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CARBON MONOXIDE MEASUREMENTS AT MACE HEAD, IRELAND

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ABSTRACT

The North Atlantic Ocean is bordered by continents which may each, under the influence of seasonal weather patterns, act as sources of natural and anthropogenic trace gas and particulate species. Photochemically active species such as carbon monoxide (CO) react to form ozone (O_3), a species of critical importance in global climate change. CO is sparingly soluble in water, and the relatively long lifetime of CO in the troposphere makes this species an ideal tracer of air masses with origin over land. We have measured CO using a nondispersive infrared gas filter correlation analyzer at Mace Head on the west coast of Ireland nearly continuously since August 9, 1991. Measurements of CO were acquired at 20-sec resolution and recorded as 60-sec averages. Daily, monthly, and diurnal variation data characteristic of CO mixing ratios observed at this site are reported. Depending on source regions of air parcels passing over this site, 60-min concentrations of CO range from clean air values of ~90 ppbv to values in excess of 300 ppbv. Data characterizing the correlation between 60-min CO and O_3 mixing ratio data observed at this site are reported also.

1. INTRODUCTION

Any meaningful assessment of the impact of continental emissions on chemical processes in the atmosphere and characterization of the climatology of tropospheric O_3 over the North Atlantic Ocean rely heavily on the acquisition of a large data base containing continuous and time-averaged values for a variety of species. Carbon monoxide has natural and anthropogenic sources contributing to observed concentrations in the atmosphere; nearly all major sources are, however, of continental origin. Carbon monoxide may act as a precursor to photochemical O_3 by reaction with the hydroxyl radical, the primary removal process for CO in the atmosphere. Carbon monoxide is sparingly soluble in water and the relatively long lifetime of CO in the troposphere makes this species an ideal tracer of air masses with origin over land. The importance of CO in the global carbon cycle and implications for global climate change is the subject of an excellent review by Khalil and Rasmussen (1990). Our research site at Mace Head, Ireland (53°19'N, 9°54'W), has an excellent westerly exposure to the North Atlantic Ocean, and suffers little by way of interferences from ship or air traffic. The site has been described in detail previously (Jennings et al., 1991). An understanding of the sources, abundance, and seasonal behavior of this species over the North Atlantic Ocean is essential to gain valuable insight into delicate biogeochemical cycles in this region, and changes in the global environment.

2. EXPERIMENTAL TECHNIQUE

For continuous measurements of ambient CO we use a commercial nondispersive infrared (NDIR) gas filter correlation analyzer (Thermo Environmental Corporation, Franklin, MA; Model 48), modified for increased sensitivity (Dickerson and Delany, 1988), equipped with a Nafion® drying tube (Perma Pure, Toms River, NJ, Model PD-625-12PS) for sample air stream drying, and a heated (to 250°C) Pd on alumina catalyst (type E 221 P/D, Degussa Corp., Plainfield, NJ) (Parrish et al., 1991) as a chemical zero for CO. A Teflon filter (5–10 µm pore size; Shelby Jones, Upper Derby, PA) is used upstream of the analyzer to keep out large particles. Laboratory and field studies of the Pd/alumina catalyst indicate that the catalyst is 100% efficient at 250°C over the dynamic range of CO mixing ratio expected at a North Atlantic regional site. We calibrate the instrument (for ~1 hr) weekly using a cylinder of compressed air of known concentration (referenced to a NIST/SRM CO standard). At intervals of six months the instrument is compared also to a NIST/SRM (1677c 9.97 ppmv CO in nitrogen, certified; NIST, Gaithersburg, MD) and a number of secondary standards (~5 ppmv CO in nitrogen; Matheson Gas, East Rutherford, NJ) referenced previously to the NIST/SRM. Measurements of ozone are provided by a commercial optical instrument using absorption of UV radiation at 254 nm (Monitor Labs Model 8810; Enviro Technology, Gloustershire, UK). Both ozone and CO are sampled at a height of 10 m.

