

Using CO₂:CO correlations to improve inverse analyses of carbon fluxes

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Received 22 September 2005; revised 2 February 2006; accepted 20 March 2006; published 30 June 2006.

[1] Observed correlations between atmospheric concentrations of CO₂ and CO represent potentially powerful information for improving CO₂ surface flux estimates through coupled CO₂-CO inverse analyses. We explore the value of these correlations in improving estimates of regional CO₂ fluxes in east Asia by using aircraft observations of CO₂ and CO from the TRACE-P campaign over the NW Pacific in March 2001. Our inverse model uses regional CO₂ and CO surface fluxes as the state vector, separating biospheric and combustion contributions to CO₂. CO₂-CO error correlation coefficients are included in the inversion as off-diagonal entries in the a priori and observation error covariance matrices. We derive error correlations in a priori combustion source estimates of CO₂ and CO by propagating error estimates of fuel consumption rates and emission factors. However, we find that these correlations are weak because CO source uncertainties are mostly determined by emission factors. Observed correlations between atmospheric CO₂ and CO concentrations imply corresponding error correlations in the chemical transport model used as the forward model for the inversion. These error correlations in excess of 0.7, as derived from the TRACE-P data, enable a coupled CO₂-CO inversion to achieve significant improvement over a CO₂-only inversion for quantifying regional fluxes of CO₂.

Citation: Palmer, P. I., P. Suntharalingam, D. B. A. Jones, D. J. Jacob, D. G. Streets, Q. Fu, S. A. Vay, and G. W. Sachse (2006), Using CO₂:CO correlations to improve inverse analyses of carbon fluxes, *J. Geophys. Res.*, 111, D12318, doi:10.1029/2005JD006697.

1. Introduction

[2] Measurements of atmospheric composition provide powerful constraints to improve understanding of surface fluxes of trace compounds and their subsequent fate in the atmosphere. Recent studies have exploited these data by employing an inverse model approach [Bousquet *et al.*, 1999; Gilliland *et al.*, 2003; Palmer *et al.*, 2003], in which a chemical transport model (forward model) is used to relate the sensitivity of an observed chemical concentration measurement to changes in particular model parameters (e.g., surface fluxes). An optimal estimation inverse model then combines this sensitivity information with the observations to yield the solution that is most consistent with the observations, the a priori information about the model parameters, and their relative errors. Estimated error vari-

ance and covariance information is included in the inversion via the a priori and observation error covariance matrices. Previous studies that analyzed correlations between different trace gases [e.g., Ciais *et al.*, 1995; Enting *et al.*, 1995] did not take advantage of these additional correlations in inverse model analyses. These correlations can arise from having similar spatial and temporal flux distributions, from chemical mass balance, or from atmospheric transport processes. Exploitation of these correlations in an inverse model involves quantifying the associated error correlation coefficients to include in the off-diagonal entries to the a priori and observation error covariance matrices.

[3] We present in this paper a method to objectively quantify error correlations between CO and CO₂ as constraints in inverse model calculations for the budgets of both gases. Carbon dioxide over continents is released by combustion and biospheric respiration, and is taken up by photosynthesis. Over many regions of the world these combustion and biogenic fluxes overlap significantly. Separation of these fluxes in inverse analyses of CO₂ observations can therefore be difficult. Combustion is a source of CO and CO₂, with the CO emission ratio decreasing with combustion efficiency. Biospheric fluxes of CO are small. Here we use the error correlation coefficients between CO and CO₂ in an inverse model analysis to estimate simultaneously CO and CO₂ fluxes with the principal purpose of reducing uncertainty of combustion and biospheric CO₂

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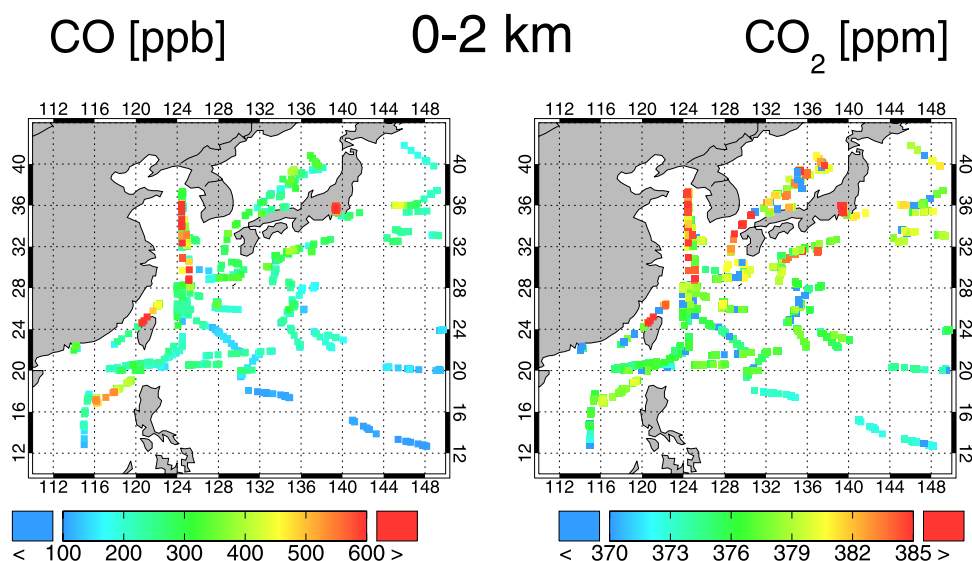


Figure 1. Mean CO and CO₂ boundary layer (0–2 km) concentrations during the TRACE-P aircraft mission in March–April 2001 [Jacob *et al.*, 2003]. The data are averaged on the GEOS-CHEM $2^\circ \times 2.5^\circ$ model grid.

flux estimates. We apply this method to CO and CO₂ concentration data from the NASA TRACE-P aircraft campaign [Jacob *et al.*, 2003], conducted over the western Pacific during February–April 2001. Two aircraft (DC8 and P3B) were used during TRACE-P to sample Asian outflow between 10° and 45°N and 0 and 12 km altitude. TRACE-P was conducted during the season of strongest outflow from mainland Asia to the Pacific, driven by frequent midlatitude cyclones and associated cold fronts and warm conveyor belts [Liu *et al.*, 2003]. The February–April period is also the biomass burning season in Southeast Asia [Heald *et al.*, 2003].

[4] Recent studies have used observed CO₂:CO slopes derived from linear regression of atmospheric composition data to identify the source origins of air masses sampled in TRACE-P [Suntharalingam *et al.*, 2004; Takegawa *et al.*, 2004]. Suntharalingam *et al.* [2004] showed strong correlations between CO₂ and CO concentrations during TRACE-P with distinct CO₂:CO slopes that they used to constrain regional flux estimates of CO₂. They interpreted the CO₂:CO correlations using the GEOS-CHEM chemical transport model (Appendix A) and identified a large underestimate in the Chinese biospheric CO₂ flux. Other TRACE-P studies have used CO observations with success to constrain east Asian source estimates of CO [Carmichael *et al.*, 2003; Palmer *et al.*, 2003; Allen *et al.*, 2004; Heald *et al.*, 2004; Tan *et al.*, 2004], but without consideration of the implications for CO₂ surface fluxes.

2. Correlations Between CO and CO₂ Errors

[5] There are two types of CO₂:CO correlations that can serve as error covariance constraints for a joint CO₂:CO inverse analysis. Correlations between CO₂ and CO combustion sources provide a constraint on the a priori fluxes used for the joint inversion. Observed correlations between atmospheric CO₂ and CO concentrations imply corresponding correlations in the source-receptor relation-

ships determining the concentrations at the observation points, i.e., in the forward model for the inversion. Therefore they provide information on model error correlations for the observation error covariance matrix. Here we derive these two types of error correlation for the Asian outflow conditions sampled by the TRACE-P mission.

