Transport-induced interannual variability of carbon monoxide determined using a chemistry and transport model

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Abstract. Transport-induced interannual variability of carbon monoxide (CO) is studied during 1989–1993 using the Goddard chemistry and transport model (GCTM) driven by assimilated data. Seasonal changes in the latitudinal distribution of CO near the surface and at 500 hPa are captured by the model. The annual cycle of CO is reasonably well simulated at sites of widely varying character. Day to day fluctuations in CO due to synoptic waves are reproduced accurately at remote North Atlantic locations. By fixing the location and magnitude of chemical sources and sinks, the importance of transport-induced variability is investigated at CO-monitoring sites. Transport-induced variability can explain 1991–1993 decreases in CO at Mace Head, Ireland, and St. David’s Head, Bermuda, as well as 1991–1993 increases in CO at Key Biscayne, Florida. Transport-induced variability does not explain decreases in CO at southern hemisphere locations. The model calculation explains 80–90% of interannual variability in seasonal CO residuals at Mace Head, St. David’s Head, and Key Biscayne and at least 50% of variability in detrended seasonal residuals at Ascension Island and Guam. Upper tropospheric interannual variability during October is less than 8% in the GCTM. Exceptions occur off the western coast of South America, where mixing ratios are sensitive to the strength of an upper tropospheric high, and just north of Madagascar, where concentrations are influenced by the strength of offshore flow from Africa.

1. Introduction

Carbon monoxide (CO) is an important trace gas for several reasons. In urban areas, high concentrations of CO pollute the air, causing health problems. Globally, CO is important because its oxidation by the hydroxyl radical (OH) can be a significant source of tropospheric ozone [Crutzen, 1973; Chameides, 1978] and a major sink for OH. Reaction with OH is the primary loss mechanism of many atmospheric pollutants and gases. An increase in CO concentrations globally could lead to a decrease in OH, resulting in a decrease in the ability of the atmosphere to cleanse itself [Sze, 1977].

CO concentrations are being monitored at over 30 ground-based stations as part of the National Oceanic and Atmospheric Administration (NOAA) Climate Monitoring and Diagnostics Laboratory (CMDL) Cooperative Air Sampling and Atmosphere Ocean Chemistry Experiment (AEROCE) networks [Novelli et al., 1992, 1994a]. CO has been measured from space by the Measurement of Air Pollution from Satellites (MAPS) [Reichle et al., 1986, 1990; Connors et al., 1996] instrument and will be measured by the Measurements of Pollution In the Troposphere (MOPITT) [Drummond and Mand, 1996] instrument as part of the Earth Observing System (EOS).

The distribution of CO has also been studied using chemistry and transport models (CTMs) driven by general circulation model (GCM) output [Pinto et al., 1983; Müller and Brasseur, 1995]. The importance of convective transport to the budget of CO has been studied over the central United States [Thompson et al., 1994] and over Brazil [Pickering et al., 1992, 1996].

Measurements of CO at monitoring sites show that CO concentrations vary seasonally and over longer timescales [e.g., Novelli et al., 1994a]. Seasonal differences are primarily due to the annual cycle of CO sources and sinks. Interannual differences are due to fluctuations and/or trends in CO emissions, sinks, and chemistry and to changes in atmospheric circulation or temperature. Short-term trends are also variable. Ground-based CO concentrations increased by 0.8 to 1.4% per year between 1981 and 1987 [Khalil and Rasmussen, 1988] but decreased by about 2% per year between June 1990 and June 1993 [Novelli et al., 1994b]. The recent decrease in CO concentrations may be due to a reduction in anthropogenic sources and biomass burning [Novelli et al., 1994b; Khalil and Rasmussen, 1994].

Interannual variability in atmospheric circulation can also lead to uncertainties in the estimation of trends. The importance of transport to interannual variability is clear over synoptic time periods and has been studied at Mace Head, Ireland [Doddridge et al., 1994b]. However, the global importance of transport-induced interannual variability could not be directly calculated until the advent of CTMs driven by assimilated data. A 6-year (1988–1993) CO calculation has been run using the Goddard CTM (GCTM) driven by assimilated data from the
2. Solution of Constituent Continuity Equation

The constituent continuity equation is solved using a 2° in latitude by 2.5° in longitude (2° x 2.5°) version of the GCTM [Lin et al., 1994; Allen et al., 1996]. This model has 20 sigma levels, (about 13 in the troposphere) chosen to match the vertical levels of the GEOS-1 atmospheric general circulation model (GEOS-1 AGCM) [Takacs et al., 1994].

Output from the multyear GEOS-1 DAS is used to drive the CTM in an off-line mode. The GEOS-1 DAS fields used to solve the continuity equation for CO are the u and v components of the wind, the surface pressure, the temperature at 0000, 6000, 1200, and 1800 UT, the 3-hour averaged planetary boundary layer (PBL) depth, and the 6-hour averaged convective mass flux. Fields are interpolated to the appropriate transport time before using. A 12-min time step is used in order to satisfy the Courant-Friedrichs-Levy (CFL) condition. In retrospect, a larger time step could have been chosen. Several 2° x 2.5° calculations with this algorithm have used a 15 min time step, and 20 min is possible for some tropospheric applications.

2.1. The Model

The mixing ratio change due to advection is solved using a multidimensional and semi-Lagrangian extension of the piecewise parabolic method (PPM) [Lin and Rood, 1995; Lin et al., 1994]. The horizontal wind components poleward of 70° are filtered with a fast Fourier transform before using to remove noise.