A digital data acquisition system (Hewlett Packard, Loveland, Colo.; Model 3421A, with HP-41CV driver and HP-9114B floppy disk drive) provide 1-min mean (of 3x20-s data) CO and ozone data. Data are stored on 3.5" floppy disks prior to further processing into calibrated time series of CO and ozone mixing ratios.

3. RESULTS

Carbon monoxide has been measured at Mace Head since August 9, 1991. Table 1 shows statistical data on 60-min means generated from the 1-min data from that time to January 17, 1992. Data arising from local sources,

Table 1. Project data summary

	Aug	Sep	1991 Oct	Nov	Dec	1992 Jan
Maximum	358	421	447	239	367	333
75th.Perc.	122	238	137	143	212	170
Median	107	123	123	134	182	153
25th.Perc.	99	114	118	128	138	147
Minimum	73	65	80	105	94	132
Mean	132	170	153	138	182	168
± 1σ †	65	73	70	16	53	39
Total Data‡	466	682	741	407	628	276

† Standard deviation in the 60-min mean
‡ Total 60-min means used (computed from 1-min data)

as characterized by relatively high frequency peaks on the CO mixing ratio time series, and data during periods of analyzer malfunction or calibration, as documented by the site operator, have been removed. Fig. 1 shows a time series of daily mean CO mixing ratio observed at Mace Head during this period. One sees a number of periods of elevated CO, over a steadily rising baseline due to the natural seasonal variation expected for Northern Hemisphere CO mixing ratio (see Khalil and Rasmussen, 1990).

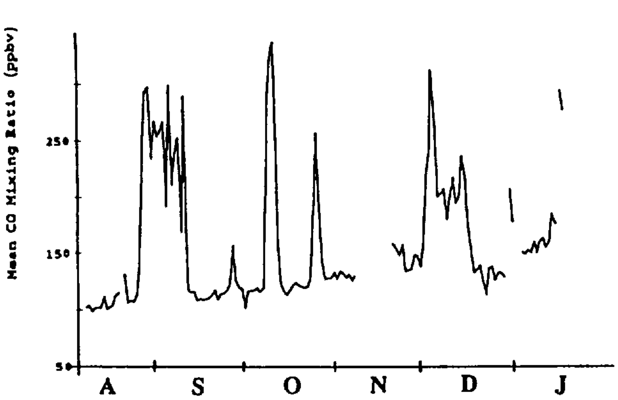

Fig. 1. Daily CO mixing ratio data from Mace Head for the period 91/08/10 – 92/01/17. Daily mean is the average of 1-min data.

On the basis of isentropic back-trajectories used for source attribution to Mace Head (Merrill, unpublished data 1992), we find that for the most part, elevated CO daily mean mixing ratios can be attributed to source regions in Europe, while westerly flow accounts for most of the baseline data.

A comparison of weekly NOAA/CMDL CO flask measurement data (analyzed using a GC/mercuric oxide reduction technique) from Mace Head with our own data has been performed. Fig. 2 shows the results of this intercomparison through the period 91/08/12 – 92/01/06 of their (grab can) data with our own (60-min mean) CO data. The

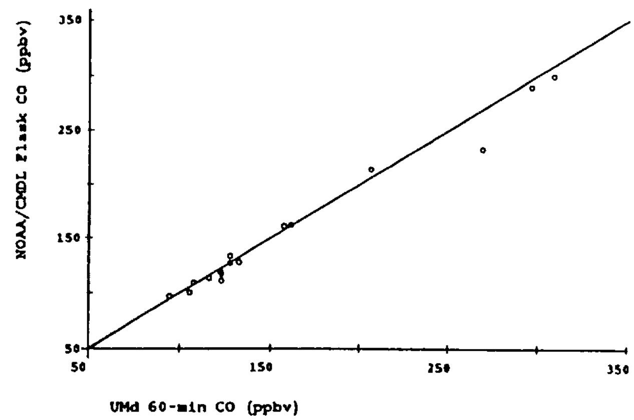

Fig. 2. Intercomparison of NOAA/CMDL calibrated flask CO data with U. Md. 60-min mean CO data from Mace Head, over the period 91/08/12 – 92/01/06. Open circles indicate data pairs and the solid line indicates 1:1 agreement between the data sets.

agreement between the two data sets is quite good, with a linear least-squares fit of the data in fig. 2 having a slope of 0.931±0.034 ($r = 0.991$). This excellent comparison with these independent data gives us a high degree of confidence in our results.

