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INTERANNUAL VARIABILITY OF ATMOSPHERIC CARBON MONOXIDE SAMPLED IN HAWAII

1. The Climate Monitoring and Diagnostics Laboratory (CMDL) of the National Oceanic and Atmospheric Administration (NOAA), Air Resources Laboratory, Boulder, Colorado, has been making meticulous measurements of several trace elements such as carbon dioxide, carbon monoxide, methane, ozone, nitrous oxide and halocarbons. In an earlier communication (Kane, 1994), it was shown that the time series of these elements showed interannual variations, roughly in the QBO (Quasi-biennial, 2-3 years) and/or QTO (Quasi-triennial, 3-4 years) ranges. However, for some elements, the data available were only annual means and for only a few (about 6) years. Recently, for carbon monoxide (CO), Khalil and Rasmussen (1994a) presented data for seasonally-averaged concentrations of CO (ppbv) at Mauna Loa and Cape Kumukahi, both in Hawaii (20^{o} N, 157^{o} W) for 1980-93. The data for Cape Kumukahi had a gap during 1982-84. But data for Mauna Loa were complete. Mauna Loa is at an altitude of 3.4 km while Cape Kumukahi is at sea level. Khalil and Rasmussen (1981) analyzed these data to study the differences of cycles and trends of CO in and above the boundary layer in the northern hemisphere tropics. Between the 1950s and middle 1980s, concentrations of CO had been increasing (Levine *et al*., 1985; Rinsland and Levine, 1985; Khalil and Rasmussen, 1984, 1988), mostly due to anthropogenic emissions. However, as shown by Khalil and Rasmussen (1994a,b) and Novelli *et al*. (1994), CO concentrations have been showing decrease since about 1985. Also, there is a strong seasonal cycle of CO, the concentrations being highest in winter and lowest in summer.

In this note, we examine the interannual variability of CO alone but during a much longer period of ~14 years (1980-93), as compared to that of ~6 years, examined in the earlier communication Kane (1994).

2. *Data* - The seasonally-averaged concentrations of CO (ppbv) at Mauna Loa and Cape Kumukahi were obtained from Table 2, page 115 of Khalil and Rasmussen (1994a). Plots of the CO concentrations for Mauna Loa and Cape Kumukahi for 1984-93 (not shown here) showed strong, roughly similar, seasonal variations, with a range of ~40 ppbv. To bring out the interannual variability, seasonal variation needs to be eliminated. For this, running averages were evaluated over four successive seasonal values, thus yielding 12-month running averages (deseasoned), centered 3 months apart (four values per year). The plots of these showed long-term trends. A rough estimate of these could be obtained by 3-year running averages. For Mauna Loa, the trend was almost zero (CO level constant) from 1980 to about 1986, followed by a downtrend upto 1990 and a constant level thereafter. For Cape Kumukahi also, there was a downtrend from 1986 to 1990 and a constant level

thereafter. When the long-term trends were subtracted from the 12-month averages, the residues for Mauna Loa (full lines) showed 6 peaks and the successive peaks were separated by 15, 24, 30, 30 and 24 months. In the earlier communication [Kane 1994, (Fig. 6)], the data for CO for only 6 years showed just two peaks with a spacing (distance of one peak from the next one, in months) of ~24 months. Now, many more peaks were seen. The limited data for Cape Kumukahi (crosses) showed obscure peaks, indicating that the two data sets could have different characteristics.

3. *Growth rates, showing QBO* - Another way of examining these variations would be to calculate the annual growth rate, a derivative of the CO concentration. This was done by subtracting every seasonal value from the fifth value ahead. Thus, the 12-month average centered at 1981 winter was subtracted from the 12-month average centered at 1982 winter, 1981 spring average was subtracted from 1982 spring average, and so on. Thus, four values of the growth rate were available for every year. The plots of these showed that the growth rate was neither constant nor steadily increasing or decreasing but instead, was oscillatory, indicating that the interannual variability of CO definitely had a QBO component of a periodicity of ~27 months (2.25 years).