The algorithm used to calculate the mixing ratio change due to turbulent mixing is described in Allen et al., 1996. Turbulent mixing in the GCTM is confined to the PBL. During a CTM time step, a fraction (α = 0.125) of material in each model layer within the PBL is mixed uniformly throughout the PBL.

The algorithm used to parameterize convective mixing is described in the appendix. Briefly, GCTM convection is parameterized using cloud mass flux information from the relaxed Arakawa-Schubert (RAS) algorithm [Moorcroft and Suarez, 1992; Arakawa and Schubert, 1974] that was used to parameterize convection in the GEOS-1 AGCM. The mixing ratio change due to convection is determined by solving iteratively a coupled linear system that defines the mass flux due to convection across the edges of model layers.

2.2. Specification of CO Sources and Sinks

Four major global sources of CO have been identified: fossil fuel combustion, biomass burning, oxidation of nonmethane hydrocarbons (NMHCs), and oxidation of methane (CH₄).

A global CO inventory is not yet available; therefore CO emission due to fossil fuel combustion is assumed to be proportional to anthropogenic odd nitrogen (NOₓ) emissions. Odd nitrogen emissions were obtained from the 1985 Global Emissions Inventory Activity (GEIA) data base [Benkovitz et al., 1996]. It is assumed that 7.9 mol of CO are emitted per mole of NOₓ emitted from fossil fuel combustion, on the basis of Environmental Protection Agency (EPA) estimates for the United States for 1985 [EPA, 1993]. The actual CO/NOₓ emission ratio is greater for mobile sources (e.g., automobiles) than for point sources (e.g., heavy industry) [Buhr et al., 1992]. Therefore the assumption of a uniform emission ratio is clearly a simplification. In addition, the use of the U.S. ratio is likely to result in an underestimation of the global source, as CO emissions are more regulated in the United States than elsewhere. In this calculation, emissions by fossil fuel combustion are assumed to be constant with time and are put into the lowest model layer.

CO emission from biomass burning is calculated assuming a CO/CO₂ volume ratio of 0.08 in biomass burning [Andreae et al., 1988]. Estimated emission ratios for savanna fires in Brazil, Ivory Coast, and Australia are between 0.053 and 0.113 [Hurst et al., 1994; see also Crutzen and Andreae, 1990]. Carbon emissions due to deforestation and savanna fires in tropical America, Africa, and Asia were obtained on a 5° x 5° grid from Hao et al. [1990]. Emissions are apportioned throughout the year using information on climatology, cultural practices, and vegetation types in 15 tropical regions [Richardson, 1994]. Hao et al. [1990] did not include Australian emissions. In this calculation, Australian CO emissions are assumed to be constant with time and equal to 8% of total tropical emissions [Hao et al., 1990].

NMHC oxidation also releases CO. Isoprene (C₅H₈) and monoterpenes (C₁₀H₁₈) emissions were obtained for each month from the 1985 GEIA inventory [Guenther et al., 1987]. Miyoshi et al. [1994] found that oxidation of 1 mol of isoprene under NOₓ-rich (NOₓ free) conditions yields 2.75 (0.55) mol of CO and estimated the global yield to be 1.5 mol of CO per mole of isoprene. In this calculation, oxidation of 1 mol of isoprene is assumed to yield 2.5 mol of CO (approximately the NOₓ-rich yield). Therefore model-calculated CO production from isoprene oxidation is overestimated in regions such as the southern hemisphere (SH), where NOₓ concentrations are usually low. Oxidation of 1 mol of monoterpane is assumed to produce 0.8 mol of CO (R. Saylor, personal communication, 1995).

The final source of CO considered is oxidation of methane (CH₄). CO is an end product of

\[ \text{CH}_4 + \text{OH} \rightarrow \rightarrow \rightarrow \text{OTP} \rightarrow \rightarrow \rightarrow \text{CO} \]  

where OTP = other products. The reaction rate constant \( k \) equals \( 2.65 \times 10^{-12} \exp \left(-1800/T\right) \) where \( T \) is temperature [DelMoro et al., 1994]. Methane concentrations are assumed to be uniform in height and longitude. Its latitudinal gradient is taken from Steele et al. [1987, Figure 6]. In order to focus on transport variability, the CH₄ mixing ratio is held fixed throughout the simulation at the values shown in Table 1. The OH distribution was obtained by monthly averaging and interpolating the OH distribution from the Harvard CTM [Spivakovskaya et al., 1990]. Harvard OH is calculated by expressing OH as a function of temperature, ultraviolet irradiance, water vapor (H₂O), CO, ozone (O₃), CH₄, and total odd nitrogen (see Spivakovskya et al., [1990] for their definition). The global tro-
pospheric mean OH concentration calculated using the Harvard OH fields was initially believed to be 15–25% too high [Spivakovsky et al., 1990]; however, more recent halocarbon-based estimates [Prinn et al., 1995] suggest that the Harvard value may actually be 20% too low (8 × 10^{-13} versus 9.7 ± 0.6 × 10^{-14} molecules cm^{-3}). The use of an equilibrium amount of OH simplifies the calculation but does not allow for feedback between CO and OH. The CO-OH feedback is not crucial for this calculation, since the effect of chemical perturbations on multiyear trends is not being calculated. Additionally, halocarbon-based estimates of OH concentrations have shown little change from 1978 to 1994 [Prinn et al., 1995].