The mean data in Table 1 seem biased by some high-[CO] data, presumably European in origin. Fig. 3 shows the upper and lower quartiles, mean, and median 60-min CO data, for each month processed thus far. A trend toward higher ambient CO mixing ratio at this site

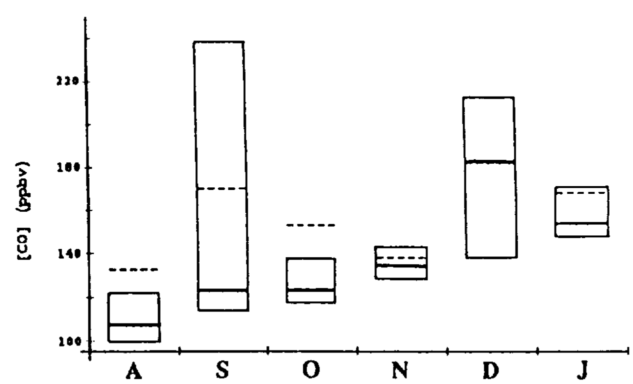

Fig. 3. Monthly variation in CO mixing ratio at Mace Head. Boxes define the upper and lower quartiles; the solid line within each box represents the median; and the dashed line represents the mean.

during winter is apparent. This fits the expected chemistry, as the primary sink for CO in the troposphere, the hydroxyl radical (OH), is most abundant during the summer months. Fig. 4 shows the monthly diurnal variation in median 60-min CO mixing ratio observed at this site. The lack of

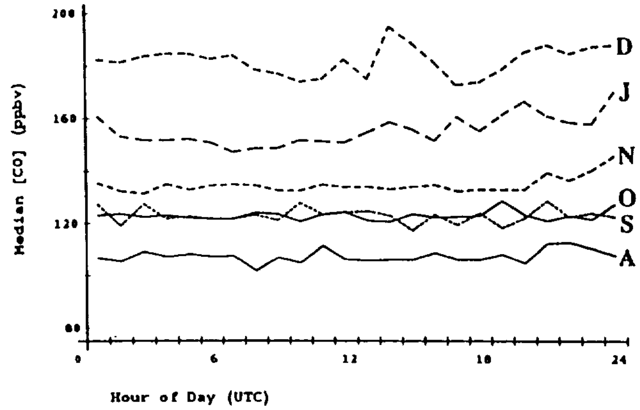

Fig. 4. Diurnal variation in 60-min median CO mixing ratio at Mace Head. Each month is indicated at right; time of day is (UTC).

diurnal variation shown in these data indicate that the origin of periods of high CO are regional in scale; local sources would be expected to show a diurnal cycle due to traffic patterns or boundary layer dynamics.

Analysis of CO data for one complete season, being Fall (September–November), is now complete. Fig. 5 shows a histogram of the Fall 60-min CO data. One

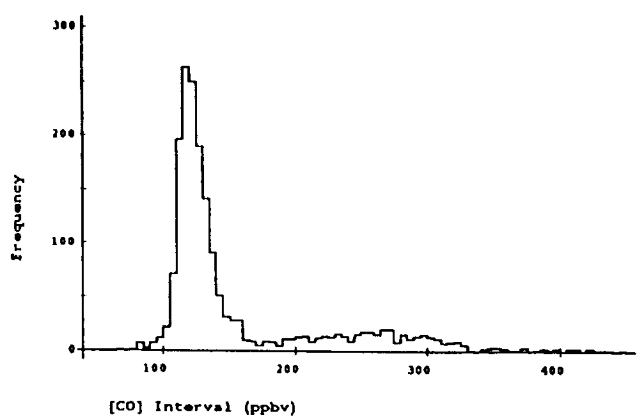

Fig. 5. Histogram of 60-min mean CO mixing ratio data for the Fall season, subject to a CO interval of 5 ppbv.

