Influence of Aerosol Scattering on the Retrieval of CO\textsubscript{2} Mixing Ratios: A Case Study Using Measurements from the California Laboratory for Atmospheric Remote Sensing (CLARS)

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Abstract

[1] Column abundances of greenhouse gases in the Los Angeles (LA) basin have recently been measured in the near-infrared spectral region using the California Laboratory for Atmospheric Remote Sensing Fourier Transform Spectrometer (CLARS-FTS) deployed at Mt. Wilson, California since August 2011. In the presence of haze, aerosol scattering causes a variable bias in the measured slant column densities (SCDs). We apply an analytic radiative transfer model and a numerical two-stream model to estimate the impact of neglecting aerosol scattering on the CO₂ and O₂ SCDs operationally retrieved from CLARS-FTS measurements. A retrieval scheme has been developed, and tested using synthetic data. The simulations are performed using a set of aerosol optical depths (AODs) that are representative of the meteorological conditions on 23 March 2013, and a viewing geometry that is nearly identical to the CLARS-FTS measurement configuration. These simulations show that the CLARS-FTS operational retrieval algorithm likely underestimates CO₂ abundances in both the planetary boundary layer and the free troposphere over the LA basin in scenes with medium aerosol loading (AOD ~ 0.1, representative of conditions on 23 March 2013). We also discuss the biases in the CLARS-FTS operational products due to neglecting aerosol scattering.
1. Introduction

[2] Measuring concentrations of greenhouse gases (GHGs, see the list of abbreviations and acronyms in Appendix A for reference) is critical to improve our understanding of their impacts on climate change [IPCC AR5, 2013]. Megacities, such as Los Angeles (LA), are immense sources of global GHGs. These areas, which contain more than 50% of the world’s population, are contributing at least 70% of fossil fuel CO\textsubscript{2} emissions and a large amount of anthropogenic CH\textsubscript{4} [Duren and Miller, 2012; Kort et al., 2012]. In the past decade, satellite observations such as those from the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY), the Greenhouse gases Observing Satellite (GOSAT) and the Orbiting Carbon Observatory-2 (OCO-2) were used or have been proposed to measure the global distribution of GHGs [Bovensmann et al., 1999; Butz et al., 1999; Crisp et al., 2004; Kuang et al., 2002; Yokota et al., 2009]. However, operational trace gas retrieval algorithms for space missions often apply simplified aerosol models to speed up data processing. To mitigate the impacts of imperfect aerosol/cloud modeling, these retrieval algorithms perform target scene screening that filters out those observations where aerosol and cloud optical depths (AOD/COD) exceed a pre-set threshold value. In the near-infrared, an optical depth of 0.3 is a typical threshold value of AOD. Over megacities where aerosols often reside in the urban planetary boundary layer (PBL), the majority of remote sensing measurements from space are usually filtered out by pre- or post-screening [Crisp et al., 2012; Yoshida et al., 2011]. Hence, there exists a need to fill in the “gap” of
satellite measurements, e.g., in the source areas that are significantly contributing to the global GHG emissions.

[3] To measure GHG concentrations in LA, the California Laboratory for Atmospheric Remote Sensing Fourier Transform Spectrometer (CLARS-FTS) was deployed on the top of Mt. Wilson, looking down at the land surface of target sites in the LA basin. There are two modes of operation as shown in Figure 1 [Fu et al., 2013, supplementary figure 1]: (1) Los Angeles Basin Surveys (LABS) mode using reflected sunlight from the LA basin that undergoes absorption and scattering by trace gases and aerosols below the CLARS site; (2) Spectralon Viewing Observation (SVO) mode using reflected sunlight from a locally positioned Spectralon plate that samples the solar beam above the CLARS site and measures the background GHG abundances in the free troposphere above Mt. Wilson. CLARS-FTS has high sensitivity to the variation of GHGs over LA basin due to the long light path traveling through the urban PBL (typically 20 km distance from CLARS site to the LA basin land surface). In the LABS mode, sunlight travels through the PBL twice, with a large viewing zenith angle, prior to being measured by the instrument. This viewing geometry offers much higher sensitivity to the atmospheric composition within the PBL than a typical satellite geometry but also makes the measurements more susceptible to the influence of aerosol scattering and absorption. The current CLARS-FTS operational retrieval algorithm (version 1.0) uses measurements of the CO$_2$ absorption band centered at 1.61 µm to estimate the CO$_2$ slant column density (SCD) along the line of sight. The SCD is defined as the total number of absorbing
gas molecules along the optical path per unit area. The effect of aerosol scattering, on the other hand, can be estimated by simultaneously retrieving the O$_2$ SCD based on measurements of the O$_2$ absorption band centered at 1.27 μm, assuming that the changes in light path due to aerosol scattering are identical in both the 1.61 μm and 1.27 μm bands. This approach leads to an underestimation of CO$_2$ and O$_2$ SCDs due to a “line filling-in” effect (see Section 3) in the absorption lines. The bias due to aerosol scattering can be reduced by estimating the column-averaged dry air mole fraction of CO$_2$ ($X_{CO_2}$), defined as 0.2095 (known O$_2$ volume mixing ratio) times the CO$_2$ SCD divided by the O$_2$ SCD. However, the wavelength dependence of aerosol scattering implies that division by O$_2$ SCD does not completely remove the aerosol scattering effect in the 1.61 μm band. The assumption that aerosol scattering is identical in the two bands leads to an observable bias in the retrieved $X_{CO_2}$. Therefore, a proper retrieval must account for wavelength-dependent aerosol scattering.

[4] Aerosol composition and mass loading in the LA area were studied during previous campaigns such as the California Research at the Nexus of Air Quality and Climate Change (CalNex) [Hersey et al., 2011, 2013] and the Southern California Ozone Study (SCOS) [Collins et al., 2000]. However, their optical properties, such as the single scattering albedo (SSA) and the asymmetry parameter (g), are poorly quantified [Andrews et al., 2006]. Most of the previous studies have focused on the effect of aerosols on the planetary energy budget [Haywood and Shine, 1995; Takemura and Nakajuma, 1995] instead of providing the optical properties needed...
for an algorithm to retrieve trace gas abundances. Recently, Seidel and Popp [2012]
studied the relationship between surface albedo and aerosol SSA and its implications
for retrieving AOD using reflected radiance. Similarly, studies on aerosol scattering
and absorption were carried out by Belton et al. [1968] and Chamberlain [1970] for
a semi-infinite planetary atmosphere without considering surface reflection.
Houweling et al. [2005] studied the retrieval bias from SCIAMACHY measurements
and confirmed that the large variability in the total column CO₂ retrieved over the
Sahara Desert was caused by mineral dust. However, they did not perform detailed
modeling to relate the optical properties of mineral dust to the observed radiance to
explain the variability in retrieved total column CO₂.

