2.4. CARBON MONOXIDE

2.4.1. MEASUREMENTS OF CARBON MONOXIDE

During 1998-1999 the study of the global distribution of CO in the lower troposphere continued using both air samples collected through the CMDL global cooperative air sampling network and in situ measurements at BRW and at MLO. In the air sampling network conversion of all sites from glass flasks with greased stopcocks to those acceptable for CO analysis (those fitted with Teflon O-ring stopcocks) was completed by 1998, and CO was measured at all active sites in the network. In situ measurements at BRW continued uninterrupted, while at MLO a rebuilt Reduction Gas Analyzer was reinstalled in late 1998. The 1998 and 1999 provisional annual mean mixing ratios from the in situ measurements at BRW (155.9 and 128.2 ppb, respectively) were equivalent to the flask results from BRW (154.7 and 129.5 ppb, respectively). At MLO interrupted measurements provide no annual mean for 1998, but the 1999 in situ results (annual mean = 86.5 ppb) agree well with the flask measurements (88.0 ppb). These provisional flask and in situ values are believed to be somewhat low and are likely to be revised upward (section 2.4.2).

The residuals from a function approximating the annual oscillations and trend (the annual cycle as represented by four harmonics, the long-term trend by a polynomial [*Thoning et al.*, 1989]) were used to examine key features in global and hemispheric CO. A high degree of interannual variation was seen during 1991-1999 (Figure 2.16). The sharp decline in global CO during 1992 (Figure 2.16a) has been attributed to the effects of the June 1991 eruption of Mt. Pinatubo [*Bekki et al.*, 1994; *Granier et al.*, 1996]. The sharp drawdown is particularly evident in the detrended residuals from the southern hemisphere (Figure 2.16b). As the effects of the eruption diminished in 1993, CO returned to previous levels [*Novelli et al.*, 1998a; *Granier et al.*, 1996]. Other variations in the time series (1994-1996) may be related, in part, to variations in large scale biomass burning.

CO mixing ratios in the southern hemisphere showed strong enhancement in late 1997. The anomaly was largely confined to the low latitudes during late 1997. Following this well-defined increase, CO remained somewhat high during early 1998 before returning to previous levels (Figure 2.16b). Strong fires in Indonesia, which burned agricultural areas, forests, and peat swamps from mid-1997 through early 1998, produced substantial amounts of CO (>77 Tg CO; *Levine et al.* [1999]). The 1997 fires provided at least 35% more CO to the troposphere than biomass burning in a typical year. As the seasonal cycle of CO in the southern hemisphere is largely driven by emissions from biomass burning [*Granier et al.,* 2000], the fires likely contributed substantially to the high CO observed during late 1997 and early 1998. In the northern hemisphere, a weak summer minimum in 1998 was followed by a strong fall maximum (Figure 2.16c). This period of high CO is also evident in the residuals calculated from in situ measurements at BRW (Figure 2.17). For the first time since CMDL measurements began at BRW in 1988, autumn mixing ratios in the high latitudes of the northern hemisphere surpassed the typical seasonal maximum in March/April. The enhancement at Barrow was nearly twice that seen in the zonally averaged northern hemisphere time series, suggesting the boreal nature of the source. Estimates of the extent of burning in Canada, northern United States, and Russia during 1998 are twice as high as any