2.1. Observation Error Correlations

[6] Atmospheric transport processes during TRACE-P moved air masses laden with CO and CO₂ from east Asia over the Pacific [Liu *et al.*, 2003; Fuelberg *et al.*, 2003], introducing correlation in the CO and CO₂ concentrations. TRACE-P took place before the onset of the growing season, hence the correlations are positive. Figure 1 illustrates the spatial distribution of TRACE-P CO and CO₂ concentration data in the boundary layer. Examination of the spatial distributions reveal strong regional correlations for individual flights (correlation coefficients >0.8) with CO₂:CO slopes ranging from 10 mol/mol in biomass burning outflow from Southeast Asia, to 20–30 mol/mol in Chinese pollution plumes and 50 mol/mol in outflow from Japan [Suntharalingam *et al.*, 2004; Takegawa *et al.*, 2004]. TRACE-P sampled relatively fresh air masses (1–2 days old) so we can assume that loss of CO by reaction with OH does not affect the CO₂:CO correlation driven by Asian outflow.

[7] Figure 2 shows correlation coefficients between CO and CO₂ concentrations measured during TRACE-P as a function of altitude and latitude. These correlation coefficients are typically >0.7 , and vary only by 5–10% as a function of altitude, with smaller values at higher altitudes where aged air masses originating from regions outside Asia play a relatively large contribution to the total CO abundances. It is useful to split the TRACE-P data into two distinct latitudinal regions, characterized by differences in sampled air masses [Blake *et al.*, 2003]. North of 30°N , air masses were heavily influenced by fossil fuel and biofuel emissions from China, Korea and Japan, with essentially no

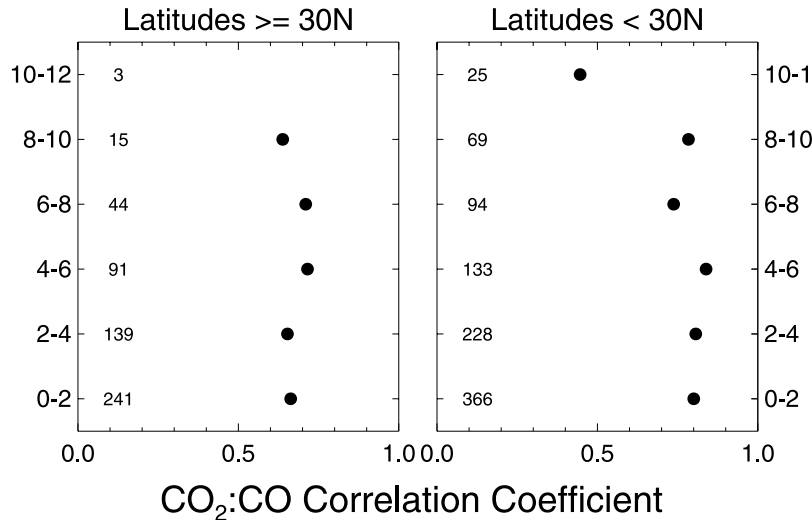


Figure 2. Correlation coefficients (r) between CO and CO₂ mixing ratios measured during TRACE-P as a function of altitude (2-km altitude bins). Numbers inset in each plot refer to the number of observations used to compute the correlation at each altitude bin. Correlation coefficients calculated from 10 or more data points are shown.

influence from biomass burning [Liu *et al.*, 2003]. South of 30°N, and particularly in the free troposphere, air masses were strongly influenced by biomass burning from South-east Asia. Correlation coefficients are larger at latitudes <30°N (Figure 2) because background concentrations are lower and less variable (Figure 1).

2.2. Source Error Correlations

[8] Combustion is a source of both CO and CO₂, and consequently introduces a correlation in emissions. We take advantage of a detailed fuel emission inventory for east Asia [Streets *et al.*, 2003] that offers an opportunity to quantify the source error correlation by providing uncertainty estimates for the sources from individual energy sectors. We do not consider error correlation for the biomass burning source, and as we will see this is justified because of large uncertainty in the CO emission factor.

[9] The emission of a gas from a combustion process (g gas emitted yr⁻¹) can be described as a product of the activity rate A (g fuel burned yr⁻¹) and the emission factor F (g gas emitted per g fuel burned). Activity rates are obtained from energy statistics. Emission factors are determined from laboratory test burns or field measurements. The activity rates and emission factors are both subject to uncertainties. Emission factors for CO₂ and CO vary with the combustion process. For example, Chinese CO emission factors range from 0.7 Gg/PJ for industrial coal burning to 7.0 Gg/PJ for gasoline-powered cars [Streets *et al.*, 2003]. Chinese CO₂ emission factors for the same processes are 24.7 Gg/PJ and 20 Gg/PJ, respectively [Streets *et al.*, 2003]. Even for inefficient forms of combustion, e.g., open biomass burning, values of F for CO₂ are an order of magnitude greater than for CO [Andreae and Merlet, 2001]. The sum of CO and CO₂ typically represents >95% of the total emitted carbon, with CH₄, and nonmethane volatile organic compounds (NMVOC) contributing the remaining few percent [Streets *et al.*, 2003].

[10] Correlation between CO and CO₂ emissions can be introduced via A or F . We assume activity rates are common to both gases, while CO and CO₂ emission factors are inversely correlated. We use the east Asian emission inventory for 2000 from Streets *et al.* [2003], which includes information about A , F , and associated 1 σ uncertainties (Δ) for different energy sectors and for individual regions. The inventory includes sector emissions from industry (coal and oil), domestic biofuel, and transportation (domestic and commercial, gas and diesel powered, vehicles). We derive error correlations for the national inventories, summing over all sectors and over all regions within a country.

[11] Table 1 presents values of ΔA and ΔF , expressed as a percentage of A and F , from Streets *et al.* [2003] for individual east Asian countries. CO emission estimates are the most uncertain, due to the uncertainty of the emission factors. The most uncertain emission estimates are from biofuels, reflecting large uncertainties in both F and A .

[12] We use a Monte Carlo approach to estimate error correlations between CO and CO₂ sources for individual countries, in which we generate a large ensemble of CO and CO₂ emissions E_i for each energy sector i within each country by perturbing the mean values for A^i and F^i by their estimated 1 σ uncertainties, ΔA^i and ΔF^i , and a population of normally distributed random numbers ϵ^i with unit variance (equation set (1)):

$$\begin{aligned} E_{CO_2}^i &= (A^i + \epsilon_A^i \Delta A^i) (F_{CO_2}^i + \epsilon_{CO_2}^i \Delta F_{CO_2}^i) \\ E_{CO}^i &= (A^i + \epsilon_A^i \Delta A^i) (F_{CO}^i + \epsilon_{CO}^i \Delta F_{CO}^i) \end{aligned} \quad (1)$$

[13] Regional CO₂:CO error correlations are calculated by first summing the ensembles of CO and CO₂ emissions generated using the Monte Carlo approach from different energy sectors within a particular country. For each energy sector i within a particular country we generate an ensemble of size 10⁴, ensuring a statistical significant correlation. In the absence of a regional and sector breakdown of CH₄ and

Table 1. Percentage Uncertainties of Activity Rates ($\Delta A/A$) and Emission Factors ($\Delta F/F$) Associated With East Asian CO and CO₂ Emissions From Fuel Consumption

Region	Biofuel				Fossil Fuel ^a				CO ₂ :CO Source Error Correlation
	CO		CO ₂		CO		CO ₂		
	$\Delta A/A$	$\Delta F/F$	$\Delta A/A$	$\Delta F/F$	$\Delta A/A$	$\Delta F/F$	$\Delta A/A$	$\Delta F/F$	
China	25	240	20	6	12	67	7	7	0.03
Korea	25	240	20	6	8	65	5	6	0.04
Japan	18	240	15	6	8	24	5	9	−0.46
Southeast Asia ^b	36	240	30	6	31	121	10	9	0.17

^aCO and CO₂ sectors include domestic coal, domestic oil, industrial coal, and transport [Streets *et al.*, 2003]. Values of ΔA and ΔF given here are national averages (Figure 4) weighted by activity rates over different sectors and regions resolved by Streets *et al.* [2003].