Model-calculated global CO sources are compared to estimates by Logan et al. [1981], Seiler and Conrad [1987], and Pacyna and Graedel [1995] in Table 2 [see also World Meteorological Organization (WMO), 1992]. The total global CO source in the GCTM is lower than tabulated estimates because of a lower estimate of the biomass burning and fossil fuel sources and the neglect of CO emission from vegetation and oceans. The biomass burning source is considerably less than the tabulated estimates because a relatively low CO/CO₂ emission factor was used; emissions due to burning of agricultural wastes, fuel wood, and charcoal were neglected; and extratropical emissions were neglected. The addition of emissions due to agricultural wastes, fuel wood, and charcoal increase total tropical CO₂ emissions by about 20% [Andreae, 1991].

The neglect of CO emission due to extratropical burning may also be important. An analysis of Arctic Boundary Layer Expedition (ABLE 3A) chemical measurements and wind trajectories showed that summertime boreal fires are a significant high-latitude source of CO [Wofsy et al., 1992; Shipham et al., 1992; Harris et al., 1992]. CO is destroyed through the reaction

\[ CO + OH \rightarrow \text{products} \]  

where \( k = 1.5 \times 10^{-13}(1 + 0.6P) \) and \( P \) is pressure in atmospheres [DeMore et al., 1994]. CO loss due to consumption by biological processes is not included. Its magnitude is believed to be less than 10% of the magnitude of loss due to reaction with OH [Logan et al., 1981].

### Table 1. Methane Mixing Ratios Used in Calculation

<table>
<thead>
<tr>
<th>Latitude</th>
<th>CH₄ Mixing Ratio, ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td>90°N</td>
<td>1.90</td>
</tr>
<tr>
<td>80°N</td>
<td>1.89</td>
</tr>
<tr>
<td>70°N</td>
<td>1.88</td>
</tr>
<tr>
<td>60°N</td>
<td>1.87</td>
</tr>
<tr>
<td>50°N</td>
<td>1.87</td>
</tr>
<tr>
<td>40°N</td>
<td>1.86</td>
</tr>
<tr>
<td>30°N</td>
<td>1.85</td>
</tr>
<tr>
<td>20°N</td>
<td>1.83</td>
</tr>
<tr>
<td>10°N</td>
<td>1.79</td>
</tr>
<tr>
<td>0°N</td>
<td>1.78</td>
</tr>
<tr>
<td>10°S</td>
<td>1.76</td>
</tr>
<tr>
<td>20°S</td>
<td>1.75</td>
</tr>
<tr>
<td>30°S</td>
<td>1.75</td>
</tr>
<tr>
<td>90-30°S</td>
<td>1.74</td>
</tr>
</tbody>
</table>

*CH₄ is assumed to be constant in height and longitude.

### Table 2. Annual Carbon Monoxide Emissions

<table>
<thead>
<tr>
<th>CO Emission, Tg/yr</th>
<th>GCTM*</th>
<th>LPWM*</th>
<th>SC*</th>
<th>PG*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Technological sources (fossil fuel combustion)</td>
<td>329</td>
<td>450</td>
<td>640 ± 200</td>
<td>440 ± 150</td>
</tr>
<tr>
<td>Natural NMVOC oxidation</td>
<td>618</td>
<td>560</td>
<td>900 ± 500</td>
<td>800 ± 400</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>370</td>
<td>655</td>
<td>1000 ± 600</td>
<td>700 ± 200</td>
</tr>
<tr>
<td>Methane oxidation</td>
<td>722</td>
<td>810</td>
<td>600 ± 300</td>
<td>600 ± 200</td>
</tr>
<tr>
<td>Ocean*</td>
<td>⋯</td>
<td>40</td>
<td>100 ± 90</td>
<td>50 ± 40</td>
</tr>
<tr>
<td>Vegetation</td>
<td>⋯</td>
<td>130</td>
<td>75 ± 25</td>
<td>75 ± 25</td>
</tr>
<tr>
<td>Oxidation of anthropogenic hydrocarbons</td>
<td>⋯</td>
<td>90</td>
<td>⋯</td>
<td>⋯</td>
</tr>
<tr>
<td>Total</td>
<td>2039</td>
<td>2735</td>
<td>3315 ± 1700</td>
<td>2700 ± 1000</td>
</tr>
</tbody>
</table>

*Estimate by Logan et al. [1981].
*Estimate by Seiler and Conrad [1987].
*Estimate by Pacyna and Graedel [1995].
* Bates et al. [1995] estimated oceanic emission to be 13 Tg/yr with an uncertainty of a factor of 2.
the northern hemisphere (NH) during the same months. The slopes of the distributions are also similar. During December–May, measured and model-calculated CO amounts increase rapidly between 60°S and 30°N. The increase is smaller during June–August, when biomass burning causes a peak between 30°S and the equator. The large peak in NOAA CMDL CO at 36°N is caused by extremely polluted air in the Qinghai Province of China. Model-calculated concentrations at this location are at least 50 ppbv less. During most seasons, model-calculated concentrations are 5–25% higher than CMDL concentrations in the SH and about the same percentage lower at mid and high latitudes of the NH. The cause of the NH low bias is unknown. Possible causes include the neglect of CO emission from boreal fires and the underestimation of CO emission by fossil fuel combustion. The high bias in the SH is partially due to an overestimation of the SH CO source from NMHC oxidation. CO concentrations constructed using model output at CMDL stations are lower than CO concentrations calculated by zonally averaging model output because most NOAA CMDL sites are placed at marine locations.