[5] One possible explanation for the retrieval bias caused by aerosols is related
to the photon path length distribution. Oshchepkov et al. [2012] studied the effect of
aerosols on optical path variations for reflected sunlight observed from space and
developed a method to filter out data highly contaminated by aerosols and clouds. In
a study by Funk and Pfeilsticker [2003], the photon path length distribution was used
to study radiative transfer in clouds. Since this method is based on statistical results,
it is difficult to quantify the relationship between gaseous absorption and aerosol
scattering.

[6] Our aim is to understand the influence of aerosol scattering on the observed
radiance using fundamental principles of radiative transfer. In Section 2, we first
demonstrate the retrieval bias in CO₂ and O₂ SCD due to neglecting aerosol
scattering, which manifests itself as a ‘U-shape’ in a plot of the retrieved SCD
against the geometric SCD. In Section 3, we present an analytic two-stream radiative transfer model [James, 1975; Liou, 1974; Meador and Weaver, 1979], employing Lorentzian absorption line shapes for O2 and CO2, to show the spectral signatures of aerosol scattering on the observed radiance. In Section 4, both the analytic model and the numerical two-stream model are used to illustrate how aerosol scattering causes an apparent reduction in the retrieved abundances of trace gases as manifested by the ‘U shape’. The retrieval biases in the PBL and the free troposphere are evaluated under different scenarios. Section 5 presents the conclusions and discusses the implications of this work.

2. Underestimation of SCDs due to aerosol scattering

[7] Here we will demonstrate the SCD retrieval bias due to the assumption of neglecting aerosol scattering. Although we perform our analysis on the CLARS-FTS measurements, the results are generally applicable to similar ground-based and space-based measurements.

[8] In the LABS mode, CLARS-FTS points at a programmed sequence of ground target locations in the LA basin. Sample CO2 SCDs along the line of sight from the CLARS site on Mt. Wilson to a target in West Pasadena retrieved during a hazy day are shown in Figure 2(a). For scenarios over the LA basin with medium aerosol loading (AOD ~ 0.1), we obtain a ‘U shape’ as the SCD of absorbing gas along the line of sight changes from the morning to the afternoon. The data are closer to the 1:1 line in the morning (A-B) and deviate from it as the haze builds up
in the afternoon (B-C). For a pure trace gas absorption scenario, i.e. with no aerosol scattering in the atmosphere, we expect the measured SCD to agree with the calculated geometric SCD. Therefore the data points, such as those in the SVO mode measurements (green "+" points in Figure 2) must fall on the 1:1 line. For the measurements over West Pasadena, the observed CO$_2$ SCDs are systematically smaller (by up to 13%) than the geometric ones from the morning to the afternoon. Figure 2(b) shows similar deviation (by up to 17%) in the O$_2$ SCD. The deviation of CO$_2$ could arise from diurnal variations (i.e., changes of CO$_2$ emission rate over the LA basin, etc). However, there are no emission sources in the LA basin for O$_2$. This suggests that the low bias is due mainly to the increase in AOD during the daytime, as indicated by the images recorded by a visible camera that was co-aligned with the CLARS-FTS. The current CLARS retrieval algorithm uses the GFIT model [Fu et al, 2013], which does not include aerosol scattering. Since aerosol scattering has wavelength dependence, we expect the O$_2$ and CO$_2$ SCD to have different deviations from the 1:1 line. Normalizing the CO$_2$ SCD by the O$_2$ SCD cannot completely eliminate the biases in $X_{CO_2}$ caused by aerosol scattering.

3. Influence of aerosols on the observed radiance

[9] Using a sophisticated numerical two-stream Radiative Transfer Model (RTM) [Spurr and Natraj, 2011], where the radiative transfer calculation is done analytically except for the boundary value problem (which is also done using a simple and fast pentadiagonal solver rather than typical matrix inversion techniques),
we simulate spectra using configurations similar to the CLARS-FTS measurements. Figure 3 shows synthetic spectra in the 1.27 µm O₂ absorption band with different AODs in the PBL. The spectra from the two-stream RTM have been validated against a full-physics RTM model VLIDORT [Spurr, 2006], which provides radiances with an accuracy higher than the two-stream RTM. There are two prominent features. First, the spectral continuum level increases with AOD (Figure 3(a)). Second, after normalizing the radiances by its maximum value, the absorption lines move upward in the regions of weak absorption, hereafter referred to as "line filling-in". The full width at half maximum (FWHM) of the spectral lines in Figure 3(b) shows that the absorption becomes weaker as AOD increases. This line filling-in is a consequence of radiance normalization. In Figure 3(c), the synthetic spectra and real measurements from CLARS-FTS on 13 March 2013 (clear) and 23 March 2013 (hazy) are shown. The measurements are made at nearly identical local times (4:30 pm) but on two days not far apart to obtain nearly identical solar zenith angles (SZAs). AOD is estimated based on images from a co-boresighted visible camera. The spectral lines measured on a hazy day (red line in Figure 3(c)) move inward and show weaker absorptions, compared with the ones recorded on a clear day (blue line in Figure 3(c)). This line filling-in is observed in both the CLARS-FTS measured spectra (Figure 3(c)) and the simulations (Figure 3(b)). Similarly, the line filling-in is apparent in spectra of the CO₂ absorption bands.

[10] The spectral features can be explained by a simple analytic model as described in Appendix B. First, to simplify the problem and show the influence of
aerosol on the magnitude of the reflected radiance, we derive the reflectance, $R$, of a single-layer atmosphere with aerosol absorption and scattering only (Appendix B.1). In this model, the incoming solar flux is absorbed by both the atmosphere and the surface, and reflected by the PBL. Simple derivations show that (equation (B15)) $R$ is a monotonic function with respect to AOD in the PBL, $\tau_1$, depending on the value of the SSA, $\omega_0$. If $\omega_0$ is high compared to the surface albedo, $\alpha$, as is the case for sulfate and sea-salt aerosols, $R$ increases with $\tau_1$. However, if $\omega_0$ is low, as is the case for black carbon, $R$ decreases with $\tau_1$.