4. *Comparison with stratospheric wind and southern oscillation* - What could be the origin of this QBO in CO? An atmospheric parameter well-known for QBO is the stratospheric low latitude zonal wind, for which a QBO was first discovered by Reed *et al*. (1961) and Veryard and Ebdon (1961). This wind QBO affects stratospheric ozone (Gray and Dunkerton, 1990; Shiotani and Hasebe, 1994 and references therein) and temperatures in the north polar region (Labitzke, 1987). Yasunari (1989) suggested possible relationships between stratospheric zonal wind QBO and tropospheric parameters. A plot of the 12-monthly running averages of the 50 hPa zonal wind, obtained by Venne and Dartt (1990, updated by us) as a four-station average of monthly zonal winds at Gan (0.7^{o} S, 73.2^{o} E), Balboa (8.9^{o} N, 79.6° E), Singapore (1.4° N, 103.9° E) and Canton (2.8° S, 171.7° W) during 1980-92, showed clear QBOs with a periodicity of ~30 months. A comparison showed that the CO maxima were one or two seasons (3-6 months) earlier than the westerly wind maxima, during 1981-87.

5. *Cross correlations* - A cross-correlation analysis between CO and 50 hPa wind indicated a very good correlation (~0.8) for a phase shift of ~2 seasons (6 months). Thus, some relationship between the CO changes and 50 hPa low latitude zonal wind is indicated, mainly during 1981-87. However, the CO QBO of ~27 months seems to be significantly less than the wind QBO of ~30 months, leaving in doubt the association of the two parameters.

Another phenomenon of interest is ENSO (El Nino-Southern Oscillation), which has a periodicity of 2-7 years. A simple parameter representing SO (Southern Oscillation) is the Tahiti (T) (18° S, 150° W) minus Darwin (D) (12° S, 131° E), mean sea level pressure difference (T-D), which is available in Parker (1983) and can be updated from Meteorological Data Reports. In the plots of the 12-month running averages of (T-D), the minima of (T-D) were associated with occurrences of El Ninos, listed in Quinn *et al.* (1987) and also with equatorial eastern Pacific sea-surface temperature (SST) maxima (Angell, 1981, and further private communication). For 1981-92, the separations between successive peaks of (T-D) minima and SST maxima were large (54, 51 months). Rasmusson *et al.* (1990) identified two dominant time-scales of ENSO variability *viz.* a biennial mode and a low frequency mode of period 4-5 years. For 1981-92, we found the biennial mode missing. The (T-D) minima were followed by CO growth rate maxima by ~2 seasons. Thus, a negative correlation between (T-D) minima and CO maxima was expected, but the correlations were generally low (less than 0.4), indicating that CO changes are not so well-related with ENSO as with stratospheric winds. The correlation between (T-D) and 50 hPa wind was low (+0.19), indicating that these two parameters are mostly unrelated.

6. *Power spectrum analysis* - Another way of comparing the characteristics of different series is to carry out a spectral analysis. For this, the CO and its growth rate were subjected to MESA (Maximum Entropy Spectral Analysis, Burg, 1967; Ulrych and Bishop, 1975) which detects periodicities very accurately. However, MESA has a drawback *viz.* the Power (or amplitude) estimates are not reliable (Kane and Trivedi, 1982). Hence MESA was used only for detecting peaks T_k (k = 1 to n) and these T_k were used in the expression:

$$\begin{aligned} f(t) &= A_o + \sum_{k=1}^{n}\left[a_k \mathrm{Sin}\left(2\pi/T_k\right) + b_k \mathrm{Cos}\left(2\pi/T_k\right)\right] + E \\ &= A_o + \sum_{k=1}^{n} r_k \mathrm{Sin}\left(2\pi/T_k + \phi_k\right) + E \qquad (1) \end{aligned}$$

where $f(t)$ is the observed series and E the error factor. A multiple regression analysis (Bevington, 1969) was then carried out which gave the best estimates of A_o (a_k, b_k) and their standard errors by a least-square fit. From these, r_k and their standard error σ_r (common to all r_k, in this methodology) were calculated and r_k