The mean (1989–1993) model-calculated latitudinal distributions of CO at 500 hPa during April and October are compared with MAPS measurements from April 9–19, 1994, and September 30 to October 11, 1994, in Figures 2a and 2b, respectively. Model output at a single layer (500 hPa) is compared with MAPS measurements because the MAPS weighting

Table 3. Carbon Monoxide Monitoring Stations Discussed in This Paper

<table>
<thead>
<tr>
<th>Site</th>
<th>Location</th>
<th>Height, m</th>
<th>First CMDL Observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrow, Alaska</td>
<td>71°N, 157°W</td>
<td>11</td>
<td>July 25, 1988</td>
</tr>
<tr>
<td>Heimaey, Iceland</td>
<td>63°N, 20°W</td>
<td>100</td>
<td>Nov. 16, 1991</td>
</tr>
<tr>
<td>Mace Head, Ireland</td>
<td>53°N, 10°W</td>
<td>25</td>
<td>June 3, 1991</td>
</tr>
<tr>
<td>Taean Peninsula, Korea</td>
<td>37°N, 126°E</td>
<td>20</td>
<td>Jan. 5, 1991</td>
</tr>
<tr>
<td>Qinghai Province, China</td>
<td>36°N, 101°E</td>
<td>3810</td>
<td>Aug. 5, 1990</td>
</tr>
<tr>
<td>St. David's Head, Bermuda</td>
<td>32°N, 65°W</td>
<td>30</td>
<td>June 11, 1991</td>
</tr>
<tr>
<td>Key Biscayne, Florida</td>
<td>26°N, 80°W</td>
<td>3</td>
<td>Aug. 9, 1991</td>
</tr>
<tr>
<td>Cape Kumukahi, Hawaii</td>
<td>20°N, 155°W</td>
<td>3</td>
<td>July 4, 1989</td>
</tr>
<tr>
<td>Guam, Mariana Islands</td>
<td>13°N, 145°E</td>
<td>2</td>
<td>Oct. 10, 1989</td>
</tr>
<tr>
<td>Christmas Island</td>
<td>02°N, 157°W</td>
<td>3</td>
<td>Dec. 25, 1989</td>
</tr>
<tr>
<td>Mahe Island, Seychelles</td>
<td>04°S, 55°E</td>
<td>3</td>
<td>Nov. 16, 1990</td>
</tr>
<tr>
<td>Ascension Island</td>
<td>08°S, 14°W</td>
<td>54</td>
<td>Feb. 2, 1989</td>
</tr>
<tr>
<td>Tutuila, American Samoa</td>
<td>14°S, 171°W</td>
<td>42</td>
<td>Sept. 23, 1988</td>
</tr>
<tr>
<td>Cape Grim, Tasmania</td>
<td>41°S, 145°E</td>
<td>94</td>
<td>June 14, 1991</td>
</tr>
</tbody>
</table>

Except for Heimaey, all sampling sites listed are included in latitudinal average (Figure 2).

\(^a\)AEROCE data are used for Figure 7, although NOAA CMDL measurements began November 16, 1991.

\(^b\)AEROCE data are used for Figure 7; NOAA CMDL data are used for remainder of study.
function [e.g., Reichle et al., 1990] is currently being revised, and MAPS concentrations are believed to be most representative of 490 hPa (V. Connors, personal communication, 1995). Model-calculated concentrations are within a standard deviation of measured concentrations at nearly all latitudes during both seasons, although significant differences do exist between the shapes of the distributions. During April, measured CO concentrations are nearly constant between 60°S and 30°S, while model-calculated concentrations increase gradually from 60°S to 30°S. In addition, the rapid increase in CO with latitude between 10°S and 10°N is underestimated by the model. Larger differences are seen during October, when model-calculated concentrations are less than MAPS concentrations by about 30 ppbv between 10°S and 25°S and 10 ppbv north of 50°N. Model-calculated SH concentrations are likely too low because the extent of biomass burning in southern Asia was underestimated [Connors et al., 1996] and because the moist convective algorithm in the GCTM tends to move too much material from the PBL to the upper troposphere directly, resulting in an underestimation of concentrations in the midtroposphere [Allen et al., 1996; Allen, 1996].

The mean model-calculated (1989–1993) distributions of CO at 500 hPa during April and October are compared in Figures 3a and 3b, respectively. During April, model-calculated concentrations exceed 120 ppbv over much of Siberia and 105 ppbv over Colombia and the Gulf of Guinea. During October, model-calculated concentrations are largest in a region extending from northern South America to western and southern Africa. CO concentrations from MAPS show an additional peak near Indonesia during October 1994 [Connors et al., 1996; Vulcan et al., 1996]. This peak is not present in the mean model-calculated distribution.

The contributions of fossil fuel combustion, oxidation of NMHCs, biomass burning, and oxidation of CH4 to the mean 500-hPa model-calculated CO distribution during October are shown in Figures 4a through 4d, respectively. CO amounts from fossil fuel combustion exceed 35 ppbv at high northern latitudes, especially over Siberia; fall off rapidly through the midlatitudes of the NH; and are as small as 5 ppbv in the SH. CO amounts from NMHC oxidation are generally 20–30 ppbv but exceed 60 ppbv in northwestern South America. CO amounts from biomass burning are largest (>50 ppbv) over and downwind of regions of extensive August–September biomass burning such as Brazil and southern Africa [e.g., Watson et al., 1990]. CO amounts from methane oxidation range from 29 ppbv at high southern latitudes to 33 ppbv at equatorial locations.

The mean model-calculated surface layer distribution of CO during October 1989–1993 is shown in Figure 5a. Surface layer concentrations exceed 350 ppbv in portions of South America and Africa where biomass burning is extensive. Monthly average measured concentrations in a region of burning near Cuiabá, Brazil, exceeded 650 ppbv [Kirchhoff et al., 1989]. Another feature of the boundary layer distribution is tongues of elevated CO extending eastward from source regions in Europe and westward from source regions in equatorial South America and Africa.