Of interest, then, is the transition point at which the derivative of $R$ with respect to $\tau_1$ changes sign. We assume that the surface albedo is fixed for most scenarios; however, the SSA of aerosols in the atmosphere may vary widely. The critical SSA, $\omega_c$, is defined as the SSA at which increasing AOD does not change the magnitude of the reflected radiance (equal to the scene without aerosol).

Mathematically we can derive it as follows.

$$\lim_{\tau_1 \to 0} R(\tau_1, \omega_c) = \frac{[\omega_c - \alpha (1 - \bar{\mu} \rho)^2]}{[(1 + \bar{\mu} \rho)^2 - \alpha \omega_c]} = \alpha$$

$$\omega_c = \frac{4\alpha}{(1 + \alpha)^2}$$

The values of $\rho$ and $\bar{\mu}$ are defined in Appendix B1. In equation (2), $\omega_c$ is a simple monotonic function of just the surface albedo. This relationship still holds in an atmosphere with both aerosol scattering and gaseous absorption. When the surface albedo is low, the aerosol SSA must be much larger than the surface albedo in order to increase the observed radiance by scattering at the top of the PBL. To confirm this
relationship and to test our analytic solution, we compare our results with the results of Seidel and Popp [2012], in which they perturb the AOD in a numerical model for different scenarios to get the value of the critical SSA. An important implication of this relationship is that if the SSA of aerosols in the PBL approaches $\omega_c$, it is difficult to retrieve the AOD even if the instrument is well calibrated. In this scenario, sensitivity of the reflected radiance to the aerosol parameters will decrease and retrieval errors will increase.

[12] To explain the line filling-in, we use a one-line absorption model for CO$_2$ and O$_2$ (Appendix B.2). Taking CO$_2$ as an example, Figure 4 shows the calculated reflectance. In this case, the absorption line becomes weaker after normalization (by the maximum value of the radiance) as shown in Figure 4(b) for $\omega_0 = 0.99$, larger than the critical value corresponding to the surface albedo of 0.1. This suggests that the gaseous absorption is reduced by aerosol scattering. This effect can be intuitively understood as follows: before the sunlight reaches the surface, it is scattered to the point of observation at the top of the PBL without going through the atmosphere below, thereby reducing the absorption optical path in the PBL. This effect is independent of aerosol type. We also calculate the reflectance with $\omega_0 = 0.2$, less than the critical value, as shown in Figures 4(a) and 4(c). The reflectance decreases with AOD, but after normalization, we can still see the line filling-in. In Figure 4(d), we obtain similar line filling-in effects by reducing the concentration of CO$_2$ in the calculation and setting AOD in the PBL to zero. For an O$_2$ absorption line centered at $\nu_0 = 7863.4$ cm$^{-1}$, all the features are similar (not shown here).
Using normalized spectra, the equivalent effects of absorption line filling-in caused either by reducing absorbing gas concentration or by aerosol scattering in the PBL are difficult to distinguish. In a model without aerosol scattering, all the changes in line width are attributed to changes in gas abundance. This explains the changes in retrieved SCDs from CLARS-FTS as AOD increases from the morning to the afternoon (Figure 2).

4. Retrieval bias caused by aerosol scattering

In order to quantify the influence of aerosol scattering on GHG retrieval and simulate the bias observed by CLARS-FTS, we employ the Levenberg-Marquardt (LM) algorithm [Rodgers, 2000] to retrieve CO₂ and O₂ concentrations. The iteration in the retrieval algorithm is:

\[
x_{i+1} = x_i + [(1 + \gamma)S_a^{-1} + K_i^T S_e^{-1} K_i]^{-1} \{K_i^T S_e^{-1}[y - F(x_i)] - S_e^{-1}[x_i - x_a]\}
\] (3)

where \(x\) is the retrieved state vector, \(x_a\) is the a priori state vector, \(y\) is the measured spectral radiance, \(S_a\) is the a priori covariance matrix, \(S_e\) is the spectral radiance noise covariance matrix, \(K\) is the Jacobian matrix, \(F(x)\) is the forward model and \(\gamma\) is the parameter determining the size of each iteration step. The number of degrees of freedom (DOF) measures how many independent pieces of information we can obtain from the measurement. It can be calculated as:

\[
DOF = \sum_i \frac{\lambda_i^2}{(1 + \gamma)}
\] (4)

where \(\{\lambda_i\}\) are the singular values of the Jacobian, \(K\).

Both the analytic and numerical models are employed in this work. We
assume nonzero AOD evenly distributed in the PBL to generate synthetic data. However, in the retrieval, the AOD is set to zero and held constant. This approach approximately simulates the influence of neglecting aerosol scattering on the retrieved values of SCD. The model configurations used in this section are listed in Table 1.

4.1 Analytic model

[16] Using the analytic model described in Appendix B (case A in Table 1), we choose a spectral window of 2 cm\(^{-1}\) around the central wavenumber of \(\nu_0 = 6243.9\) cm\(^{-1}\) for CO\(_2\) and \(\nu_0 = 7863.4\) cm\(^{-1}\) for O\(_2\). The sampling interval is 0.001 cm\(^{-1}\), therefore, 2000 channels are used. Synthetic data are generated using normalized spectra for a signal-to-noise ratio (SNR) of 300, similar to that of a CLARS-FTS measured spectrum. The model sampling interval (spectral point spacing) is much smaller than the CLARS-FTS sampling interval; however, it provides a DOF close to 2 for both CO\(_2\) and O\(_2\) with only one absorption line, thereby enabling us to retrieve trace gas abundances in the PBL and the free troposphere simultaneously. In the retrieval algorithm, the \textit{a priori} and the first guess of CO\(_2\) concentrations in the two layers are set at 400 ppm, which are different from the true values of 410 ppm in the PBL and 390 ppm in the free troposphere. For the O\(_2\) concentration, the \textit{a priori} and the true values in both the layers are set at 0.2095.