^bSEA in Figure 4.

other VOC emission factors, we assume that CO₂ and CO represents 97.5% of the total carbon emitted [Streets *et al.*, 2003], and that CH₄ and other VOCs contribute the remaining 2.5%. In perturbations to this best estimate we require that the sum of the CO₂ and CO emission factors is between 95% and 100%, ensuring that we only consider physically realistic realizations, e.g., the total carbon emitted does not exceed the carbon content of the fuel burned.

[14] The value of the CO₂:CO error correlation for a particular sector i depends on the relative uncertainties associated with A^i and F^i . In the limiting case, where values of F^i are known perfectly the correlation will be +1 because ΔA is common to both CO and CO₂. Conversely, if A^i is known perfectly, uncertainties in F^i will lead to correlation coefficients between −1 and +1. In practice, there are significant uncertainties associated with both A^i and F^i , and error correlations between CO₂ and CO sources represent a balance between the relative magnitudes and uncertainties of A^i and F^i , e.g., $F_{CO_2}^i$ is a smaller factor of variability for CO₂ emission than the activity rate, while the converse holds for CO.

[15] We find that the error correlations on the a priori sources of CO₂ and CO, corresponding to values of ΔA^i and ΔF^i prescribed by Streets *et al.* [2003], are negligible or weakly negative (Table 1). This is due primarily to large values of ΔF_{CO}^i . However, analyses of the TRACE-P CO data indicate that the Streets *et al.* [2003] inventory under-

estimated A and F [Tan *et al.*, 2004], so we explored the sensitivity of the CO₂:CO source error correlation to the range of possible values of ΔA^i and ΔF^i (Figure 3) using the same percentage change in ΔA^i and ΔF^i over all sectors i and over all regions. As we will show later, source error correlation coefficients need to be greater than 0.5 before we get a significant improvement in the inverse analysis for CO₂ fluxes. Such correlations are unrealistic, given constraints on A from the CO₂ concentrations [Suntharalingam *et al.*, 2004].

3. Inverse Model

[16] Our inverse model aims to achieve the best estimate of CO and CO₂ fluxes that is consistent with the TRACE-P concentration measurements of CO and CO₂, the a priori CO and CO₂ flux estimates, and their respective uncertainties. It builds on our previous CO-only inverse model that used the TRACE-P observations to estimate east Asian CO fluxes [Palmer *et al.*, 2003].

3.1. Model Description

[17] Anthropogenic sources of CO and CO₂ include burning of fossil fuels and biofuels, and biomass burning (Tables 2 and 3). We use a priori anthropogenic emission estimates of CO and CO₂ from Streets *et al.* [2003] for east Asia and from Palmer *et al.* [2003] and Suntharalingam *et*

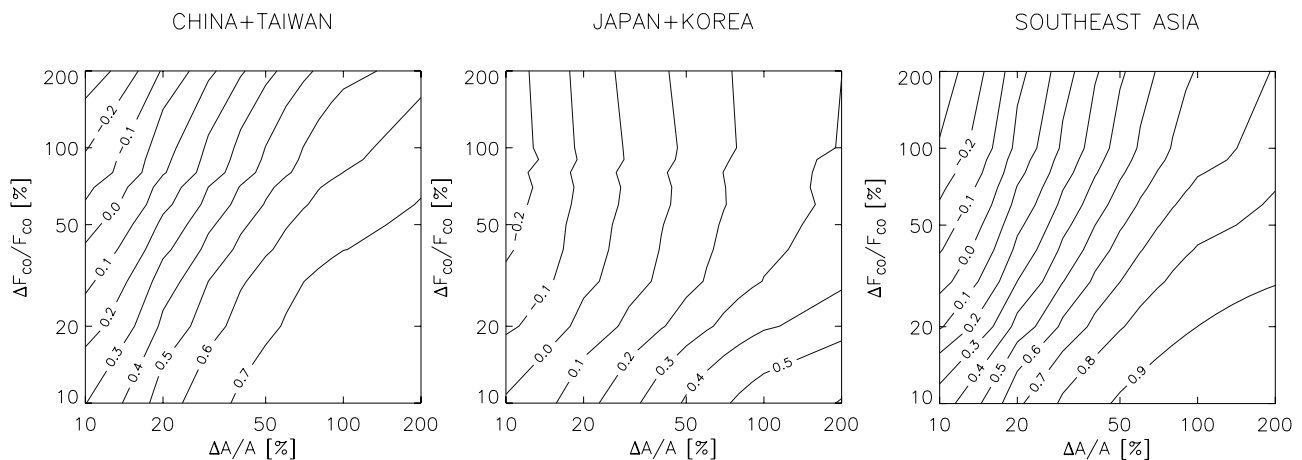


Figure 3. Regional error correlation coefficients r between bottom-up emission estimates for CO₂ and CO from fuel consumption as a function of relative uncertainties in activity rates A and emission factors F . These illustrative calculations assume the same relative uncertainties for all energy sectors within the region.

Table 2. A Priori Sources of CO for the Inverse Model Analysis

Region	Biofuels (BF), ^a Tg CO yr ⁻¹	Fossil Fuels (FF), ^a Tg CO yr ⁻¹	Biomass Burning (BB), ^a Tg CO yr ⁻¹	Global CH ₄ and Biogenic NMVOCs, Tg CO yr ⁻¹
China (CH)	49 ± 38	59 ± 46	18 ± 9	-
Korea (KR)	3 ± 1	3 ± 1	0.08 ± 0.04	-
Japan (JP)	3 ± 1	6 ± 1	0.3 ± 0.1	-
Southeast Asia (SEA)	23 ± 23	10 ± 10	81 ± 40	-
Boreal Asia (BA)	-	-	12 ± 6	-
Rest of world (ROW)	124 ± 26	301 ± 78	396 ± 198	1205 ± 301

^aSources from BF, BB, and FF include the secondary source of CO from the oxidation of NMVOCs coemitted with CO.

al. [2004] for the rest of the world (ROW). We use the same biomass burning emission estimates as *Palmer et al.* [2003], based on daily satellite fire count data for the TRACE-P period [*Heald et al.*, 2003]. We account for the secondary source CO from oxidation of anthropogenic VOCs coemitted with CO by scaling up fossil fuel and biofuel (19%) and biomass burning (16%) [*Heald et al.*, 2004]; these scaling factors are different from those used by *Palmer et al.* [2003] and are reflected in the a priori emissions presented in Table 2. The ROW represents a background of CO and CO₂, including sources outside of Asia and chemical production of CO from CH₄. ROW also includes the chemical production of CO from biogenic NMVOCs, representing a small diffuse source over the TRACE-P period (which was mainly outside the growing season). Daily mean terrestrial biosphere fluxes of CO₂ are provided by the CASA balanced biosphere model [*Randerson et al.*, 1997]. TRACE-P data are a few days downwind of continental sources and at this offshore distance the influence of diurnal variation from the terrestrial biosphere is weak [*Suntharalingam et al.*, 2004]. For the TRACE-P season (March) there is a net positive flux of CO₂ from the east Asian biosphere [*Suntharalingam et al.*, 2004]. Ocean CO₂ fluxes, prescribed by *Takahashi* [1999], are assumed not to contribute significantly to the magnitude and variability of TRACE-P data [*Suntharalingam et al.*, 2004]. We aggregate the CO₂ flux from the global ocean with ROW.