observes two distinct distributions within these data with a division at ~180 ppbv; air with origin over the North Atlantic Ocean with a median CO mixing ratio of ~120 ppbv accounting for 78% of the data, and (presumably) European air with median CO mixing ratio ~260 ppbv making up the other 22%. A study by Piotrowicz et al. (1990) of CO over the mid-latitude North Atlantic Ocean during late-summer and early-fall indicated an average CO mixing ratio of ~124 ppbv under conditions of westerly flow, which is consistent with our interpretation. We have made a comparison of 60-min mean CO data with hourly mean ozone data from Mace Head for the Fall season, and the resulting scatter plot is shown in fig. 6. Most of the data can be placed in a box bounded by CO 100–150 ppbv and O_3 25–45 ppbv, and these data appear anticorrelated;

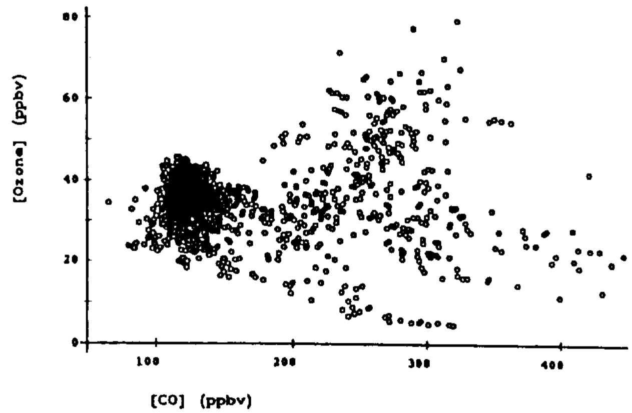

Fig. 6. Comparison of observed 60-min CO and O_3 data from Mace Head, for the Fall season. Data pairs are shown as open circles.

most of these data are certainly of North Atlantic origin. At higher CO mixing ratios there is some indication of two processes operating, ozone destruction by titration with NO and hydrocarbons (indicated by negative correlation), and photochemical ozone production (positive correlation), but without a detailed analysis of back-trajectory data, it is not possible to resolve these regimes at this stage. A conditional mean (Poulida et al., 1991) of the Fall CO data, relative to 1-ppbv intervals of ozone mixing ratio, is more instructive, and is shown in fig. 7. We see three distinct

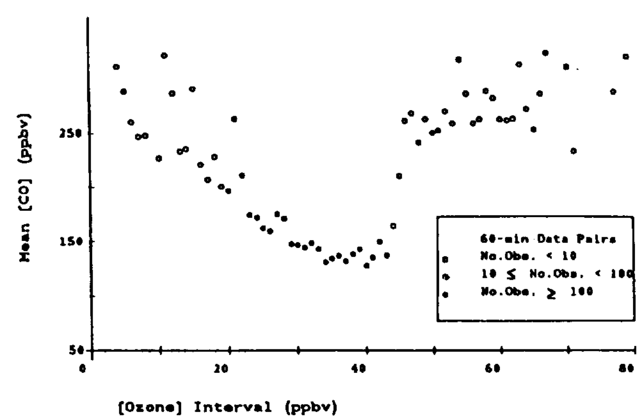

Fig. 7. Conditional mean of 60-min CO mixing ratio relative to 1-ppbv interval of O_3 at Mace Head, for the Fall season. The number of individual CO data averaged to produce that mean for each O_3 interval is indicated by the figure legend.

regimes in these data. For O_3 < ~25 ppbv, the curve has a large negative slope, representative of periods of relatively high CO input, presumably European in origin, to the area. For O_3 > ~45, the curve has a positive slope, indicative of photochemical ozone production. At intermediate levels of O_3, the curve is relatively flat, with a slope near zero, suggesting that photochemical production and loss are similar in magnitude, and probably both slow in this season of sparse solar radiation.