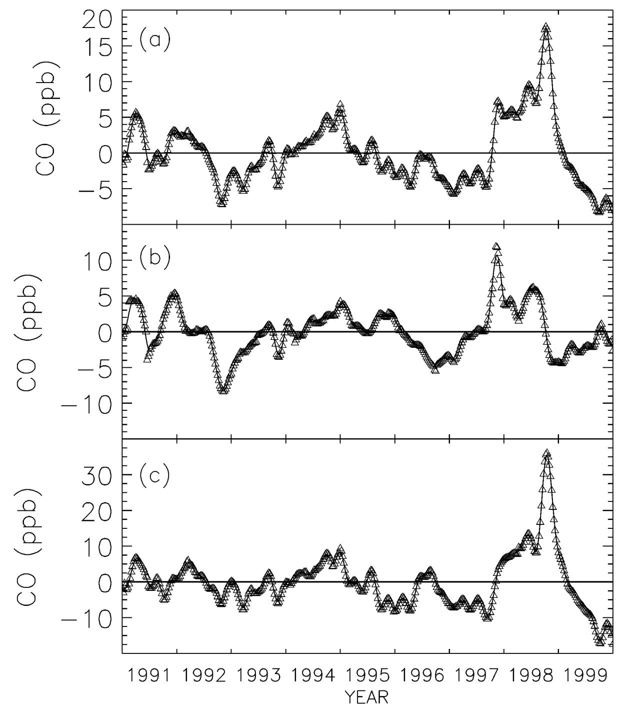

Fig. 2.16. Residuals from zonal average time series, after the average seasonal cycle and a third-order polynomial fit to the trend have been subtracted, and a smooth curve fit to those residuals (solid line): (a) global, (b) southern hemisphere, and (c) northern hemisphere.

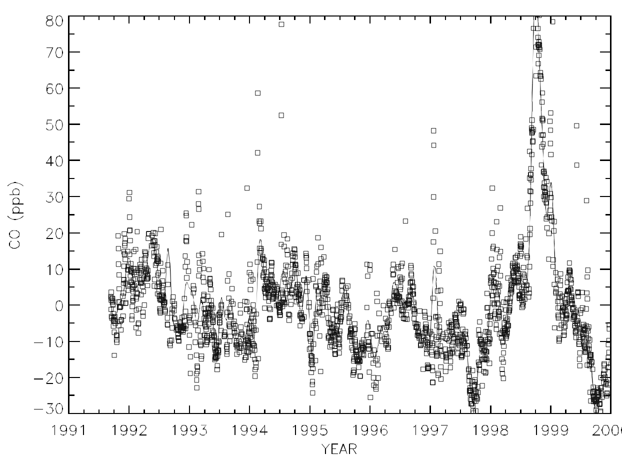

Fig. 2.17. Residuals, determined as in Figure 2.16, from the in situ measurements at Point Barrow, Alaska. The solid line is the smooth fit to the residuals.

in the depth of the northern hemispheric seasonal CO minimum (defined as the July/August average mixing ratio) are highly correlated with the annual land area burned in the temperate and boreal forests (G. Wotawa et al., Boreal forest fires and their contribution to northern hemispheric summertime CO background concentrations during the 1990s, submitted to *Nature*, 2000). The effect of boreal forest fires on the Arctic troposphere was also shown in a comparison between CMDL CO surface measurements at BRW and total column spectroscopic measurements made at Poker Flats, Alaska. In winter and late spring 1995 surface measurements of CO were greater than the equivalent column average. However, during May and through September (the primary burning season in Canada and Russia) the column measurements were enhanced relative to the surface. Emissions from forest fires were suspected of providing CO to the free troposphere over Alaska [*Yurganov et al.*, 1998].

2.4.2. CO REFERENCE GASES

A set of eight CO standards was prepared using gravimetric methods by the CMDL Halocarbons and other Atmospheric Trace Species (HATS) group in late 1999 and early 2000. Mixing ratios assigned to CMDL working standards referenced against the new gravimetrics were significantly greater than those previously assigned based upon the original scale. The CMDL reference scale used in our measurements of atmospheric CO is based upon 17 standards prepared during 1989-1990 by gravimetric methods [*Novelli et al.*, 1991]. The scale was transferred to a set of ten natural air secondary standards with mixing ratios between 32 and 201 ppb CO. The standard scale was found to be in good agreement with our gravimetric dilutions of a NIST 9.7 ppm CO Standard Research Material (SRM), and dynamic dilutions of a NIST 10 ppm SRM made at the U.S. National Aeronautics and Space Administration (NASA) Langley Research Center and at the Fraunhofer Institute in Garmisch-Partenkirchen, Germany.