[17] Figure 5 shows retrieved CO\(_2\) concentrations in both the PBL and the free troposphere with increasing AOD. It is worthwhile to note that this is performed prior to normalizing the CO\(_2\) column by the O\(_2\) columns, i.e., completely neglecting the
impacts of aerosol scattering on light path computations. When the AOD is identical to zero, we can retrieve the true values of CO$_2$ concentrations in both layers, showing that our retrieval algorithm is robust. Since the AOD decreases from the surface to higher altitudes, the bias in the PBL (solid line) is much larger than that in the free troposphere (dashed line). The analytic model requires identical slant path optical depths in the incoming and outgoing directions. Therefore, the model requires the viewing zenith angle always to match the SZA. In the LABS mode measurements, the viewing zenith angles are larger than the SZA (greater than 60°). When the SZA and the viewing angle are increased from 0° to 60°, the CO$_2$ concentration differences between the retrieved and true states also increase (Figure 5). This shows that both AOD and SZA are important factors affecting the retrieval of absorbing gas concentrations.

[18] In Figure 6, we retrieve the CO$_2$ and O$_2$ SCDs assuming the SZA varies linearly from 60° to 0° and back to 60° with the AOD increasing linearly from 0 to 0.1 in the PBL. It shows approximately one day of simulated measurements from the morning to the afternoon (8:00 am to 4:00 pm). The SCD is defined in equation (5), where $P_s$ is the surface pressure, $P_1$ is the pressure at the top of PBL, $\chi_1$ is the absorbing gas concentration in the PBL, $\chi_2$ is the absorbing gas concentration in the free troposphere, $M = 2.067 \times 10^{22}$ molecule cm$^{-2}$ hPa$^{-1}$ is the total number of air molecules per unit area per unit pressure. Our model is approximate in many ways. Therefore, if we compare Figure 6 with the measurements in Figure 2, we can expect only qualitative agreement.
\[ SCD = \frac{2\chi_s(P_s - P) + \chi_s P}{\cos(SZA)} M \]  

[19] As the AOD increases, the retrieved SCD falls off the 1:1 line of geometric SCD, similar to the daily trend of SCD measured by the CLARS-FTS on 23 March 2013 over West Pasadena. The CLARS-FTS operational retrieval algorithm uses the O\(_2\) SCD to normalize the CO\(_2\) SCD. This method can eliminate the uncertainties in light path computation to first order. However, some errors persist because the aerosol scattering depends on wavelength. In addition, because the spectroscopic parameters such as line strength and pressure broadening coefficients for O\(_2\) and CO\(_2\) are different, the two biases are likely not identical. When the aerosol SSA is decreased to 0.2, the retrieval also underestimates the true SCD, consistent with the analysis in section 3 on spectral line filling-in for low SSA scenarios. However, the biases are much smaller compared with the cases with higher SSA because for a given AOD, the filling in is less significant (see Figure 4c).

4.2 Numerical model

[20] The analytic model provides an explanation for the retrieval bias caused by aerosol scattering. However, there are several approximations in this first-order analytic model. The incoming solar flux is approximated by an isotropic diffusive flux at the top of the model. In the PBL, the viewing zenith angle and SZA must be identical in order to ensure the same slant path optical depths for the incoming and outgoing beams. These assumptions may cause the model to deviate from the measurements. In order to better simulate CLARS-FTS measurements, and to explore
the effects of aerosol scattering in a more realistic parameter space, we use a numerical two-stream RTM [Spurr and Natraj, 2011] to simulate the observed spectra in a spectral interval broader than those in Figures 3 – 4. The CO₂ and O₂ spectral ranges shown in Figure 7 are based on Fu et al. [2013] and each covers 25 cm⁻¹ (the CLARS-FTS operational algorithm used spectral regions wider than 25 cm⁻¹). In this model, the a priori atmospheric profile has 70 layers from the surface up to 70 km and is derived from NCEP-NCAR reanalysis data [Kalnay et al., 1996]. We calculate the optical depth for each layer using the Reference Forward Model [Dudhia et al., 2002], and then simulate the reflected radiance observed by the CLARS-FTS. We assume the surface reflection to be Lambertian with a surface albedo of 0.23, as measured for West Pasadena [Fu et al., 2013]. The model takes into consideration Rayleigh scattering by air molecules. The viewing zenith angle, a constant parameter, is 83.1° for the target scene over West Pasadena. SZAs at a given date can be calculated as shown in equations (6)-(7):

\[
cos(SZA) = \cos(L)\cos(\delta)\cos(H) + \sin(L)\sin(\delta) \tag{6}
\]

\[
H = \frac{(\text{minutes past midnight}) - 720}{4 \text{ min/deg}} \tag{7}
\]

where L is the latitude (34.2° for West Pasadena) and δ is the declination angle (0.2° for 23 March 2013). H is the hour angle measuring the time difference from the local noon.

[21] In the forward model, we apply the CLARS-FTS instrument line shape (ILS) with FWHM = 0.22 cm⁻¹ [Fu et al., 2013] to the simulated radiances and Jacobian matrices for absorbing gas concentrations. The sampling interval is 0.06 cm⁻¹, and the
SNR is 300. To investigate the impacts of aerosol scattering on the SCD of CO₂ and O₂, the algorithm retrieves the two species separately. For each species, two scaling factors are retrieved, one for the mean gas concentration in the PBL and the other for the free tropospheric concentration.

[22] We selected a target scene with a SZA of 54.1° to study the retrieval bias as a function of AOD. Figure 8 shows the influence of aerosol scattering on the retrieved concentrations of CO₂ and O₂. We assume an idealized aerosol with SSA = 0.99 and asymmetry parameter g = 0 (case B in Table 1). For CO₂, the true values of the concentration scale factors in the PBL and the free troposphere are set to 1.1 and 0.9 respectively, which are different from the a priori vertical profile. Without the influence of aerosols, we retrieve the true values as shown in Figure 8(a). The features shown here for the decrease in concentration with increasing AOD are similar to the analytic model (Section 4.1, Figure 5). The retrieval bias in the PBL is much larger than that in the free troposphere. It is worthwhile to note that the bias in the O₂ retrieval is slightly larger than that in the CO₂ retrieval, due to the wavelength dependence of aerosol scattering. Figure 8(c) shows $X_{CO₂}$ as a function of AOD. The sign of this bias is dependent on the AOD. An algorithm that calculates $X_{CO₂}$ (equation (8)), i.e., the approach used in the CLARS-FTS operation algorithm, can greatly reduce the bias due to aerosol scattering. However, the scaling factor of $X_{CO₂}$ shown in Figure 8(c) still deviates from the true value. The biases between retrieved $X_{CO₂}$ and the true values are up to 3%, because this approach (equation (8)) neglects
wavelength dependence of aerosol scattering between the CO$_2$ and O$_2$ absorption bands.