Locations where interannual CO variability is large were identified by calculating standard deviations of October monthly means from 1989–1993. The relative importance of interannual variability is shown in Figure 5b which shows the normalized standard deviations as a function of longitude and latitude. Model-calculated interannual variability exceeds 12% over the eastern north Atlantic, the southern tip of South Africa, and western India; however, variability at most locations is less than 6%. In general, variability is largest where horizontal gradients of CO are largest. Possible causes of large variability in the eastern North Atlantic (Mace Head, Ireland) were studied as part of AEROCE.
3.2. Atmospheric Variability

As part of AEROCE, CO was measured almost continuously between September 1992 and September 1993 at Heimaey, Iceland (63°N, 20°W), and between August 1991 and January 1993 at Mace Head, Ireland (53°N, 10°W). The experimental technique and sampling protocol are discussed by Doddridge et al. [1994a, b]. Descriptions of the Mace Head and Heimaey measurement sites are given by Jennings et al. [1991, 1993] and Prospero et al. [1995], respectively. Surface layer model output at these sites and daily average AEROCE measurements are compared in Figures 6a and 6b. A seasonal cycle is evident at both locations and is captured by the model, although model-calculated summertime concentrations are lower than measurements at Heimaey. The most striking feature of the CO distributions at Mace Head and Heimaey are the abrupt increases that occur when polluted European air reaches these sites [Jennings et al., 1993, 1996; Doddridge et al., 1994b]. The amplitude, length, and timing of most of these events are captured by the model, with only a few springtime events missed. A major strength of the GCTM is its ability to resolve the transport of pollutants to island sites in the northern Atlantic [e.g., Allen et al., 1996].

Fall (September–November) CO measurements are available at Mace Head, during 1991 and 1992. Statistics from the AEROCE measurements [Doddridge et al., 1994b] and from the model for the fall seasons are shown in Table 4. Flow from Europe was more common during 1991, resulting in larger concentrations and a larger standard deviation. Model-calculated means were slightly lower than observed means, but interannual variability in mean CO concentrations and in CO variability was well captured by the model. Measured (model-calculated) 1991 means exceed 1992 means by 42 (34) ppbv. Standard deviations calculated from 1991 measurements and 1991 model output exceed 1992 standard deviations by a factor of 3.5. Interannual variability is especially large at Mace Head owing to its proximity to large CO sources in Europe. The ability of the GCTM to simulate variability at other locations where measurements are less frequent and CO gradients are smaller is examined by comparing model output with NOAA CMDL measurements.
3.3. Annual Cycle at NOAA Sites

Because of the approximations used in specifying chemical sources and sinks, the investigation of interannual variability will be limited to the marine and coastal locations shown in Figure 7. Longitudes and latitudes of these sites are listed in Table 3. Model-calculated and observed monthly average means at these sites are compared in Figures 8a through 8k. Model-calculated means were obtained by averaging daytime surface layer model output for each day of the month. Measured means were calculated by Novelli et al. [1991, 1994a] using a curve-fitting technique. Measured means are likely to be biased low, since measurements are usually taken during periods when "background" air is expected. Measurements were taken 2–4 times per month; the date of the first measurement at each site is listed in Table 3.

The observed annual cycle of CO is reproduced reasonably well at all locations except Christmas Island, where it is completely missed. Measured CO concentrations at Christmas Island show a strong peak during the late NH winter and a much smaller peak during the late NH summer. Model-calculated CO concentrations show a strong peak during the late NH summer and fall. The amplitude of the annual cycle at Ascension Island is overestimated, possibly because of an overestimation of CO emission by savanna fires in southern Africa [Scholes et al., 1995]. The seasonal cycle is also overestimated at Cape Grim and underestimated at Seychelles. In general, model-calculated concentrations are too low in the NH and too high in the SH.

Table 4. Mace Head, Ireland, CO for Fall 1991 and Fall 1992

<table>
<thead>
<tr>
<th></th>
<th>Fall 1991 CO, ppbv</th>
<th>Fall 1992 CO, ppbv</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Measures</td>
<td>Model</td>
</tr>
<tr>
<td>Minimum</td>
<td>65</td>
<td>78</td>
</tr>
<tr>
<td>25th percentile</td>
<td>118</td>
<td>99</td>
</tr>
<tr>
<td>Median</td>
<td>127</td>
<td>114</td>
</tr>
<tr>
<td>75th percentile</td>
<td>157</td>
<td>145</td>
</tr>
<tr>
<td>Maximum</td>
<td>447</td>
<td>474</td>
</tr>
<tr>
<td>Mean</td>
<td>156</td>
<td>140</td>
</tr>
<tr>
<td>Standard deviation</td>
<td>64</td>
<td>71</td>
</tr>
</tbody>
</table>

4. Interannual Variability

4.1. NOAA/CMDL Sites

The importance of transport-induced interannual variability at NOAA CMDL sites is assessed by evaluating how well a model without interannual chemical variability and interannual variability in CO emissions reproduces interannual fluctuations in seasonal CO concentrations.

Since the lifetime of CO is long in comparison with the lifetime of synoptic systems, CO concentrations away from source regions are determined to a large extent by atmospheric flow patterns. Flow patterns are variable because of barotropic and baroclinic instabilities. Mean CO concentrations vary from year to year as the location, strength, and timing of disturbances caused by instabilities change. Causes of interannual variability in atmospheric flow patterns are varied. Doddridge et al. [1994b] speculate that interannual variations in flow to
Locations of selected sites in NOAA/CM DL Network

Figure 7. Model grid point containing AEROCE and NOAA CMDL measuring sites discussed in this paper. Locations are approximate; see Table 3 for actual latitudes and longitudes of sites.