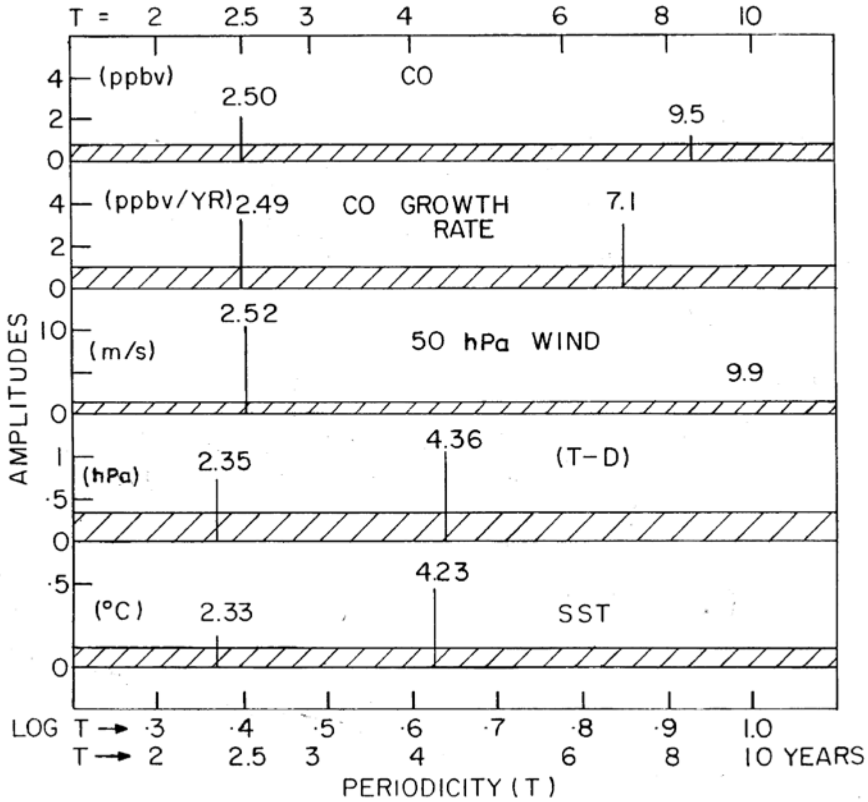


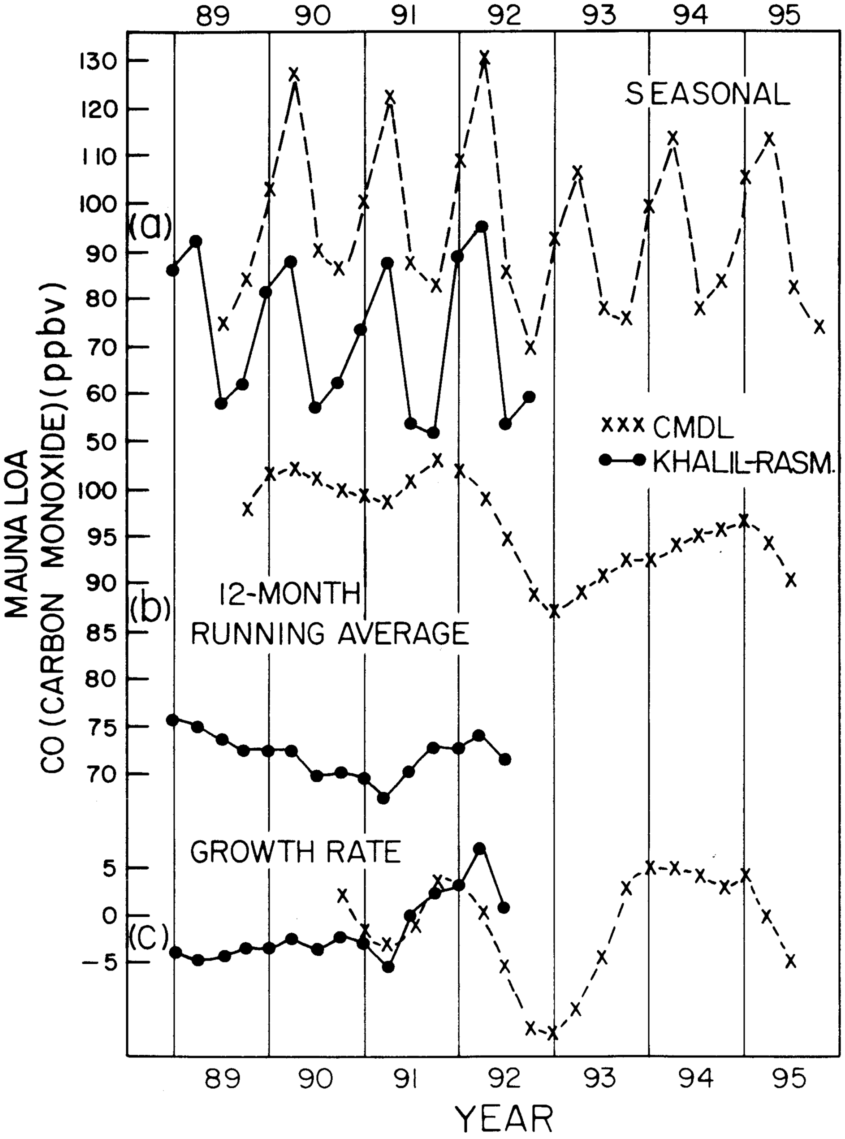
Fig. 1. Amplitudes of the periodicities detected by a Maximum Entropy Spectral Analysis of the time series of CO, CO Growth rate, 50 hPa, T-D, SST