\[ X_{CO_2} = 0.2095 \frac{SCD_{CO_2}}{SCD_{O_2}} \]  

(8)

[23] For non-isotropic aerosol scattering, we explore the retrieval bias in the SSA-g parameter space (case C in Table 1) as shown in Figure 9. We assume that the aerosol scattering has a Henyey-Greenstein type phase function [Boucher, 1998; Henyey and Greenstein, 1941] with SSA $\omega_0$ and asymmetry parameter $g$. The AOD is kept constant at 0.1. We find that the retrieved SCD is always less than the geometric SCD calculated from the true atmospheric profile. This is because aerosol scattering causes absorption line filling-in, as described in Section 3. When calculating $X_{CO_2}$ using equation (8) without taking the wavelength dependence into account, the mean mixing ratio could be either over- or under-estimated, depending on the relative magnitude of biases in the CO$_2$ and O$_2$ SCDs. The bias in $X_{CO_2}$ is much smaller than that in the CO$_2$ SCD. This indicates that dividing the CO$_2$ SCD by that of O$_2$ removes some of the biases due to aerosol scattering. However, the wavelength dependence of aerosol scattering still causes biases in $X_{CO_2}$, the magnitude of which is dependent on the AOD. At constant AOD, the biases in both $X_{CO_2}$ and SCDs are dependent on both SSA and $g$. The retrieval bias of SCD increases with SSA, consistent with Figure 6, and decreases with $g$. The latter can be intuitively understood as follows: for smaller $g$, the scattering phase function is more isotropic (less forward peaked). By using the delta-Eddington approximation [Hansen and Travis, 1974; Kylling et al, 1995; Wiscombe, 1977], we can get the equivalent isotropic AOD $\tau'_s$ and
SSA ω' for the forward peaked scattering as shown in equations (9)-(10) [Goody and Yung, 1999; Liou, 2002]:

\[
\tau_\omega' = (1 - f) \tau_s \tag{9}
\]

\[
\omega' = \frac{1 - f}{1 - f \omega} \tag{10}
\]

where f is the fraction of scattered energy residing in the forward peak. Therefore a more forward-peaked phase function with large g value will lead to smaller aerosol scattering as well as smaller retrieval bias.

[24] To simulate the observed 'U shape' and match the CLARS-FTS retrieved SCD as shown in Figure 2, AOD data are taken from measurements from the AErosol RObotic NETwork (AERONET) station at Caltech on 23 March 2013 [Holben et al., 1998; Holben et al., 2001]. AERONET measurements cover the wavelength range from 340 to 1020 nm. However, neither the CO2 nor O2 near-infrared band used in our retrievals is included in the AERONET measurements. To calculate the AOD in these two bands, we use the Angstrom exponent law to extrapolate the data [Seinfeld and Pandis, 2006]

\[
\frac{\tau}{\tau_0} = \left( \frac{\lambda}{\lambda_0} \right)^{-\kappa} \tag{11}
\]

where \(\lambda_0\) and \(\tau_0\) are the reference wavelength and the corresponding AOD, and \(\kappa = 0.78\) is the Angstrom coefficient. The AOD in the CO2 band starting at 1607 nm is 0.0708, while the AOD in the O2 band starting at 1264 nm is 0.0854.

[25] Aerosol properties in the LA basin were obtained from simulations using the Weather Research and Forecasting [WRF; Skamarock et al., 2005] model. The Modal
[Ackermann et al., 1998; Schell et al., 2001] was used to obtain specific values for 5 aerosol types (black carbon, organic carbon, sulfate, coarse and accumulation mode sea salt). The aerosol single scattering properties were computed using the Meerhoff Mie code [de Rooij and van der Stap, 1984], with size distribution parameters taken from the Optical Properties of Clouds and Aerosols [OPAC; Hess et al., 1998] database. Table 2 shows the typical aerosol compositions (measured by optical depth) and optical parameters in this region. In the forward model (case D in Table 1), we vary the hour angle $H$ in equation (7) from $-75^o$ to $75^o$ to simulate different measurements from the morning to the afternoon (7:00 am to 5:00 pm). We assume that the total AOD increases from zero to the value extrapolated from the AERONET station measurements. The temporal variation of AOD is simulated by an idealized function as shown in equation (12).

$$\tau_s = \frac{AOD}{2} + \frac{AOD}{2} \tanh\left(\frac{H}{30^o}\right)$$  \hspace{1cm} (12)

[26] The simulated variations of CO$_2$ and O$_2$ SCD (Figure 10) match the data. Furthermore, the 'U shape' of O$_2$ SCD also shows larger low bias than CO$_2$ SCD for the same AOD conditions. This demonstrates that aerosol scattering is the cause of the low bias in the CO$_2$ and O$_2$ SCD.

5. Discussion and conclusion

[27] The effects of aerosol scattering on GHG retrievals are analyzed. Analytic solutions provide clear insights into the physical mechanism of aerosol scattering,
while the more complex numerical models are more realistic and match the data more accurately. We conclude that in an environment with aerosols, the effect of aerosol scattering is equivalent to a decrease in absorption line width. When using normalized radiances in the retrieval, the retrieved gas abundances show a low bias regardless of the value of aerosol SSA. The observed 'U shape' is simulated with both analytic and numerical models. We compute the SCD retrieval bias in an SSA-g parameter space to analyze the influence of different kinds of aerosols; the results reinforce the conclusion that the retrieved SCD always shows a low bias when using normalized radiance. This result is different from that reported by Houweling et al. [2005], who concluded that aerosols over a bright reflective surface will on average extend the light path length. The difference is mainly due to the non-normalized reflected radiance used in their study. As shown in Appendix B.1, if we use the non-normalized radiance instead, aerosols, to first order will cause a decrease in the magnitude of the radiance. To fit the decreased radiance, retrieved gas abundances will show a high bias. This has been tested using our analytic model. An examination of CLARS-FTS measurements on other days confirms that all retrievals of CO₂ and O₂ SCD show low biases without exception.