[18] Observed CO and CO₂ mixing ratios (measurement vector *y*) are related to CO and CO₂ surface fluxes (state vector *x*) by

$$\mathbf{y} = \mathbf{K}\mathbf{x} + \epsilon, \quad (2)$$

where *K* is the Jacobian matrix describing the forward model sensitivity. We use the GEOS-CHEM CTM as the forward model. Loss of CO is computed with fixed 3-D OH fields from GEOS-CHEM to enforce linearity as described by equation (2). The linearized CO and linear

CO₂ models allow us to describe total CO and CO₂ model concentrations as a linear sum of contributions from different countries and different sources.

[19] The state vector *x* comprises annual mean CO and CO₂ anthropogenic (including biomass burning) source estimates assuming seasonal variations [*Duncan et al.*, 2003; *Streets et al.*, 2003]. It also includes CO₂ biospheric surface fluxes for March 2001 from the different geopolitical regions of Figure 4.

[20] The state vector components were chosen on the ability of the TRACE-P data to independently resolve source regions (Figure 4) and processes (fuel FL and biomass burning BB), as derived formally by *Palmer et al.* [2003] and *Heald et al.* [2004]. For CO we use six components: CHFL, KRJP, SEA, CHBB, BABB, and ROW. For CO₂ we add regional biospheric terms (BS) and use eight components: CHFL, KRJP, CHBB, BABB, ROW, CHBS, KRJPBS, BABS. Observed CO₂ signatures for biomass burning from China (CHBB), boreal Asia (BABB), and for SEA are too weak to be resolved independently.

[21] The measurement vector *y* consists of the TRACE-P CO and CO₂ mixing ratio data. CO and CO₂ mixing ratios are measured using a differential absorption tunable diode laser system [*Sachse et al.*, 1987] and a nondispersive infrared analyzer [*Vay et al.*, 2003], respectively. The data used for the inversion includes 299 hours of measurements from the two aircraft over 28 flights between 27 February and 3 April, 2001. We use the data for individual flights averaged on the GEOS-CHEM 2° × 2.5° model grid.

[22] Errors associated with *K* and *y* (the sum of which is described by *ε*), include measurement accuracy, subgrid variability of observations (representation error), and model error. The ensemble characteristics of these errors are described by the observation error covariance, *S_y*, representing a sum of the covariance matrices from individual sources of error. This will be discussed further in the next section.

Table 3. A Priori Surface Fluxes of CO₂ for the Inverse Model Analysis

Region	Biofuels, Tg CO ₂ yr ⁻¹	Fossil Fuels, Tg CO ₂ yr ⁻¹	Biomass Burning, Tg CO ₂ yr ⁻¹	Terrestrial Biosphere, ^a Tg CO ₂ /March 2001	Global Oceans, Tg CO ₂ yr ⁻¹
China (CH)	856 ± 69	2553 ± 638	294 ± 147	693 ± 520	-
Korea (KR)	43 ± 3	335 ± 84	1 ± 0.7	20 ± 15	-
Japan (JP)	30 ± 1	813 ± 203	6 ± 3	41 ± 31	-
Southeast Asia (SEA)	419 ± 189	608 ± 274	1320 ± 660	23 ± 17	-
Boreal Asia (BA)	-	-	197 ± 99	360 ± 270	-
Rest of world (ROW)	1800 ± 900	17137 ± 4741	6467 ± 3331	698 ± 524	-8050 ± -8050

^aNet flux for March 2001.

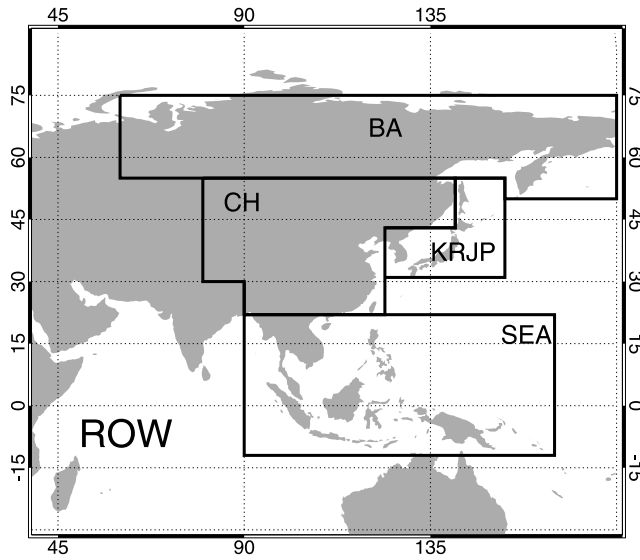


Figure 4. Source regions for tagged CO and CO₂ simulations. See Tables 2 and 3 for flux estimates.

[23] The maximum a posteriori solution [Rodgers, 1976] is given by

$$\hat{\mathbf{x}} = \mathbf{x}_a + (\mathbf{K}^T \mathbf{S}_\Sigma^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1} \mathbf{K}^T \mathbf{S}_\Sigma^{-1} (\mathbf{y} - \mathbf{K} \mathbf{x}_a) \quad (3)$$

$$\hat{\mathbf{S}} = (\mathbf{K}^T \mathbf{S}_\Sigma^{-1} \mathbf{K} + \mathbf{S}_a^{-1})^{-1}, \quad (4)$$

where \mathbf{S}_a is the a priori error covariance matrix, $\hat{\mathbf{x}}$ is the optimized a posteriori state vector, $\hat{\mathbf{S}}$ is the a posteriori error covariance matrix describing the error associated with $\hat{\mathbf{x}}$, and other variables are as defined previously. Source and observation CO₂:CO error correlations, as derived in section 2, are implemented in the inversion as off-diagonal terms in \mathbf{S}_a and \mathbf{S}_Σ , respectively.

[24] Inverse modeling using Bayesian synthesis generates artificially small a posteriori errors, due to the assumption that observational errors are random, Gaussian, representatively sampled by the observations, and described accurately by its covariance [Heald et al., 2004]. Here we use the a posteriori errors as a qualitative measure of the constraint provided by the CO₂:CO error correlations.

3.2. Error Variance and Covariance Specification

[25] Error variance and covariance information is included in the inversion as diagonal and off-diagonal terms in \mathbf{S}_a and \mathbf{S}_Σ , respectively. We specify a priori emission error variances for Asia following Streets et al. [2003]. We assign an uncertainty of 25% on the global source of CO from the oxidation of CH₄ and biogenic NMVOCs [Palmer et al., 2003], and further assume flux uncertainties for CO₂ from the ocean and terrestrial biosphere of 100% and 75%, respectively.

[26] Observation error variances are quantified using the mean statistics of the relative difference between the observed and model concentrations as a function of altitude and latitude [Palmer et al., 2003; Heald et al., 2004]. The mean bias between the model and observed concentration is

assumed to reflect errors in model fluxes to be retrieved by the inversion, while the standard deviation about the mean bias (residual relative error, RRE) is assumed to reflect total observation error. RRE values for CO are typically 20–30% [Palmer et al., 2003]. Similar analysis for CO₂ shows RRE values of 1–2%, with little variability as a function of altitude or latitude. The observation error variance for an individual observation y_i is given by $(\text{RRE} \times y_i)^2$.