Mace Head during the fall are caused by changes in external forcing from the tropics. Interannual variability in mean NOAA CMDL CO concentrations may be especially large because measurements are taken infrequently, allowing fluctuations in CO concentrations due to synoptic systems to remain.

Seasonal means at NOAA CMDL stations are constructed by averaging measurements with unique sampling times from each season. Seasonal means are calculated because too few measurements exist to accurately determine monthly means. Measurements flagged by NOAA as nonbackground or erroneous are not included in the average. In order to lessen possible sampling biases, measurements taken before the beginning of the first full season and after the end of the last full season are not included. For example, although measurements

Figure 8. Monthly average CO for 1989–1993 at (a) Barrow, Alaska; (b) Mace Head, Ireland; (c) St. David's Head, Bermuda; (d) Key Biscayne, Florida; (e) Cape Kumukahi, Hawaii; (f) Guam, Mariana Islands; (g) Christmas Island; (h) Mahe Island, Seychelles; (i) Ascension Island; (j) Tutuila, American Samoa; and (k) Cape Grim, Tasmania. CMDL measurements are shown with solid lines. Model-calculated surface layer CO at nearest grid point are shown with dashed lines.
at Barrow, Alaska, began July 1988 and ended June 1993, seasonal means were calculated using output between September 1988 and May 1993. Seasonal means are available for as few as 7 seasons at Key Biscayne, Florida, to as many as 19 seasons at Barrow and American Samoa. The number of complete seasons at each site (N) is listed in Table 5. In order to lessen sampling biases, seasonal means from the model are calculated by sampling the surface layer of the model at the same time the observations were taken.

The average seasonal means from measurements and model output are calculated by averaging seasonal means from each year. Residuals from the average seasonal mean are calculated by subtracting the average seasonal mean from the actual seasonal mean. A quadratic function is then fitted to each residual.

Table 5. Residual Information

<table>
<thead>
<tr>
<th>Site</th>
<th>N</th>
<th>r</th>
<th>r²</th>
<th>0.05</th>
<th>Trend</th>
<th>CMDL</th>
<th>Model</th>
<th>r*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Barrow, Alaska</td>
<td>19</td>
<td>0.59</td>
<td>0.35</td>
<td>yes</td>
<td>-3.3</td>
<td>+0.1</td>
<td>0.27</td>
<td></td>
</tr>
<tr>
<td>Mace Head, Ireland</td>
<td>8</td>
<td>0.90</td>
<td>0.81</td>
<td>no</td>
<td>-2.8</td>
<td>-3.1</td>
<td>0.86</td>
<td></td>
</tr>
<tr>
<td>St. David’s Head, Bermuda</td>
<td>8</td>
<td>0.92</td>
<td>0.85</td>
<td>no</td>
<td>-3.5</td>
<td>-4.2</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>Key Biscayne, Florida</td>
<td>7</td>
<td>0.97</td>
<td>0.94</td>
<td>no</td>
<td>+6.2</td>
<td>+4.6</td>
<td>0.91</td>
<td></td>
</tr>
<tr>
<td>Cape Kumukahi, Hawaii</td>
<td>15</td>
<td>-0.01</td>
<td>xx</td>
<td>no</td>
<td>-3.5</td>
<td>+0.3</td>
<td>0.02</td>
<td></td>
</tr>
<tr>
<td>Guam, Mariana Islands</td>
<td>14</td>
<td>0.83</td>
<td>0.68</td>
<td>yes</td>
<td>-4.1</td>
<td>-0.7</td>
<td>0.66</td>
<td></td>
</tr>
<tr>
<td>Christmas Island</td>
<td>14</td>
<td>-0.50</td>
<td>xx</td>
<td>no</td>
<td>-0.8</td>
<td>-1.6</td>
<td>-0.49</td>
<td></td>
</tr>
<tr>
<td>Mahé Island, Seychelles</td>
<td>10</td>
<td>0.57</td>
<td>0.32</td>
<td>no</td>
<td>-2.7</td>
<td>-0.5</td>
<td>0.66</td>
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</tr>
<tr>
<td>Ascension Island</td>
<td>17</td>
<td>0.72</td>
<td>0.52</td>
<td>yes</td>
<td>-2.4</td>
<td>+0.4</td>
<td>0.48</td>
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<tr>
<td>Tutuila, American Samoa</td>
<td>19</td>
<td>-0.11</td>
<td>xx</td>
<td>no</td>
<td>-3.7</td>
<td>-0.7</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Cape Grim, Tasmania</td>
<td>8</td>
<td>0.55</td>
<td>0.31</td>
<td>no</td>
<td>-6.7</td>
<td>-0.4</td>
<td>0.03</td>
<td></td>
</tr>
</tbody>
</table>

Here "N" is number of seasons with measurements available throughout (19, fall 1988 to spring 1993; 15, fall 1989 to spring 1993; 11, fall 1990 to spring 1993; and 7, fall 1991 to spring 1993); "r" and "r*" are linear correlation coefficients between model-calculated and measured time series after (and before) removal of linear and quadratic terms, respectively; "r²" is the variance explained by linear correlation; "0.05" is significance at the 0.05 level calculated using t test with N - 8 degrees of freedom; and "trend" is mean percent change per year in residuals calculated from NOAA CMDL measurements (CMDL) and model output (Model), calculated using fields from N seasons.
Figure 9. Interannual fluctuations in monthly mean CO after removal of mean and “trend” over measurement period at (a) Barrow, Alaska; (b) Mace Head, Ireland; (c) St. David's Head, Bermuda; (d) Key Biscayne, Florida; (e) Cape Kumukahi, Hawaii; (f) Guam, Mariana Islands; (g) Christmas Island; (h) Mahe Island, Seychelles; (i) Ascension Island; (j) Tutuila, American Samoa; and (k) Cape Grim, Tasmania. Residuals calculated from measurements (model output) are shown with solid (dashed) lines.