[28] This study has implications for current and future missions measuring GHG abundances such as GOSAT and OCO-2. For these instruments, many measurements with aerosol or cloud contaminations are rejected. With high enough spectral resolution and wide enough spectral range, as in the case of OCO-2, there is great potential to retrieve the GHG vertical profile. Our results (Figure 5 and Figure 8)
show that, for a profile retrieval, the bias in the free troposphere is very small, even if we use a RTM that does not include aerosol scattering, such as the GFIT model. Therefore it is possible that many of the rejected measurements could be reanalyzed to yield useful results. Since megacities are important areas of GHG sources, a better remote sensing technique will greatly improve our estimation of the global GHG budget.

[29] As a fast approach to correct the $X_{\text{CO}_2}$ retrieval bias, we can develop a look up table that stores scaling factors as a function of AOD, such as shown in Figure 8(c). It is also possible to retrieve aerosol properties simultaneously with GHG abundances, thereby eliminating the bias caused by aerosol scattering. However, current full-physics radiative transfer models with aerosol scattering are not fast enough to be used operationally for processing data on a large scale. With a full-physics model, we can calculate the radiance more accurately and match the real measurements. It is also possible to account for the state of polarization to gain extra DOFs and improve the retrieval quality.

[30] Furthermore, the simulated retrievals uncover the degeneracy between SSA and surface albedo Jacobians, making the determination of these parameters more difficult. There are several possible solutions. First, calibrating the instrument to obtain absolute radiance can increase the DOF by approximately 1 and the information content by several bits. Second, in principle, the surface albedo can be assumed to be constant for most of the target scenes, thereby mitigating the degeneracy issue. In this work, when using normalized radiance, the bias always tends
to underestimate the retrieved GHG abundances in all scenes with different
types/amounts of aerosols. Our preliminary study shows that, even if some aerosol
parameters are not accurately retrieved, the retrieval biases for gas abundances can
still be greatly mitigated when aerosol parameters are incorporated into the retrieval
algorithm. By using more accurate \textit{a priori} aerosol information, such as
measurements from the Multiangle Imaging Spectro Radiometer (MISR) and
AERONET [Kahn et al., 2005], the retrieval biases can be further reduced. These
issues will be the topics of subsequent papers.
[31] We thank C. Wong, J. Margolis, S. Newman, C. Miller, D. Crisp, M. Gerstell, X. Xi, P. Kopparla, P. Gao, R. Hu and L. Kuai for helpful comments. This research was supported in part by NASA grant NNX13AK34G to the California Institute of Technology, grant P1367828 from the Jet Propulsion Laboratory and and the KISS program of Caltech.
### Appendix A: Abbreviations and acronyms

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>AERONET</td>
<td>Aerosol Robotic Network</td>
</tr>
<tr>
<td>AOD</td>
<td>Aerosol Optical Depth</td>
</tr>
<tr>
<td>CalNex</td>
<td>California Research at the Nexus of Air Quality and Climate Change</td>
</tr>
<tr>
<td>CLARS</td>
<td>California Laboratory for Atmospheric Remote Sensing</td>
</tr>
<tr>
<td>COD</td>
<td>Cloud Optical Depth</td>
</tr>
<tr>
<td>DOF</td>
<td>Degree of Freedom</td>
</tr>
<tr>
<td>FTS</td>
<td>Fourier Transform Spectrometer</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>g</td>
<td>Asymmetry Parameter</td>
</tr>
<tr>
<td>GHG</td>
<td>Greenhouse Gas</td>
</tr>
<tr>
<td>GOSAT</td>
<td>Greenhouse Gases Observing Satellite</td>
</tr>
<tr>
<td>ILS</td>
<td>Instrument Line Shape</td>
</tr>
<tr>
<td>LA</td>
<td>Los Angeles</td>
</tr>
<tr>
<td>LABS</td>
<td>Los Angeles Basin Surveys</td>
</tr>
<tr>
<td>LM</td>
<td>Levenberg-Marquardt</td>
</tr>
<tr>
<td>MADE</td>
<td>Modal Aerosol Dynamics Model</td>
</tr>
<tr>
<td>MISR</td>
<td>Multiangle Imaging Spectro Radiometer</td>
</tr>
<tr>
<td>OCO-2</td>
<td>Orbiting Carbon Observatory-2</td>
</tr>
<tr>
<td>Term</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>---------------------------------------------------------------------------</td>
</tr>
<tr>
<td>PBL</td>
<td>Planetary Boundary Layer</td>
</tr>
<tr>
<td>RTM</td>
<td>Radiative Transfer Model</td>
</tr>
<tr>
<td>SCD</td>
<td>Slant Column Density</td>
</tr>
<tr>
<td>SCIAMACHY</td>
<td>Scanning Imaging Absorption Spectrometer for Atmospheric Chartography</td>
</tr>
<tr>
<td>SCOS</td>
<td>Southern California Ozone Study</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal-to-Noise Ratio</td>
</tr>
<tr>
<td>SORGAM</td>
<td>Secondary Organic Aerosol Module</td>
</tr>
<tr>
<td>SSA</td>
<td>Single Scattering Albedo</td>
</tr>
<tr>
<td>SVO</td>
<td>Spectralon Viewing Observation</td>
</tr>
<tr>
<td>SZA</td>
<td>Solar Zenith Angle</td>
</tr>
<tr>
<td>(X_{CO_2})</td>
<td>Column-Averaged Dry Air Mole Fraction of CO(_2)</td>
</tr>
</tbody>
</table>
Appendix B: Two-stream analytic model

1. Influence of aerosols on radiance

[32] We solve a simplified radiative transfer equation without the source term as shown in equation (B1) to explain the change of radiance due to aerosols [Goody and Yung, 1989; Liou, 2002]. We assume that the scattering is isotropic and the single scattering albedo $\omega_0$ is a constant. In this equation $I$ is the radiance, $\tau$ is the optical depth and $\mu=1/\cos(\theta)$, where $\theta$ is the viewing zenith angle or the SZA. This approximation is accurate only to the first order. We neglect the term associated with the incoming solar irradiance and assume that it is the same as the isotropic diffusive flux at the top of the atmosphere.