[27] Observed correlations between CO₂ and CO concentrations imply corresponding observation error correlations (section 2 and Figure 2), which we use to specify the off-diagonal elements in \mathbf{S}_Σ . Correlations in CO and CO₂ emission errors provide similar information to construct the off-diagonal elements of \mathbf{S}_a (section 2). These CO₂:CO error correlation coefficients, r , are included as off-diagonal elements in \mathbf{S}_Σ and \mathbf{S}_a following

$$s_{ij} = r_{ij} \sqrt{s_{ii}} \sqrt{s_{jj}}. \quad (5)$$

We neglect the spatial correlations of observations as previous work for CO during TRACE-P has shown that it decays on a length scale of 150 km [Jones et al., 2003; Heald et al., 2004], which is short relative to the $2^\circ \times 2.5^\circ$ grid over which the observations are sampled here.

4. Inversion Results

4.1. Best-Case Estimate

[28] Figure 5 shows results for our best-case inversion of CO and CO₂ fluxes that uses the state vector defined in section 3, and the CO₂:CO error correlations derived in section 2. The results for CO are generally the same as those presented by Palmer et al. [2003], including a 72% increase in the anthropogenic source from China but the 45% decrease in Southeast Asia obtained here is less than the 60% decrease inferred from using only TRACE-P CO data, and is more consistent with the constraints from the MOPITT data [Heald et al., 2004]. The CO source from Chinese biomass burning is weakly negative but is not significantly different from zero, given that $\hat{\mathbf{S}}$ underestimates actual a posteriori errors.

[29] A posteriori emissions of CO₂ show a 18% decrease in Chinese anthropogenic sources and a 10% increase in sources from Korea and Japan. The a posteriori decrease (increase) in Chinese anthropogenic CO₂ (CO) source estimates implies an overestimate of sources with high CO₂:CO signatures, and a missing source with a low CO₂:CO signature, e.g., which could be contributed by small heavily polluting power plants [Tan et al., 2004] or burning of domestic coal and biofuels [Carmichael et al., 2003]. There is also a 95% reduction in the net Chinese biospheric CO₂ source for March 2001 relative to the CASA model, consistent with the results of Suntharalingam et al. [2004], and a 10% increase in CO₂ from the boreal Asia biosphere.

4.2. Sensitivity Studies

[30] Here we assess the added value of CO₂:CO error correlations by comparing our best-case estimates with sensitivity calculations using modified correlations, i.e., modified off-diagonal terms in \mathbf{S}_Σ and \mathbf{S}_a . The uncorrelated inversion (best-case inversion but with off-diagonal terms

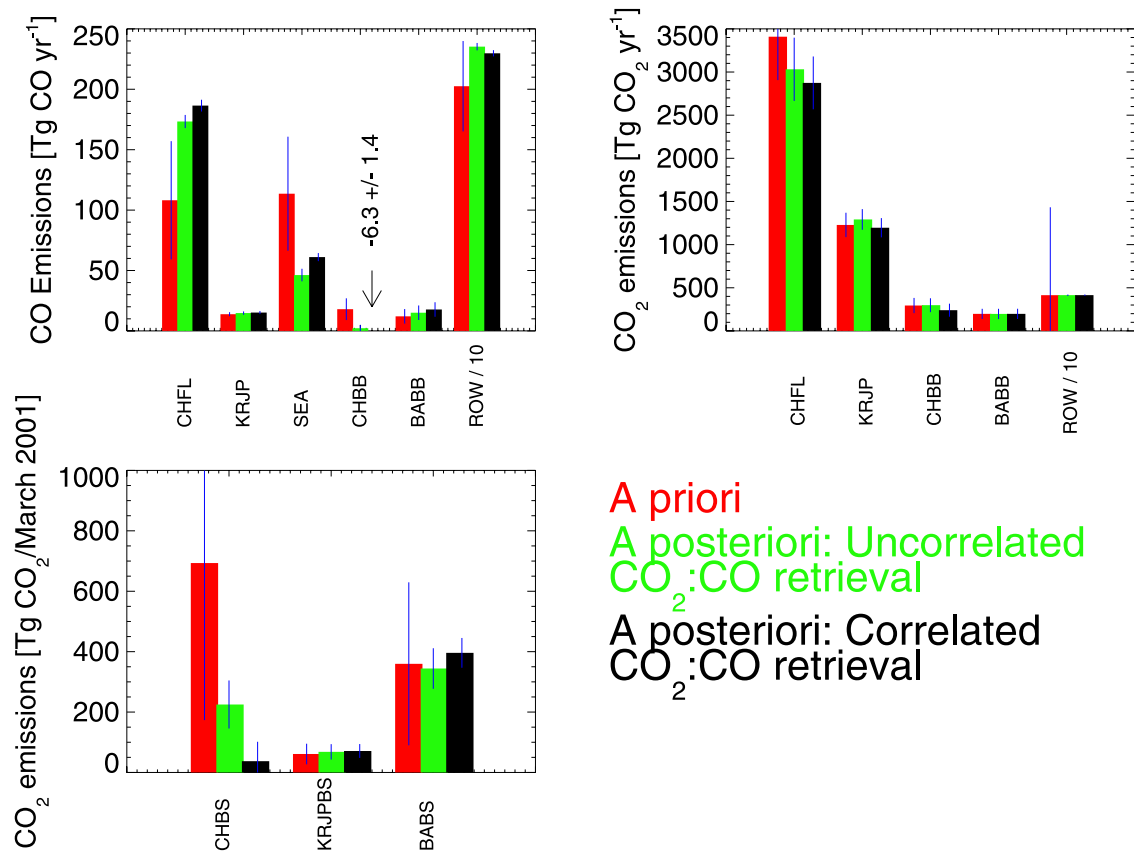


Figure 5. A priori (red), uncorrelated a posteriori (green), and best-case a posteriori (black) CO and CO₂ flux estimates. The vertical lines superimposed on each estimate denotes the 1 σ uncertainty.

set to zero) estimates independently the optimal flux estimates of CO and CO₂ (Figure 5). A posteriori emissions of CO are within a few percent of the best case inversion analysis, with the exception of biomass burning from Southeast Asia, as described above. A posteriori CO estimates are tightly constrained by the CO concentration data and are largely insensitive to changes in S_a and S_Σ introduced by the CO₂:CO error covariances. In the case of the Southeast Asian source, transport to the TRACE-P sampling region involved lifting to the free troposphere by convection and warm conveyor belts [Liu *et al.*, 2003]. Consideration of the CO₂:CO correlations in other geopolitical regions appears to help reduce the model transport errors associated with the Southeast Asian source, resulting in better agreement with the CO inversions that use the much denser MOPITT data [Heald *et al.*, 2004].

[31] Including CO₂:CO correlations further reduces the Chinese biospheric flux by 80%, while KRJPBS and BABS estimates are not significantly different from the uncorrelated inverse analyses. Examination of the a posteriori correlation matrix (normalized \hat{S}) shows a particularly strong anticorrelation (−0.8) between CO₂ fluxes from anthropogenic and biospheric sources. Consideration of the CO₂:CO error correlation in the inversion facilitates the separation of these two sources by reducing the correlation between biospheric and anthropogenic sources. Figure 6 illustrates for China the strong anticorrelation between CHFL and CHBS remains until source or observation CO₂:CO error

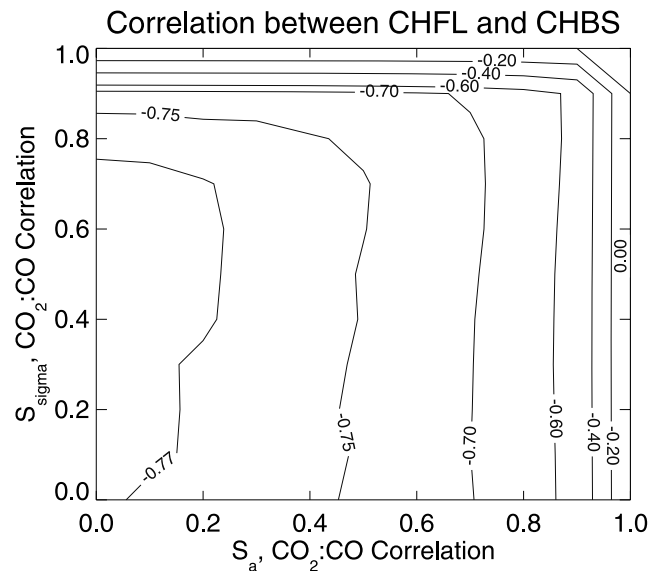


Figure 6. Sensitivity of the a posteriori correlation between Chinese anthropogenic (CHFL) and biospheric (CHBS) CO₂ flux estimates to the source (S_a) and observation (S_Σ) CO₂:CO error correlations.