Time series in order to determine the change in residuals during the N seasons. Annually averaged model-calculated and observation-calculated changes in CO residuals at each site are listed in Table 5. Residuals calculated from NOAA CMDL measurements decrease at all locations but Key Biscayne. Model- and observation-calculated 1991–1993 changes at Mace Head, Key Biscayne and St. David's Head, Bermuda, are nearly the same, suggesting that transport alone is responsible...
for summer 1991 to spring 1993 changes in CO concentrations at these locations. In addition, model- and observation-calculated residual time series at these three sites are highly correlated, with \( r^* \approx 0.9 \) at each location (see Table 5). Model-calculated CO concentrations also decrease at most SH locations; however, the magnitudes of the decreases are much less than the magnitudes of observation-calculated decreases (see Table 5). Transport-induced variability is responsible for only a small portion (or quite possibly none) of the SH decreases. Changes in model-calculated CO concentrations at NOAA CMDL sites are not caused by changes in the total amount of CO in the model. The global surface layer CO burden in the model varies by less than 1% per year between 1989 and 1993. Global trends in CO during the late 1980s and early 1990s are discussed by Novelli et al. [1994b] and Khalil and Rasmussen [1994].

In order to focus on interannual variability, linear and quadratic terms were fitted to and removed from each 7- to 19-season time series. In general, this process reduced total variability by 20-40%, although the variability in observation-calculated residuals at Barrow, Bermuda, Cape Kumukahi, and Guam was reduced by \( \approx 60\% \). Time series of detrended CO residuals at the selected NOAA CMDL sites are shown in Figures 9a to 9k. The correlation coefficient between model-calculated and NOAA CMDL-calculated residuals (\( r \)), the percent of variance in NOAA CMDL residuals explained by the model (\( r^* \)), and the significance of correlations at the 0.05 significance level are shown in Table 5.

The explained variance is an estimate of the fraction of interannual variability explained by transport. The estimate is most reliable at locations where the GCTM is able to simulate day to day fluctuations in CO accurately. It is likely to be low in regions where atmospheric variability is not captured. Transport-induced interannual variability explains more than 80% of total interannual variability at Mace Head, St. David's Head, and Key Biscayne. The model calculation explains about 50% of variability in detrended NOAA CMDL residuals at Ascension Island. The importance of transport-induced variability at Ascension Island is somewhat surprising given the importance of biomass burning to its distribution. However, the amount of CO reaching Ascension Island is dependent on both the strength and location of biomass burning and atmospheric transport [Fishman et al., 1991; Novelli et al., 1992].

Residuals calculated from model output and measurements are negatively correlated at Christmas Island and uncorrelated at American Samoa and Cape Kumukahi. The poor agreements are not necessarily evidence that interannual chemical variability dominates interannual transport variability at these locations. They may also indicate that meteorological variability is poorly simulated by the model at these locations.

Model-calculated and observation-calculated residuals at Guam and Cape Grim are correlated, although the agreement is likely fortuitous, since the magnitudes of model-calculated residuals are usually substantially smaller than the magnitudes of observation-calculated residuals. Transport may also explain a significant fraction (30%) of interannual variability at Seychelles; however, the actual contribution of transport is highly uncertain, since the correlation is not significant at the 0.05 significance level.

### 4.2. Upper Tropospheric Variability in GCTM

Upper tropospheric CO measurements are too scarce to evaluate interannual variability; however, processes responsible for upper tropospheric interannual variability in the GCTM can be identified.

The mean (1989–1993) model-calculated CO distribution for October at 300 hPa is shown in Figure 10a. The CO distribution has the most structure in the tropics where a combination of biomass burning, NMHC oxidation, and convection creates a CO peak over equatorial South America and Africa. Strong upper tropospheric winds advect a substantial portion of this CO as far east as Australia.

Locations where upper tropospheric interannual variability is large during October were identified by calculating normalized standard deviations of residuals from the October mean (see Figure 10b). In general, transport-induced variability is most important near the coasts of continents, especially in regions where horizontal CO gradients are large. In these areas, small interannual changes in atmospheric circulation can lead to substantial changes in CO.

Upper tropospheric interannual variability during October rarely exceeds 4% in the NH, where horizontal CO gradients are small; however, variability exceeds 12% to the north and east of Madagascar (15°S, 50°E) and off the western coast of South America (10°S, 80°W) (see Figure 10b). Interannual variability in upper tropospheric winds is the primary cause of both peaks. Most CO in the upper troposphere near Madagascar was originally emitted in eastern Africa and subsequently lofted by convection (Figure 11c). Upper tropospheric 1993 CO concentrations to the northeast of Madagascar exceed 1990 concentrations by over 30 ppbv (Figure 11d). The cause is strong offshore flow during 1993 (Figure 11b) and weak offshore flow during 1990 (Figure 11a). The situation is a bit more complicated off the western coast of South America. CO emissions are largest in eastern Brazil (Figure 12c), but variability is largest in the eastern Pacific (Figure 10b), where 1990 CO...
concentrations exceed 1993 amounts by up to 50 ppbv (Figure 12d). A strong anticyclone is located over South America during 1990 (Figure 12a). Convectively lofted CO is transported around the high and into the Pacific, where some CO is transported to the west and some to the south. The strength of the southward component of the anticyclonic circulation is especially variable from year to year. CO concentrations off the western coast of South America are larger during 1990 because the anticyclonic circulation is much stronger in 1990 than 1993 (compare Figures 10a and 10b). Direct transport of CO to the Atlantic is larger in 1993, when the upper tropospheric high is weaker.
5. Summary