We have just begun using isentropic back-trajectory analysis data (Merrill, unpublished data 1992) to determine if a valid correlation exists between air mass origin and observed CO mixing ratios at Mace Head, even from as far away as North America. As an example, fig. 8 shows two back-trajectories, with arrival times at Mace Head 24 hr apart, but with differing source regions on the North American continent. The 60-min mean CO mixing ratio

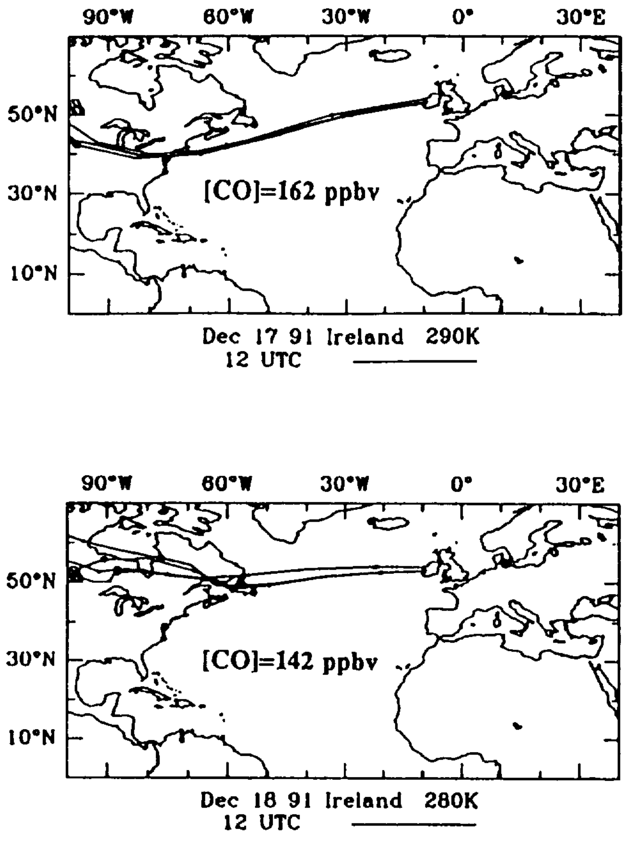

Fig. 8. Isentropic back-trajectories to Mace Head, Ireland, and observed 60-min mean CO mixing ratios at arrival times of 12 UTC on 12/17/91 and 12/18/91. Trajectories supplied by Merrill (unpublished data 1992).

observed at Mace Head at 12 UTC on 12/17/91 was 162 ppbv, with the trajectory passing over heavily industrialized regions of the northeastern U.S. A significantly lower CO mixing ratio of 142 ppbv was observed at 12 UTC on 12/18/91, with the trajectory passing over sparsely populated areas of northern Canada and Newfoundland. In contrast, a trajectory arriving at Mace Head at 00 UTC on 12/05/91, of European origin as shown in fig. 9, is characterized by a much higher observed CO mixing ratio of 306 ppbv.

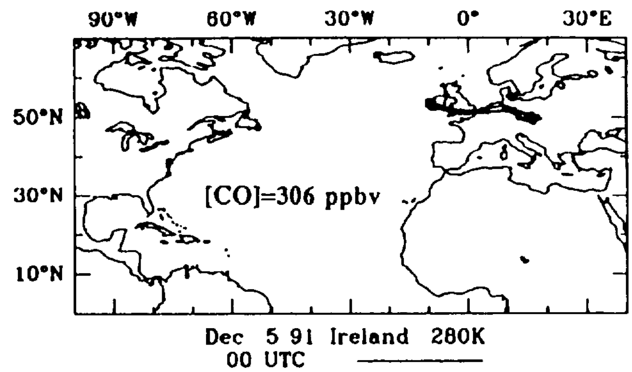

Fig. 9. Isentropic back-trajectory to Mace Head, Ireland, and observed 60-min mean CO mixing ratio at an arrival time of 00 UTC on 12/05/91. Trajectory supplied by Merrill (unpublished data 1992).

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