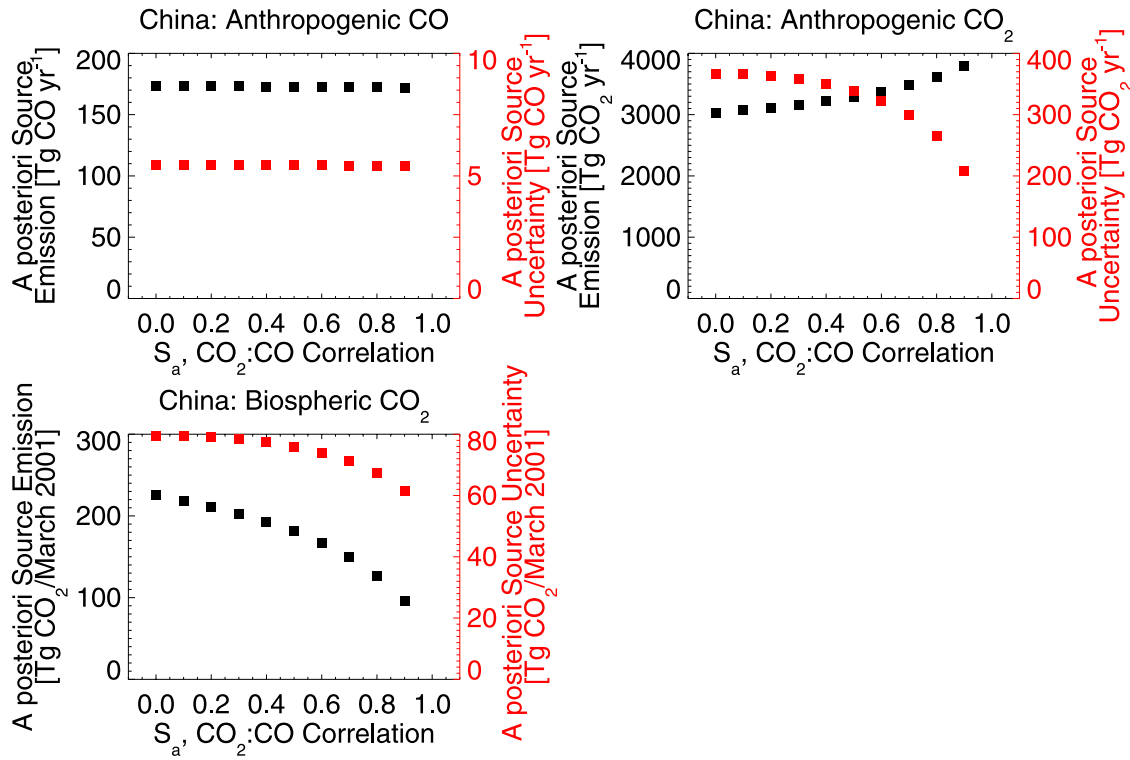


Figure 7. Sensitivity of a posteriori Chinese anthropogenic source estimates and their uncertainties to the source CO₂:CO error correlation (S_a).

correlations are greater than 0.7–0.8, after which it drops rapidly to zero. The source CO₂:CO error correlation is the more effective constraint for separating biospheric and anthropogenic sources but as discussed earlier this error correlation is weak. Our best estimate, which uses both source and observation CO₂:CO error correlations, leads to a CHFL:CHBS correlation 10% less than the uncorrelated inversion.

[32] Figures 7 and 8 illustrate the sensitivity of a posteriori Chinese fluxes to the strengths of the source and observation CO₂:CO error correlations. Source CO₂:CO error correlation (Figure 7) provides little improvement in a posteriori CO source estimates, since CO atmospheric concentration signals are much stronger than for CO₂ and the transport from China to the TRACE-P sampling region is principally by boundary layer advection [Liu *et al.*, 2003] which has low transport error. Anthropogenic and biospheric CO₂ flux estimates are statistically significantly different from the uncorrelated inversion where the source CO₂:CO error correlation is greater than 0.5. However, with the emission uncertainty for CO contributed mostly by emission factor [Streets *et al.*, 2003] the source CO₂:CO error correlation is much less than 0.5 (Table 1). We conclude that the source CO₂:CO error correlation is unlikely to offer much benefit for joint CO₂:CO inversions. In contrast, accounting for forward model error CO₂:CO correlation (i.e., off-diagonal terms of S_Σ) effectively reduces the uncertainty of the observations (Figure 8). The magnitude of a posteriori CO estimates increases slightly with increasing CO₂:CO error correlation, with the associated uncertainties decreasing. This reduction in

CO emission uncertainty is observed only with changes in S_Σ because the observation uncertainties dominate the calculation of \hat{S} (equation (4)). The magnitude of the Chinese biospheric CO₂ flux reduces as the observation error CO₂:CO correlation increases and is a CO₂ sink at correlations greater than 0.8. The magnitude of the a posteriori Chinese anthropogenic CO₂ estimate is not significantly affected by increasing the observation error CO₂:CO correlation. Separation of the biospheric and anthropogenic CO₂ sources, indicated by the a posteriori correlation matrix (Figure 6), occurs at correlations coefficients >0.7, similar to observed CO₂:CO correlation (Figure 2). The importance of the CO₂:CO error correlations in the TRACE-P inverse problem lies in their role of reducing model transport error and subsequently reducing uncertainty on a posteriori CO₂ flux estimates.

5. Closing Remarks

[33] Accurately quantifying CO₂ exchanges with the terrestrial biosphere represents an important challenge for understanding the global carbon cycle. A standard method has been to use inverse models constrained with atmospheric observations of CO₂, and occasionally CO₂ isotopes. Strong observed correlations between CO₂ and CO in atmospheric data, as well as CO₂:CO correlations in combustion sources, suggest that a joint CO₂:CO inversion might provide information to improve the separation of combustion and biospheric CO₂ surface flux estimates. We showed here that such an inversion, using concurrent observations of CO₂ and CO in Asian outflow from the

