks for O_2 in the southern hemisphere compared to CO_2.

A_{NP} air masses arriving at Samoa [*Halter et al.*, 1988]. By contrast even when air masses are entirely of southern hemispheric origin, APO variability is still high because regional sources and sinks prevent the air from becoming as well homogenized in APO. Figure 4a shows little distinction in APO variability between Samoa and Cape Grim, further supporting this conclusion. 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, this altitudinal variability in air mass origin will contribute further to the variability observed in the APO signal at Samoa. Furthermore, the frequency of occurrence of air arriving from the A_{ANZ} anticyclone was higher during austral winter and spring, coinciding with the lowest CO_2 variability.

Thus APO variability is a function of the interhemispheric gradient, the frequency of occurrence of air masses originating from A_{NP} when this gradient is large, and the frequency of occurrence of air masses originating from A_{ANZ}. These three effects, with regional sources and sinks of comparable magnitude in both hemispheres, combine to result in higher variability in the APO signal than the CO_2 signal, and very little if any seasonal pattern to this APO variability.

SUMMARY

A 7-yr record of atmospheric O_2/N_2 ratios and CO_2 concentrations measured from flask samples collected at American Samoa have been presented. These data show O_2/N_2 ratios decreasing and CO_2 concentrations increasing because of the combustion of fossil fuels. O_2/N_2 ratios are decreasing at a faster rate than the observed CO_2 increase because of the uptake of some fossil fuel-emitted CO_2 by the oceans. Uptake of CO_2 by the land biosphere also influences both the O_2/N_2 and CO_2 trends. When compared to other stations in the flask sampling network, data from Samoa are unusual, exhibiting higher short-term variability and seasonal cycles not in phase with other stations. This has been noted before from measurements of CO_2, methyl chloroform, and ozone and has been attributed to the unique geographical position of Samoa in relation to the IPCZ and SPCZ, whose positions vary seasonally, resulting in different air masses arriving at Samoa at different times of the year. The Scripps atmospheric O_2 data, expressed as APO, exhibit characteristics different from other atmospheric gases. The main differences are greater magnitude in the short-term variability, but, in contrast, almost no seasonal pattern to this variability. This is explained by significant regional sources and sinks existing for APO in both hemispheres, in contrast to CO_2, and related to this, a dependence on the altitudinal origins of air masses arriving at Samoa in addition to a dependence on the latitudinal origins.

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