$$\mu \frac{\partial I(\tau, \mu)}{\partial \tau} = I(\tau, \mu) - \frac{1}{2} \omega_0 \int_1^\tau I(\tau, \mu) d\mu$$  \hspace{1cm} (B1)

Separating upward and downward streams using two-stream approximation as

$$\bar{\mu} \frac{dI^+(\tau, \bar{\mu})}{d\tau} = I^+(\tau, \bar{\mu}) - \frac{1}{2} \omega_0 [I^+(\tau, \bar{\mu}) + I^-(\tau, -\bar{\mu})]$$ \hspace{1cm} (B2)

$$-\bar{\mu} \frac{dI^-(\tau, -\bar{\mu})}{d\tau} = I^-(\tau, -\bar{\mu}) - \frac{1}{2} \omega_0 [I^+(\tau, \bar{\mu}) + I^-(\tau, -\bar{\mu})]$$ \hspace{1cm} (B3)

we can solve for general solutions as below, where $I^+(\tau) = I^+(\tau, \bar{\mu})$, $I^-(\tau) = I^-(\tau, \bar{\mu})$.

$$I^+(\tau) = (1 - \bar{\mu} \rho)c_1 e^{\rho \tau} + (1 + \bar{\mu} \rho)c_2 e^{\rho \tau}$$ \hspace{1cm} (B4)

$$I^-(\tau) = (1 + \bar{\mu} \rho)c_1 e^{-\rho \tau} + (1 - \bar{\mu} \rho)c_2 e^{-\rho \tau}$$ \hspace{1cm} (B5)

$$\rho^2 = \frac{1 - \omega_0}{\bar{\mu}^2}$$ \hspace{1cm} (B6)
Applying the boundary conditions to account for the reflection at the surface, where \( \alpha \) is the surface albedo and \( F \) is the incoming solar flux, we can get the two-stream general solution with surface albedo at arbitrary optical depth

\[
(1 + \overline{\mu} \rho) c_1 + (1 - \overline{\mu} \rho) c_2 = \frac{1}{2\pi} F \tag{B8}
\]

\[
(1 - \overline{\mu} \rho) c_1 e^{-\rho} + (1 + \overline{\mu} \lambda) c_2 e^{\rho} = \alpha [(1 + \overline{\mu} \rho) c_1 e^{-\rho} + (1 - \overline{\mu} \rho) c_2 e^{\rho}] \tag{B9}
\]

Then we can get the two-stream general solution with surface albedo at arbitrary optical depth

\[
I^+(\tau) = \frac{1}{2\pi} F \frac{[\omega_0 - \alpha(1 - \overline{\mu} \rho)^2] e^{\rho} - [\omega_0 - \alpha(1 + \overline{\mu} \rho)^2] e^{-\rho}}{[(1 + \overline{\mu} \rho)^2 - \alpha \omega_0] e^{\rho} - [(1 - \overline{\mu} \rho)^2 - \alpha \omega_0] e^{-\rho}} \tag{B10}
\]

\[
I^-(\tau) = \frac{1}{2\pi} F \frac{[(1 + \overline{\mu} \rho)^2 - \alpha \omega_0] e^{\rho} - [(1 - \overline{\mu} \rho)^2 - \alpha \omega_0] e^{-\rho}}{[(1 + \overline{\mu} \rho)^2 - \alpha \omega_0] e^{\rho} - [(1 - \overline{\mu} \rho)^2 - \alpha \omega_0] e^{-\rho}} \tag{B11}
\]

At the top and bottom, emergent radiances are shown by equation (B13)-(B14).

\[
I^+(0) = \frac{1}{2\pi} F \frac{[\omega_0 - \alpha(1 - \overline{\mu} \rho)^2] e^{\rho} - [\omega_0 - \alpha(1 + \overline{\mu} \rho)^2] e^{-\rho}}{[(1 + \overline{\mu} \rho)^2 - \alpha \omega_0] e^{\rho} - [(1 - \overline{\mu} \rho)^2 - \alpha \omega_0] e^{-\rho}} \tag{B13}
\]

\[
I^-(\tau_1) = \frac{2\overline{\mu} \rho F}{\pi} \frac{1}{[(1 + \overline{\mu} \rho)^2 - \alpha \omega_0] e^{\rho} - [(1 - \overline{\mu} \rho)^2 - \alpha \omega_0] e^{-\rho}} \tag{B14}
\]

The non-dimensional value of reflectance is calculated in equation (B15).

\[
R(\tau_1, \omega_0) = \frac{[\omega_0 - \alpha(1 - \overline{\mu} \rho)^2] e^{\rho} - [\omega_0 - \alpha(1 + \overline{\mu} \rho)^2] e^{-\rho}}{[(1 + \overline{\mu} \rho)^2 - \alpha \omega_0] e^{\rho} - [(1 - \overline{\mu} \rho)^2 - \alpha \omega_0] e^{-\rho}} \tag{B15}
\]

2. One-line spectra

[33] Only pressure broadening is considered in this model as Doppler and natural broadenings are weak in the troposphere where most of the absorption occurs. [Goody}
The atmosphere is divided into two layers: a free troposphere with absorption only and a PBL with absorption and scattering. We define the pressure at the top of PBL to be \( P_1 \). In this model \( P_1 \) is defined to be 800 hPa, which is consistent with the pressure level of CLARS instrument at the altitude of 1.7 km.

[34] The absorption coefficient of a Lorentzian absorption line shape is

\[
k = S \frac{\alpha_L}{\pi} \frac{1}{\alpha_L^2 + (\nu - \nu_0)^2}
\]  

(B16)

where \( \alpha_L = \alpha_L^0 \frac{p}{p_0} \) is half-width of the line at the half-maximum [Liou, 2002], \( p \) is the pressure and \( \alpha_L^0 \) is the line width at the reference pressure \( p_0 \). The optical depth of the free troposphere is given by

\[
\tau_1 = \tau_{\text{free}} = \frac{S \chi}{\pi mg} \int_0^P \frac{Ap}{(Ap)^2 + (\nu - \nu_0)^2} dp = \frac{S \chi}{2\pi mgA} \ln \frac{P_1^2 + [(\nu - \nu_0)/A]^2}{[(\nu - \nu_0)/A]^2}
\]  