exceeding $2\sigma_r$ were considered as significant at a 95% (a priori) confidence level.

Fig. 1 shows the MESA results. Both CO and CO (Growth rate) show prominent peaks at 2.50 and 2.49 years, which match very well with the prominent peak at 2.52 years for 50 hPa wind. The (T-D) and SST have prominent peaks at 4.36 and 4.23 years and less prominent peaks at 2.35 and 2.33 years. Thus (T-D) and SST have very similar characteristics, as expected, but these do not match with CO periodicities, indicating once again that CO variations (mainly QBO) match with 50 hPa wind but not with ENSO phenomena.

A spectral analysis of TOMS total ozone data (Kane *et al*., 1998) indicated a peak at ~2.50 years for the period 1979-92, same as that for CO and the 50 hPa wind. Thus, these three parameters may be interrelated.

7. *Comparison with CMDL data* - The NOAA-CMDL is also measuring carbon monoxide on routine basis, at various locations around the globe, including Hawaii. It seems there are calibration differences between various laboratories (Novelli *et al*., 1992). At CMDL, Dr. Novelli developed a carbon monoxide standard scale (Novelli *et al*., 1991), an informally accepted protocol for workers measuring CO in the troposphere. The data of Khalil and Rasmussen are not intercalibrated with CMDL protocol and needed changes in reference scales (Khalil and Rasmussen, 1990). It would be interesting to see if the CO measurements at CMDL for Mauna Loa match with those of Khalil and Rasmussen and show QBO. Dr. Novelli kindly provided the flask measurements of CO for July 1989 onwards. Fig. 2 shows a plot of the CO values at CMDL (crosses) and the values of Khalil and Rasmussen (full lines). There are differences in the absolute values, with the CMDL values higher by ~30 (ppbv). Fig. 2(a) shows the seasonal (winter, spring, summer, fall) values. The crosses and full lines show similar patterns, though absolute values are different. Fig. 2(b) shows the 12-monthly running averages. For the common period 1989-92, the patterns are roughly similar. Fig. 2(c) shows the growth rates. The common period is very small and the values tally fairly well. From 1991 onwards, the CMDL values show one full cycle of QBO, with a QBO of ~27 months. Thus, a QBO seems to exist;



Figs. 2(a-c). (a) CO concentration at Mauna Loa from CMDL data (crosses) and Khalil and Rasmusson (1994a, full lines), (b) 12-month running averages and (c) Growth rate

but a better estimate of the periodicity involved will need much longer data. For Mauna Loa, there is a gap (interruption) in the *in situ* data in 1998. However, Tans *et al.* (2001, page 36) have given a plot of the global and hemispherical average CO values corrected for seasonal effects and long-term trends, for 1991-99. Their plots look similar to those of our Fig. 2 upto 1995.