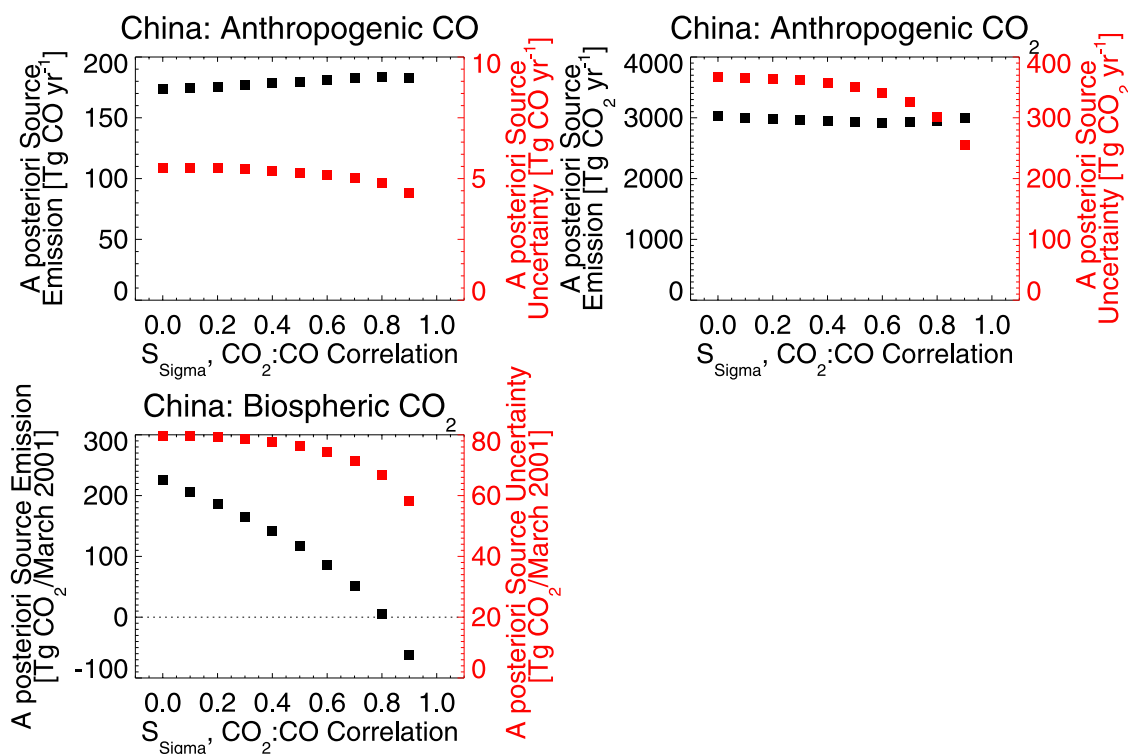


Figure 8. Sensitivity of a posteriori Chinese anthropogenic source estimates and their uncertainties to the observation CO₂:CO error correlation (S_{Σ}).

TRACE-P aircraft campaign in Spring 2001, does indeed provide useful additional constraints for improving a posteriori CO₂ regional flux estimates.

[34] Observed correlations between CO₂ and CO concentrations in atmospheric data imply a corresponding correlation in source-receptor relationships, and therefore in the forward model errors for the inversion. Mathematically, they can be used to estimate off-diagonal terms in the observation error covariance matrix (S_{Σ}) of a joint CO₂:CO inversion. Observed CO₂:CO correlation coefficients during TRACE-P are generally larger than 0.7 [Suntharalingam *et al.*, 2004; Takegawa *et al.*, 2004] and enable significant improvement of a posteriori flux estimates. CO₂:CO correlations may be different for other regions and during other seasons.

[35] Correlation between CO₂ and CO combustion sources in a priori estimates could also provide constraints to the joint inversion. We used a Monte Carlo approach to quantify the resulting CO₂:CO source error correlations in individual Asian countries on the basis of uncertainties in activity rates and emission factors for individual energy sectors and source regions reported by the east Asia emission inventory of Streets *et al.* [2003]. We find that these correlation coefficients are weak ($r < 0.2$) because CO emission factors are the largest contribution to the overall uncertainty. Significant improvements in a posteriori CO₂ and CO would require correlation coefficients > 0.7 but these would require unrealistic uncertainties in activity rates.

[36] We find that the benefit of including CO₂:CO error correlations in joint CO₂:CO inversions is mainly for

improving retrievals of CO₂ surface fluxes, not CO sources. Atmospheric variability of CO is far greater than that of CO₂, and separation of biospheric and combustion terms is not an issue, so that information on CO₂ has little benefit for the CO source inversion.

[37] Satellite observations of CO₂ have the potential to improve quantitative understanding of the global carbon cycle [e.g., Pak and Prather, 2001; Rayner and O'Brien, 2001]. Our work shows that this potential can be enhanced by exploiting correlations with concurrent satellite observations of CO, where CO information may be coretrieved from the measured spectra of one instrument (e.g., SCIAMACHY and AIRS), retrieved from another instrument aboard the same satellite platform, or taken from an instrument in the same orbit (e.g., OCO and TES).

Appendix A: Forward Model

[38] The GEOS-CHEM version used here (6.01, <http://www-as.harvard.edu/chemistry/trop/geos/index.html>) has a horizontal resolution of $2^{\circ} \times 2.5^{\circ}$, with 48 vertical levels ranging from the surface to the mesosphere, 20 of which are below 12 km. The model is driven by GEOS-3 assimilated meteorology data from the Global Modeling and Assimilation Office GCM based at NASA Goddard. The 3-D meteorological data are updated every 6 hours, and the mixing depths and surface fields are updated every 3 hours.

[39] The CO and CO₂ simulation are as described by Palmer *et al.* [2003] and Suntharalingam *et al.* [2004], respectively. The main sink for CO is oxidation by OH,

leading to a lifetime of a few months. We prescribe global monthly mean OH fields calculated from a full chemistry model simulation (GEOS-CHEM v4.33) and consistent with observational constraints [Prinn *et al.*, 2001]. The CO sink has little effect for the inversion of TRACE-P measurements, which are only a few days downwind of the Asian sources. The impact of the OH sink on the CO background is effectively taken into account by the adjustment of the ROW CO source [Palmer *et al.*, 2003]. Suntharalingam *et al.* [2005] showed that not properly accounting for reduced carbon species (CO, CH₄ and NMVOCs) in CO₂ inversion analyses can significantly bias a posteriori flux estimates. This bias arises for two reasons: not accounting for the 3-D production of CO₂ from the oxidation of reduced carbon species and neglecting that reduced carbon species are often included in bottom-up combustion and biospheric CO₂ flux inventories. Air masses sampled during TRACE-P are relatively fresh and so the oxidation effect will only affect observations that sample the background atmosphere. The Streets *et al.* [2003] combustion emission inventory only accounts for direct emissions of CO₂, however the terrestrial biospheric fluxes from CASA do account for reduced carbon species.

[40] The Jacobian matrix for the inversion is constructed by transporting separately CO and CO₂ from individual sources describing the state vector. This required initialization of the corresponding “tagged tracers.” The CO simulation is initialized in January 2000 and integrated for 16 months (through April 2001). The 14 months prior to TRACE-P effectively remove the influence of initial conditions. In the case of CO₂, we adopt the model initialization approach previously used by Xiao *et al.* [2004] for CH₄ in GEOS-CHEM. We use the total CO₂ simulation to define a background CO₂ tracer as the CO₂ present in the atmosphere on 1 January 2001. The background tracer has no surface fluxes after January 2001 and is allowed to mix. The other tagged tracers are initialized with zero concentration on 1 January 2001. Their concentrations evolve over the course of the simulation as a result of surface fluxes. We also included an additional initialization to the CO₂ simulation to correct the model bias introduced by not accounting for the net uptake of CO₂ by the land biosphere. We make this correction by comparing the 20th percentile (assumed to represent the CO₂ background) in the model and observed CO₂ concentration data (east of 150°W) as a function of latitude (5° increments), and remove it from the model values. The corresponding model bias ranges from 4 to 5 ppm and is consistent with the values calculated using GLOBALVIEW CO₂ data [Suntharalingam *et al.*, 2004].

[41] **Acknowledgment.** This work was supported by the NASA and NOAA carbon cycle programs.