Over time the original gravimetric standards, made in high-pressure cylinders of a smaller size, were found to drift at rates of up to several ppb yr^{-1}, and the scale was maintained through the secondary and working standards. Drift in these standards was evaluated in two ways: (1) frequent intercomparison of the suite of standards maintained at CMDL, and (2) periodic preparation of new gravimetric standards. In 1991 the instrument with a linear response was changed to a new one that exhibited nonlinearity below ~125 ppb. Therefore, a multipoint calibration procedure was necessary to define the instrument response. In addition to exhibiting nonlinearity, response characteristics changed over time requiring frequent calibration of the instrument. This procedure used six to eight standards (mixing ratios between 50 and 200 ppb) plus a blank (zero air passed through Schutze reagent) and daily calibration curves. A straight line, second-, and third-order polynomial were used to define instrument response [*Novelli et al.*, 1998a]; the first two curve fits were used for diagnostics, and the reported mixing ratios were based upon the third-order fit.

In 1992 three gravimetric standards were prepared, and their assigned mixing ratios, based on the gravimetric method, agreed well with the CO mixing ratios assigned to the secondary standards [*Novelli et al.*, 1994]. The long-term calibration histories of the CMDL standards showed no evidence of drift. Figure 2.18 shows the calibration history of one 50 ppb working standard (ID CC114712). A significant drift was not detected through the first half of 1998 (Fig. 2.18a), however, higher mixing ratios determined in 1999 suggest an increase of 0.2 ppb yr^{-1} (Figure 2.18b).

In 1996 a new set of five standards was prepared using gravimetric methods. The mixing ratios assigned to the secondary and working standards when referenced against the 1996 gravimetrics were somewhat higher than those previously assigned. In 1999 and 2000 eight gravimetric standards with

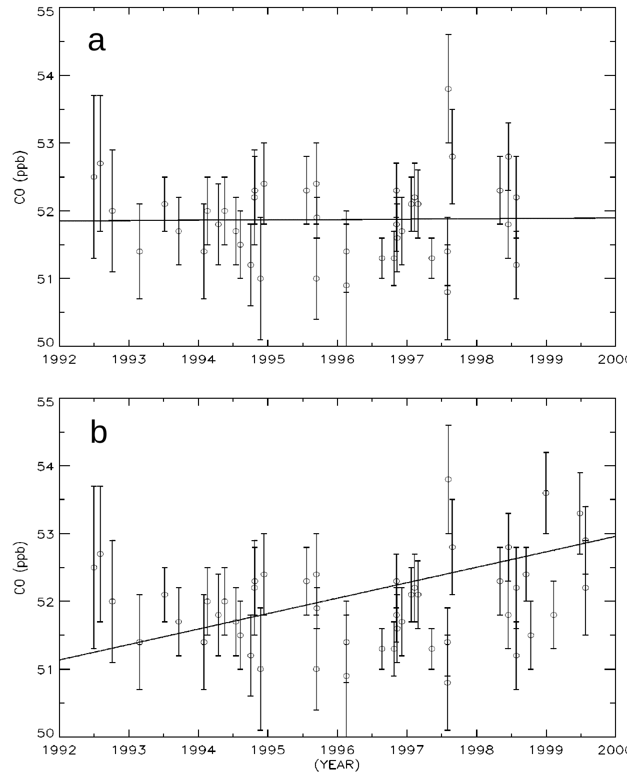

Fig. 2.18. The calibration history of CMDL working standard CC114712 (assigned a mixing ratio = 51.9 ppb in 1992). Each point represents a calibration based upon ten or more analyses. Error bars represent one standard deviation. (a) History through the first half of 1998, Y = 51.9 (±0.37) + 5.3 × 10^{-3} (±0.086)(X –1992); (b) History through 1999; Y = 51.2 (±0.31) + 0.22 (±0.55)(X-1992).

mixing ratios ranging from 53 to 205 ppb were prepared at CMDL. The mixing ratios assigned to the secondary and working standards referenced to the new gravimetric standards were greater than the 1996 results and definitely greater than the original values (Table 2.9). Calibration of the new gravimetrics using dynamic dilution of a NIST 9.7 ppm SRM confirmed their values based on the gravimetric preparation. This surprising result lead to a re-evaluation of the CO scale extending back to the original standards prepared in 1989 and 1990. Confidence in both the original scale and the 1999 gravimetric standards suggests drift in both the secondary and working standards over time. Calculations of linear drift at rates of 0.8 ± 0.3 ppb yr^{-1} between 1992 and 1999 are consistent with the 1996 gravimetric standards and with intercomparisons involving several other laboratories [*Novelli et al.*, 1998b] (K. Masarie et al., The NOAA/CSIRO Flask Air Intercomparison Experiment: A strategy for directly assessing consistency among atmospheric measurements made by independent laboratories, submitted to *Journal of Geophysical Research*, 2000). However, drift rates of about 1 ppb yr^{-1} are not evident in the calibration histories of the working standards because the working standards and the CMDL secondary standards were both drifting at comparable rates.