Besides the QBO caused by whatever mechanism, there are other factors which seem to cause significant CO variations. Thus, the sharp decline of CO during 1991-92 [Fig. 2(b)] is attributed to the effects of the June 1991 eruption of Mt. Pinatubo (Granier *et al.*, 1996). The recovery occurred by 1993-94, but this has resulted into two peaks (end of 1991 and middle of 1994) of a possible QBO. Later, there was a strong peak in early 1998 (plot in Tans *et al.*, 2001, page 36) which would fit as a third QBO peak (end of 1991, middle of 1994, end of 1997), but can be attributed to CO production by strong fires in Indonesia, which burned agricultural areas, forests, and peat swamps from mid 1997 through early 1998 (Levine *et al*., 1999). Thus, what are seen as QBO effects could be atleast partially due to interference by natural disasters.

9. *Conclusions* - The results of the present work may be summarized as follows :

9.1. The CO concentrations at Mauna Loa and Cape Kumukahi show a strong seasonal variation. When this is eliminated by evaluating 12-month running averages, and further, when 3-year averages are subtracted from the 12-month averages, the residues show QBO (Quasi-biennial oscillations). The growth rates, obtained by subtracting the 12-month averages centered at any month of any year, from similar averages centered at the same month of next year, also show similar QBO.

9.2. The QBO periodicity of CO is ~2.50 years (30 months) and matches with similar peaks in stratospheric (50 hPa) low latitude zonal winds and tropospheric ozone. Matching with peaks in the southern oscillation index is not good. However, the data length investigated is small (only 12 years) and the finer comparison may not be fully justified. Overall, a QBO of periodicity 27-30 months seems to exist in CO.

10. *Discussion* - Changes in CO concentration can occur due to removal of CO by reaction with OH (decreases), anthropogenic effects like vehicle emissions, biomass burning etc. (increases) and variations due to transport. Seasonal changes of CO can be due to seasonal changes in all these factors, while long-term trends (earlier increases and recent decreases) may be attributed mainly to changes in human consumption of vehicle fuels, though some effect due to long-term increases of OH may also be involved (Madronich and Granier, 1992). The interannual variability in CO could be associated with similar variability in OH and/or in the transport processes. As shown by Madronich and Granier (1992), changes in stratospheric ozone are reflected inversely in the UV radiation received not only at the surface but also throughout the troposphere. Thus, ozone decreases (increases) in the stratosphere would cause increases (decreases in the UV radiation, which, in turn, would cause (by photodissociation of tropospheric ozone to molecular and excited atomic oxygen) increases (decreases) in OH radicals, which would cause larger (smaller) destruction of trace gases like CO or CH_4. For the long-term trends, this sequence seems to be already operative. On a smaller time scale, stratospheric ozone is known to have QBO. This should, therefore, be reflected in the UV radiation and subsequently in the OH concentration and its effect on the CO concentration. It would thus seem that the QBO seen in CO might have its origin in the QBO of stratospheric ozone which is known to be related to QBO of stratospheric zonal wind (Shiotani and Hasebe, 1994).

Regarding the transport processes, convective cloud activity is known to be associated with the ENSO (El Nino-southern oscillation) cycle. Though ENSO is an ocean-atmosphere-coupled variation confined mainly to the tropical Pacific, there is evidence for influences on extratropical circulation and stratospheric circulation (Randel and Cobb, 1994). Carbon monoxide would be affected by these circulations and hence by ENSO. Barnett (1991) and Ropelewski *et al.* (1992) feel that tropospheric QBO is an integral part of ENSO. Incidentally Servain (1991) mentions that SST index of the whole tropical Atlantic basin shows a QBO of an average spacing of ~26 months. This matches with the QBO spacing of CO in the present analysis.

In recent years, NOAA/CMDL have produced data from several sites (North Pole to South Pole) in CO program (Novelli *et al*., 1998). The plot of global CO given in Tans *et al.* (2001, page 36) indicates QBO during 1991-99, but some of the maxima and minima can be attributed to natural disasters (volcano eruptions, biomass burning, etc.). Thus, the evidence for QBO related to stratospheric wind and ENSO becomes unreliable.

There is another important aspect, namely the calibration problems. CO standards are prepared by CMDL-HATS groups, using gravimetric methods (Tans *et al*., 2001, page 37). Seventeen CO standards were prepared during 1989-90 (Novelli *et al*., 1991). Over time, the standards were found to drift at rates upto several ppb per year. In 1992, three gravimetric standards were prepared, which resulted into more reliable results (Novelli *et al*., 1994). Since then, further improvements have been made and new sets of standards are prepared (for example, eight CO standards in 1999-2000). A re-evaluation of the CO scale extending back to 1989 suggested drifts in both the secondary and working standards over time, of about 1 ppb per year during 1992-99. Thus, uncertainties of a few ppb are involved in the observed CO values (Novelli *et al*., 1998; Masarie *et al.* 2001, page 20458). However, in calculating 12-month moving averages, the errors would be reduced and the QBO effects reported here are most probably fairly reliable, atleast qualitatively.