References

- Allen, D., K. Pickering, and M. Fox-Rabinovitz (2004), Evaluation of pollutant outflow and CO sources during TRACE-P using model-calculated, aircraft-based, and Measurements of Pollution in the Troposphere (MOPITT)-derived CO concentrations, *J. Geophys. Res.*, **109**, D15S03, doi:10.1029/2003JD004250.
- Andreae, M. O., and P. Merlet (2001), Emission of trace gases and aerosols from biomass burning, *Global Biogeochem. Cycles*, **15**, 955–966.
- Blake, N. C., *et al.* (2003), NMHCs and halocarbons in Asian continental outflow during TRACE-P: Comparison to PEM-West B, *J. Geophys. Res.*, **108**(D20), 8806, doi:10.1029/2002JD003367.
- Bousquet, P., P. Ciais, P. Peylin, M. Ramonet, and P. Monfray (1999), Inverse modeling of annual atmospheric CO₂ sources and sink: 1. Method and control inversion, *J. Geophys. Res.*, **104**, 26,161–26,178.
- Carmichael, G. R., *et al.* (2003), Evaluating regional emission estimates using TRACE-P observations, *J. Geophys. Res.*, **108**(D21), 8810, doi:10.1029/2002JD003116.
- Ciais, P., P. P. Tans, M. Troler, J. W. C. White, and R. J. Francey (1995), A large Northern Hemisphere terrestrial CO₂ sink indicated by the ¹³C/¹²C ratio of atmospheric CO₂, *Science*, **269**, 1098–1102.
- Duncan, B. N., R. V. Martin, A. C. Staudt, R. Yevich, and J. A. Logan (2003), Interannual and seasonal variability of biomass burning emissions constrained by satellite observations, *J. Geophys. Res.*, **108**(D2), 4100, doi:10.1029/2002JD002378.
- Enting, I. G., C. M. Trudinger, and R. J. Francey (1995), A synthesis inversion of the concentration and delta-C-13 of atmospheric CO₂, *Tellus, Ser. B*, **47**, 35–52.
- Fuehlberg, H. E., *et al.* (2003), Meteorological conditions and transport pathways during Transport and Chemical Evolution over the Pacific (TRACE-P) experiment, *J. Geophys. Res.*, **108**(D20), 8782, doi:10.1029/2002JD003092.
- Gilliland, A. B., R. L. Dennis, S. J. Roselle, and T. E. Pierce (2003), Seasonal NH₃ emission estimates for the eastern United States based on ammonium wet concentrations and an inverse modeling method, *J. Geophys. Res.*, **108**(D15), 4477, doi:10.1029/2002JD003063.
- Heald, C. L., D. J. Jacob, P. I. Palmer, M. J. Evans, G. W. Sachse, H. B. Singh, and D. R. Blake (2003), Biomass burning emission inventory with daily resolution: Application to aircraft observations of Asian outflow, *J. Geophys. Res.*, **108**(D21), 8811, doi:10.1029/2002JD003082.
- Heald, C. L., *et al.* (2004), Comparative inverse analysis of satellite (MOPITT) and aircraft (TRACE-P) observations to estimate Asian sources of carbon monoxide, *J. Geophys. Res.*, **109**, D23306, doi:10.1029/2004JD005185.
- Jacob, D. J., *et al.* (2003), The Transport and Chemical Evolution over the Pacific (TRACE-P) mission: Design, execution and overview of results, *J. Geophys. Res.*, **108**(D20), 9000, doi:10.1029/2002JD003276.
- Jones, D. B. A., K. W. Bowman, P. I. Palmer, J. R. Worden, D. J. Jacob, R. N. Hoffman, I. Bey, and R. M. Yantosca (2003), Potential of observations from the Tropospheric Emission Spectrometer to constrain continental sources of carbon monoxide, *J. Geophys. Res.*, **108**(D24), 4789, doi:10.1029/2003JD003702.
- Liu, H., D. J. Jacob, I. Bey, R. M. Yantosca, B. N. Duncan, and G. W. Sachse (2003), Transport pathways for Asian combustion outflow over the Pacific: Interannual and seasonal variations, *J. Geophys. Res.*, **108**(D20), 8786, doi:10.1029/2002JD003102.
- Pak, B. C., and M. J. Prather (2001), CO₂ source inversions using satellite observations of the upper troposphere, *Geophys. Res. Lett.*, **28**, 4571–4574.
- Palmer, P. I., D. J. Jacob, D. J. A. Jones, C. L. Heald, R. M. Yantosca, J. A. Logan, G. W. Sachse, and D. G. Streets (2003), Inverting for emissions of carbon monoxide from Asia using aircraft observations over the western Pacific, *J. Geophys. Res.*, **108**(D21), 8828, doi:10.1029/2003JD003397.
- Prinn, R. G., *et al.* (2001), Evidence for substantial variation of atmospheric hydroxyl radicals in the past two decades, *Science*, **292**, 1882–1888.
- Randerson, J. T., M. V. Thompson, T. J. Conway, I. Y. Fung, and C. B. Field (1997), The contribution of terrestrial sources and sinks to trends in the seasonal cycle of atmospheric carbon dioxide, *Global Biogeochem. Cycles*, **11**, 535–560.
- Rayner, P. J., and D. M. O'Brien (2001), The utility of remotely sensed CO₂ concentration data in surface source inversions, *Geophys. Res. Lett.*, **28**, 175–178.
- Rodgers, C. D. (1976), Retrieval of atmospheric temperature and composition from remote measurements of thermal radiation, *Rev. Geophys.*, **14**, 609–624.
- Sachse, G. W., G. F. Hill, L. O. Wade, and M. G. Perry (1987), Fast-response, high-precision carbon monoxide sensor using a tunable diode laser absorption technique, *J. Geophys. Res.*, **92**, 2071–2081.
- Streets, D. G., *et al.* (2003), An inventory of gaseous and primary aerosol emissions in Asia in the year 2000, *J. Geophys. Res.*, **108**(D21), 8809, doi:10.1029/2002JD003093.
- Suntharalingam, P., *et al.* (2004), Improved quantification of Chinese carbon fluxes using CO₂/CO correlations in Asian outflow, *J. Geophys. Res.*, **109**, D18S18, doi:10.1029/2003JD004362.
- Suntharalingam, P., J. T. Randerson, N. Krakauer, D. J. Jacob, and J. A. Logan (2005), The influence of reduced carbon emissions and oxidation

- on the distribution of atmospheric CO₂: Implications for inversion analysis, *Global Biogeochem. Cycles*, *19*, GB4003, doi:10.1029/2005GB002466.
- Takahashi, T. (1999), Net air-sea CO₂ flux over the global oceans, in *Proceedings of 2nd International Symposium CO₂ in the Oceans: CGER 1037*, pp. 9–15, Natl. Inst. for Environ. Stud., Tsukuba, Japan.
- Takegawa, N., et al. (2004), Removal of NO_x and NO_y in Asian outflow plumes: Aircraft measurements over western Pacific in January 2002, *J. Geophys. Res.*, *109*, D23S04, doi:10.1029/2004JD004866.
- Tan, Q., W. L. Chameides, D. Streets, T. Wang, J. Wu, M. Bergin, and J. Woo (2004), An evaluation of TRACE-P emission inventories from China using a regional model and chemical measurements, *J. Geophys. Res.*, *109*, D22305, doi:10.1029/2004JD005071.
- Vay, S. A., et al. (2003), Influence of regional-scale anthropogenic emissions on CO₂ distributions over the western North Pacific, *J. Geophys. Res.*, *108*(D20), 8801, doi:10.1029/2002JD003094.
- Xiao, Y., J. S. W. D. J. Jacob, J. A. Logan, P. I. Palmer, P. Suntharalingam, R. M. Yantosca, G. W. Sachse, D. R. Blake, and D. G. Streets (2004), Constraints on Asian and European sources of methane from CH₄-C₂H₆-CO correlations in Asian outflow, *J. Geophys. Res.*, *109*, D15S16, doi:10.1029/2003JD004475.
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