Transport-induced interannual variability of CO must be considered when calculating changes in mean CO concentrations using data from only a few years and when evaluating the representativeness of satellite measurements taken over a few days. The fraction of interannual CO variability attributable to transport was estimated by comparing output from a GCTM calculation having a fixed annual cycle of sources and sinks with NOAA CMDL measurements. The latitudinal distribution of CO obtained by averaging model output at NOAA CMDL sites was realistic during all seasons, although SH concentrations were typically 5-15 ppbv too high and NH concentrations were 10-40 ppbv too low. Mean model-calculated CO concentrations at 500 hPa are within 1 standard deviation of 1994 MAPS measurements at nearly all latitudes during both April and October, although the magnitude of a SH peak due to biomass burning is underestimated.

Day to day fluctuations in trace species are well simulated by the GCTM at north Atlantic sites (Mace Head, Ireland; Key Biscayne, Florida; and St. David's Head, Bermuda), and these three sites are ideal for estimating the importance of transport to interannual variability. Transport-induced interannual variability explains 80-90% of total interannual variability at these sites. The estimation is less reliable at sites where day to day variations are not as well simulated; however, it appears that transport is responsible for about 50% of interannual CO variability at Guam and Ascension Island. Transport-induced variability can explain decreases in CO during 1991-1993 at Mace Head and Bermuda and an increase in CO at Key Biscayne. Transport-induced variability is responsible for little (or possibly none) of the observed decrease in CO at SH locations.

Monthly mean model-calculated CO concentrations are most variable in regions where emissions vary strongly with location. Upper tropospheric variability during October is largest off the western coast of South America and off the eastern coast of Africa. The variability off the South American coast was traced to the strength of an upper tropospheric high, while the variability off of Africa was traced to the strength of upper tropospheric offshore flow from Africa.

Appendix

Cumulus convection in the GCTM is parameterized using cumulus mass flux output from the RAS algorithm [Moorthi and Suarez, 1992; Arakawa and Schubert, 1974] used to parameterize convection in the GEOS-1 AGCM.

The conservation of mass principle is invoked in order to calculate the mixing ratio change due to convection. Consider layer k in Figure A1. From mass conservation it follows that the upward flux due to convection ($C_k$) is balanced by compensating large-scale subsidence ($S_k$). This circulation moves $\Delta t C_k q_k$ kg of tracer upward and out of layer k and $\Delta t C_{k-1} q_{k-1}$ kgs of tracer downward and into layer k ($\Delta t$ is the dynamic time step; $q_k$ is the mixing ratio of tracer within the cloud, assumed to be constant; and $q_{k-1}$ is the mixing ratio of tracer in layer k). Similar arguments can be applied to calculate the mass flux at the lower edge of the layer. The mass of tracer in layer k after $\Delta t$ is given by

\[ M_{q_k}^{n+1} = M_{q_k}^n + \Delta t \left( C_k \cdot [q_k^{n+1} - q_k^n] - C_{k-1} [q_{k-1}^{n+1} - q_{k-1}^n] \right) \] (A1)

where $M_q = 100 \Delta p / g$ is the background air mass per unit area, in kilograms per square meter; $\Delta p_k$ is the depth of model layer k in hPa; and g is the gravitational acceleration in meters per second squared. At the fixed cloud base (the top of layer NLAY-1), k = c, and equation (A1) reduces to

\[ M_{q_c}^{n+1} = M_{q_c}^n - \Delta t C_c [q_c^{n+1} - q_c^n] \] (A2)

The equations for each model layer from cloud base to cloud top form a coupled linear system that is similar to a discretized flux form transport equation for a time implicit differencing scheme. In the limit $\Delta t \to 0$ and $\Delta p \to 0$ (i.e., the continuous case), the cloud transport equation becomes

\[ \frac{\partial q_c}{\partial t} = \frac{g}{100 \Delta p} C(q_c - q) \] (A3)

This equation is analogous to Schneider and Lindzen’s [1976] equation for computing the “apparent momentum source” due to cloud motions. The equations for each layer (A1) form a coupled linear system that is solved iteratively using a time step of $\Delta t / ns$, where ns is the number of iterations. The equations can be written in a discretized form as

\[ M_{q_k}^{n+1} = M_{q_k}^n + \frac{\Delta t}{ns} \left( C_k \cdot [q_k^{n+1/ns} - q_k^n] - C_{k-1} [q_{k-1}^{n+1/ns} - q_{k-1}^n] \right) \] (A4)

where the intermediate cloud mixing ratio $q_c^{n+1/ns}$ is obtained by directly solving (A2) after replacing $q_c^{n+1/2}$ with $q_c^{n-1/2}$.

\[ q_c^{n+1/2} = \left[ M_{q_c}^n + \Delta t C_c (q_c - q_{c-1}) / ns \right] / (M_c + \Delta t C_c / ns) \] (A5)

Equations (A4) and (A5) are integrated from the cloud base to the cloud top ns times in order to obtain a more accurate solution. In practice, $ns = 3$, which results in a cumulus transport step of 4 min for $\Delta t = 12$ min.

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References


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