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References

Angell, J. K., 1981, "Comparison of variations in atmospheric quantities with sea surface temperature variations in the equatorial eastern Pacific", *Mon. Wea. Rev.*, **109**, 230-243.

Barnett, T. P., 1991, "The interaction of multiple time scales in the tropical climate system", *J. Climate*, **4**, 269-285.

Bevington, P. R., 1969, "Data reduction and error analysis for the physical sciences", McGraw Hill, New York, 164-176.

Burg, J. P., 1967, "Maximum Entropy Spectral Analysis, paper presented at the 37th Meeting", *Soc. Explor. Geophys.,* Oklahoma City, October.

Gray, L. J. and Dunkerton, T. J., 1990, "The role of the seasonal cycle in the quasi-biennial oscillation of ozone", *J. Atmos. Sci.*, **47**, 2429-2451.

Granier, C., Muller, J. F., Madronich, S. and Brasseur, G., 1996, "Possible causes of the 1990-93 decrease in the global tropospheric carbon monoxide abundance: A three dimensional sensitivity study", *Atmos. Environ.*, **30**, 1673-1692.

Kane, R. P., 1994, "Interannual variability of some trace elements and surface aerosol", *Int. J. Climatology*, **14**, 691-704.

Kane, R. P. and Trivedi N. B., 1982, "Comparison of maximum entropy spectral analysis (MESA) and least-square linear prediction (LSLP) methods for some artificial samples", *Geophys.*, **47**, 1731-1736.

Kane, R. P., Sahai, Y. and Casiccia, C., 1998, "Latitude dependence of the QBO and QTO characteristics of total ozone measured by TOMS", *J. Geophys. Res.*, **103**, 8477-8490.

Khalil, M. A. K. and Rasmussen, R. A., 1981, "Differences in the concentrations of trace gases in and above the tropical boundary layer", *Pure Appl. Geophys.*, **119**, 990-997.

Khalil, M. A. K. and Rasmussen, R. A., 1984, "Carbon monoxide in the earth's atmosphere: Increasing trend", *Science*, **224**, 54-56.

Khalil, M. A. K. and Rasmussen, R. A., 1988, "Carbon monoxide in the earth's atmosphere: Indications of a global increase", *Nature*, **332**, 242-245.

Khalil, M. A. K. and Rasmussen, R. A., 1990, "Atmospheric carbon monoxide: Latitudinal distribution of sources", *Geophys. Res. Lett.*, **17**, 1913-1916.

Khalil, M. A. K. and Rasmussen, R. A., 1994a, "Trends of CO Hawaii: Seasonal cycles and decreasing concentrations. Summary report 1993", Climate Monitoring and Diagnostics Laboratory No. 22, Boulder, CO, 114-117.

Khalil, M. A. K. and Rasmussen, R. A., 1994b, "Global decrease of atmospheric carbon monoxide", *Nature*, **370**, 639-641.

Labitzke, K., 1987, "Sunspots, the QBO and the stratospheric temperature in the north polar region", *Geophys. Res. Lett.*, **14**, 535-537.

Levine, J. S., Rinsland, C. P. and Tenille, G. M., 1985, "The photochemistry of methane and carbon monoxide in the troposphere 1950 and 1985", *Nature*, **318**, 254-257.

Levine, J. S., Bobbe, T., Ray, N., Singh, A. and Witt, R. G., 1999, "Wildland fires and the environment: A global synthesis", UNEP/DEIAEW/TR.99-1, UNEP (WMO), Geneva.

Madronich, S. and Granier, C., 1992, "Impact of recent total ozone changes on tropospheric ozone photodissociation, hydroxyl radicals and methane trends", *Geophys. Res. Lett.*, **19**, 465-467.

