4.2.3. EVIDENCE OF O_3 TITRATION DURING BRW WINTER DARK PERIODS

Trace gas measurements from BRW during the winter dark periods of 1986-1997 were examined. After ensuring that local pollution from the Barrow town site was not present in the data set, a smooth curve consisting of a function and filtered residuals was removed from each data record. The smooth curve was designed so that its removal leaves residuals containing only the highest frequency variations on the order of synoptic scale changes [*Thoning et al.*, 1989]. Variability caused by changes in transport can be examined with these residuals.

Figure 4.12 shows a negative correlation between O_3 and CO_2 residuals for Siberian transport. CO_2, CO, and CH_4 residuals were positively correlated with one another (e.g., Figure 4.13). On the basis of trajectory analysis, it is speculated that the positive correlations among CO_2, CO, and CH_4 indicate industrial sources either in Siberia or further upwind (e.g., the Ural region). By limiting the data to transport from this direction, the slope of the fitted line did not change much in comparison to that derived from all transport types, and the correlation of the fit improved slightly. This may reflect the fact that winter transport conditions result in the Siberian pollution signature becoming regionally widespread throughout the Alaskan Arctic. The other transport pathways to Barrow yield few or no man-made sources within 10 days.

The negative correlations between O_3 and the other species may be caused by chemical removal of O_3 by NO_X (titration) that occurs when NO_X is plentiful in the absence of sunlight.

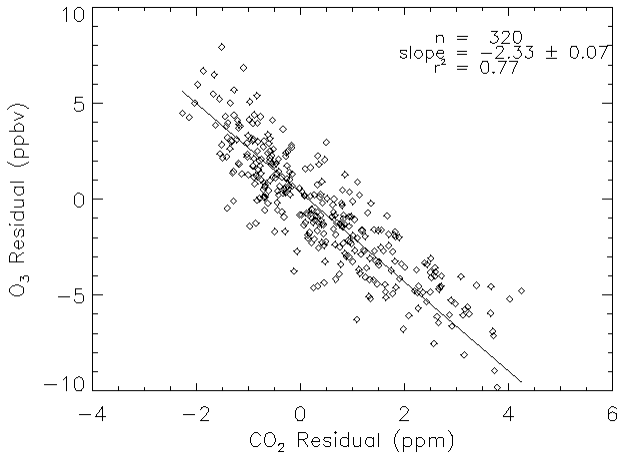

Fig. 4.12. O_3 versus CO_2 residuals for the winter dark periods, 1986-1997, at BRW. Only data corresponding to transport from the direction of Siberia are included.

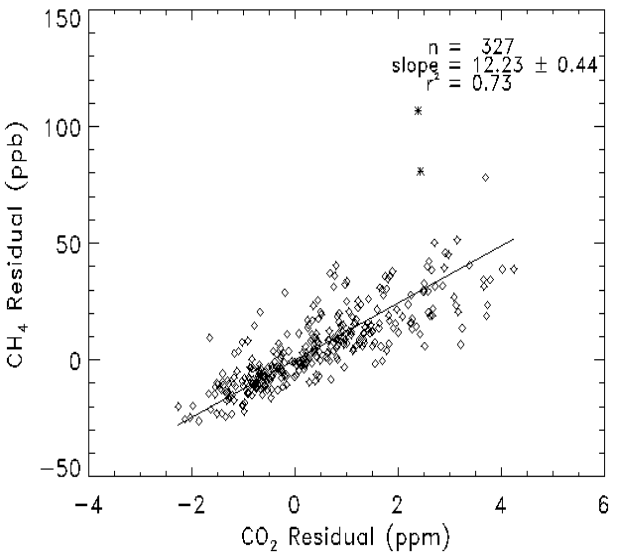

Fig. 4.13. CH_4 versus CO_2 residuals for the winter dark periods, 1986-1997, at BRW. Only data corresponding to transport from the direction of Siberia are included.

Based on the chemical reactions that likely take place, the range of 1.5-2 O_3 molecules destroyed per NO molecule emitted was used. There is negligible NO_X in the remote Arctic near Barrow. However, it is surmised that O_3 is being destroyed within pollution plumes generated in Siberia or upwind from there. As a check on this assumption, the molar ratio of NO_X to CO_2 was calculated. The delta (Δ) symbol is used to denote a change in concentration over time or an emission rate: $\Delta NO_X/\Delta CO_2 = \Delta NO_X/\Delta O_3 \times \Delta O_3/\Delta CO_2$. Inverting the titration factor and with the empirical slope of $\Delta O_3/\Delta CO_2$ determined from the Barrow data (-2.33×10^{-3}), $\Delta NO_X/\Delta CO_2 = (1.2\text{-}1.6) \times 10^{-3}$ is obtained. This is close to, or within, the lower end of the range expected from coal-fired industrial processes $(1.39\text{-}3.49) \times 10^{-3}$ (W. Barbour, Environmental Protection Agency, personal communication, 1999). It is possible that the natural gas burned in this region causes the $\Delta NO_X/\Delta CO_2$ ratio to be lower than that for pure coal burning. Likewise, with the empirically derived slope for $\Delta O_3/\Delta CO$ (-3.45×10^{-1}), $\Delta NO_X/\Delta CO$ = 0.17-0.23 is obtained and is consistent with the ratio determined for eastern North America of 0.19 [*Saeger et al.*, 1989]. The empirical ratios indicate air measured at Barrow during the winter has a pollution component and that the negative O_3 correlations could be caused by titration that occurs days upwind of Barrow.