To examine whether drift in a sample could be masked by drift in the standards, a sensitivity study examined the effects of drifting standards on the calibration of simulated samples. Artificial area responses of eight standards comprising a calibration curve were allowed to change while the assigned

TABLE 2.9. Mixing Ratios Assigned to the CMDL Secondary Standards*

Tank ID	1989/1990, 1992		1996		1999		NIST Dilution, 1999	
121999	51.7	(1.1)	56.2	(0.7)	60.4	(0.5)	61.5	(1.2)
105460	100.5	(1.2)	107.5	(0.9)	110.9	(1.1)	111.3	(1.1)
68734	159.7	(1.1)	164.4	(1.0)	167.7	(1.3)	167.0	(1.7)
73110	200.8	(1.7)	202.9	(0.9)	205.3	(0.5)	207.3	(1.5)

*Mixing ratios assigned to secondary standards by comparison to gravimetric standards prepared in 1989/1990 and 1992; 1996, 1999, and by comparison to dynamic dilution of a NIST 9.7 ppm SRM. Uncertainties (1σ) are in parentheses. All mixing ratios are in ppb by mole fraction (gravimetric calibrations) or ppb by volume (NIST dilutions).

mixing ratios were kept constant. When upward standard drift was not accounted for, the calculated sample mixing ratios were lower than the actual value. Combinations of drift in the simulated standards, on the order of the apparent rates seen in the CMDL standards, and drift in samples at various rates between 0 and 3 ppb yr^{-1}, resulted in a range of results. In general if samples were drifting at rates similar to those of the standards, the appearance of drift was largely hidden within the precision of the measurements. Beginning late 1999 a number of standards were assigned mixing ratios referenced to both the CMDL working standards and the new gravimetric standards. The relationship defined by these calibrations (Figure 2.19) relates mixing ratios assigned during mid-1999 to mid-2000 by the original (but drifting) scale to mixing ratios defined by the new gravimetric standards. Correcting the time series data is more difficult, but several options are available. Most promising is a linear adjustment between 1992 and 1999. Results from this approach are consistent with both the 1996 and 1999 gravimetric standards.

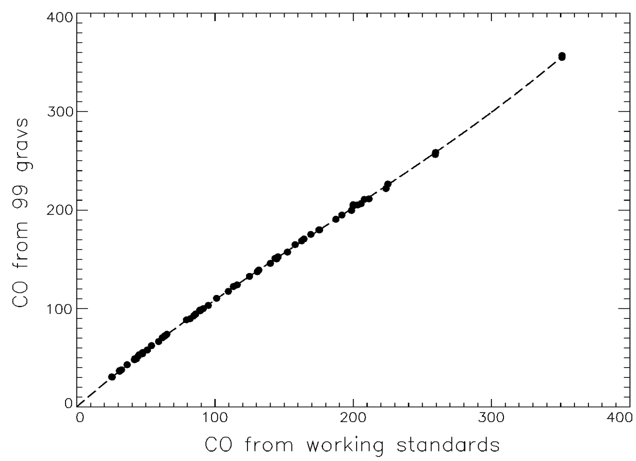

Fig. 2.19. Scatter plot of CO mixing ratios assigned to various natural air mixtures based upon the 1999 gravimetric standards versus the original CMDL CO scale. The dashed line shows a third order fit to the data and is defined by $Y = 0.320 + 1.217 X - 0.00163 X^2 + 2.972 \times 10^{-6} X^3$. The solid line represents the one-to-one relationship between the 1999 gravimetric standards and the CMDL CO working standards.