Masarie, K. A., Langenfelds, R. L., Allison, C. E., Conway, T. J., Dlugokencky, E. J., Francey, R. J., Novelli, P. C., Steele, L. P., Tans, P. N., Vaughn, B. and White, J. W. C., 2001, "NOAA/CSIRO flask air intercomparison experiment: A strategy for directly assessing consistency among atmospheric measurements made by independent laboratories", *J. Geophys. Res.*, **106**, 20445-20464.

Novelli, P. C., Elkins, J. W. and Steele, L. P., 1991, "The development and evaluation of a gravimetric reference scale for measurements of atmospheric carbon monoxide", *J. Geophys. Res.*, **96**, 13109-13121.

Novelli, P. C., Steele, L. P. and Tans, P. P., 1992, "Mixing ratios of carbon monoxide in the troposphere", *J. Geophys. Res.*, **97**, 20731-20750.

Novelli, P. C., Massarie, K. A., Tans, P. P. and Lang, P. M., 1994, "Recent changes in atmospheric carbon monoxide", *Science*, **263**, 1587-1590.

Novelli, P. C., Massarie, K. A. and Lang, P. M., 1998, "Distribution and recent changes of carbon monoxide in the lower troposphere", *J. Geophys. Res.*, **103**, 19015-19033.

Parker, D. E., 1983, "Documentation of southern oscillation index", *Meteor. Mag.*, **112**, 184-188.

Quinn, W. H., Neal, V. T. and Antunes de Mayolo, S. E., 1987, "El Nino occurrences over the past four and a half centuries", *J. Geophys. Res.*, **92**, 14449-14461.

Randel, W. J. and Cobb, J. B., 1994, "Coherent variation of monthly mean total ozone and lower stratospheric temperature", *J. Geophys. Res.*, **99**, 5433-5447.

Rasmussen, E. M., Wang, X. and Ropelewski, C. F., 1990, "The biennial component of ENSO variability", *J. Marine Systems*, **1**, 71-96.

Reed, R. J., Campbell, W. J., Rasmussen, L. A. and Rogers, D. G., 1961, "Evidence of downward propagating annual wind reversals in the equatorial stratosphere", *J. Geophys. Res.*, **66**, 813-818.

Rinsland, C. P. and Levine, J. S., 1985, "Free tropospheric carbon monoxide in 1950 and 1951 deduced from infrared total column amount measurements", *Nature*, **318**, 250-254.

Ropelewski, C. F., Halpert, M. S. and Wang, X., 1992, "Observed tropospheric biennial variability and its relationship to southern oscillation", *J. Climate*, **5**, 594-614.

Servain, J., 1991, "Simple climate indices for the tropical Atlantic ocean and some applications", *J. Geophys. Res.*, **96**, 15137-15146.

Shiotani, M. and Hasebe, F., 1994, "Stratospheric ozone variations in the equatorial region as seen in stratospheric aerosol and gas experiment data", *J. Geophys. Res.*, **99**, 14575-14584.

Tans, P. P., Bakwin, P. S., Bruhwiler, L., Conway, T. J., Dlugokencky, E. J., Guenther, D. W., Kitzis, D. R., Lang, P. M., Masarie, K. A. and Miller, J. B., 2001, "Carbon cycle, CMDL (Climate Monitoring and Diagnostics Laboratory) Summary Report No. 25", 1998-1999, U. S. Dept. of Commerce, NOAA, Boulder Colorado, 24-46.

Ulrych, T. J. and Bishop, T. N., 1975, "Maximum entropy spectral analysis and autoregressive decomposition", *Rev. Geophys.*, **13**, 183-200.

Venne, D. E. and Dartt, D. G., 1990, "An examination of possible solar cycle – QBO effects in the northern hemisphere troposphere", *J. Climate*, **3**, 272-281.

Veryard, R. G. and Ebdon, R. A., 1961, "Fluctuations in tropical stratospheric winds", *Meteorol. Mag.*, **90**, 125-143.

Yasunari, T., 1989, "A possible link of the QBOs between the stratosphere, troposphere and the surface temperature in tropics", *J. Meteorol. Soc.*, Japan, **67**, 483-493.

R. P. KANE

Instituto Nacional de Pesquisas Espaciais – INPE,
C.P. 515, São José dos Campos – 12245-970, SP, Brazil

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