(B17)

where \( S \) is the line strength constant, \( A = \alpha_L / p = \alpha_L^0 / p_0 \). The two constants \( A \) and \( S \) can be obtained from the HITRAN database [Rothman et al., 2008]. In this model, for the CO\(_2\) absorption line \( \nu_0 = 6243.9 \) cm\(^{-1}\), \( S = 1.52 \times 10^{-23} \) cm\(^{-1}\)Pa\(^{-1}\), \( A = 7.2 \times 10^{-7} \) cm\(^{-1}\)Pa\(^{-1}\); for the O\(_2\) absorption line \( \nu_0 = 7863.4 \) cm\(^{-1}\), \( S = 4.78 \times 10^{-26} \) cm\(^{-1}\) A\(^{-1}\), \( A = 5.5 \times 10^{-7} \) cm\(^{-1}\)Pa\(^{-1}\). \( \chi \) is the volume mixing ratio of the absorbing gas (CO\(_2\) and O\(_2\)). We set \( \chi \) to be 400 ppm for CO\(_2\) and 0.21 for O\(_2\). In the equation \( m = 4.8 \times 10^{-26} \) kg is the mean molecular weight of air, \( g \) is 9.8 m/s\(^2\). Note that \( mg = 4.7 \times 10^{-21} \) cm\(^2\)Pa is a constant. Transmittance of the free troposphere is

\[
T_1 = e^{-\tau_1}
\]  

(B18)

In the PBL, the total optical depth is

\[
\tau_{2a} = \frac{S \chi}{\pi mg} \int_0^P \frac{Ap}{(Ap)^2 + (\nu - \nu_0)^2} dp = \frac{S \chi}{2\pi mgA} \ln \frac{P_1^2 + [(\nu - \nu_0)/A]^2}{[(\nu - \nu_0)/A]^2}
\]  

(B19)
\[ \tau_2 = \tau_{2a} + \tau_s \]  
(B20)

\[ \gamma = \frac{\tau_s}{\tau_{2a} + \tau_s} = \frac{\tau_s}{\tau_2} \]  
(B21)

where \( P_s = 1030 \) hPa is the surface pressure. According to equation B(17), at the center of the absorption line where \( \nu = \nu_0 \), we have a singular point with infinite absorption optical depth. In the retrieval, most of the channels are away from the singular point (\( |\nu - \nu_0| > 0.001 \text{cm}^{-1} \)) where Lorentzian line shape is still a good approximation. This problem can be avoided in our numerical model where we have more realistic line shapes. The parameter \( \gamma \) is defined to be the ratio of AOD in the PBL to the total optical depth in this layer. We can modify the radiative transfer equation as

\[ \mu \frac{dI(\tau, \mu)}{d\tau} = I(\tau, \mu) - \frac{1}{2} \omega_0 \gamma \int_{-1}^{1} I(\tau, \mu) d\mu \]  
(B22)

[35] Repeating the calculations of the two-stream approximation, we can get the reflectance of the PBL as equation (B23).

\[ R_2 = \frac{[\omega_0 \gamma - \alpha(1 - \mu \rho)^2]}{[(1 + \mu \rho)^2 - \alpha \omega_0 \gamma]} e^{\mu \tau_2} - \frac{[\omega_0 \gamma - \alpha(1 + \mu \rho)^2]}{[(1 - \mu \rho)^2 - \alpha \omega_0 \gamma]} e^{-\mu \tau_2} \]  
(B23)

Finally, what we observe as the reflectance at the top of the PBL is

\[ R = T_1 \cdot R_2 = e^{-\tau_1} \frac{[\omega_0 \gamma - \alpha(1 - \mu \rho)^2]}{[(1 + \mu \rho)^2 - \alpha \omega_0 \gamma]} e^{\mu \tau_2} - \frac{[\omega_0 \gamma - \alpha(1 + \mu \rho)^2]}{[(1 - \mu \rho)^2 - \alpha \omega_0 \gamma]} e^{-\mu \tau_2} \]  
(B24)

where \( \tau_1, \tau_2 \) and \( \gamma \) are wavelength dependent. To incorporate the variation of solar zenith angle \( \theta \), we assume in each layer the optical depth

\[ \tau_i(\theta) = \frac{\tau_i(0)}{\cos(\theta)} \]  
(B25)
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Table captions:

Table 1. Model configurations for retrieval.

Table 2. Aerosol composition and optical properties in the LA region.
Table 1. Model configurations for retrieval.

<table>
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<tr>
<th></th>
<th>model</th>
<th>$\alpha$</th>
<th>SSA</th>
<th>$g$</th>
<th>phase function</th>
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<td>Case A</td>
<td>analytic</td>
<td>0.1</td>
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<td>Case B</td>
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<tr>
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<td>0~0.99</td>
<td>0~1</td>
<td>Henyey-Greenstein</td>
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<tr>
<td>Case D</td>
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<td>0.23</td>
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Table 2. Aerosol composition and optical properties in the LA region.

<table>
<thead>
<tr>
<th></th>
<th>Organic</th>
<th>Seasalt (accum)</th>
<th>Seasalt (coarse)</th>
<th>Soot</th>
<th>Sulfate</th>
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<tr>
<td>percentage</td>
<td>4.9%</td>
<td>31.7%</td>
<td>38.1%</td>
<td>7.9%</td>
<td>17.4%</td>
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<tr>
<td>SSA</td>
<td>0.872</td>
<td>0.998</td>
<td>0.985</td>
<td>0.040</td>
<td>0.999</td>
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<tr>
<td>$g$</td>
<td>0.55</td>
<td>0.79</td>
<td>0.82</td>
<td>0.15</td>
<td>0.69</td>
</tr>
</tbody>
</table>

[Ackermann et al., 1998; Schell et al., 2001]
Figure captions:

Figure 1. Schematic figure of CLARS measurement geometries.

Figure 2. Variations of CLARS measured SCD v.s. geometric SCD from the morning to the afternoon, for (a) CO₂ and (b) O₂. A, B and C indicate morning, noon and afternoon. Units for CO₂ and O₂ SCDs are scaled by 10²² and 10²⁵ molecule/cm², respectively. The red lines indicate 1:1 correspondence between measured and geometric SCDs.

Figure 3. Spectra of the O₂ absorption band with different AOD in the PBL. (a) Absolute radiance from the numerical model. In the model surface albedo is 0.23, SSA is 0.99 and g is 0. The absolute radiance assumes that the radiance at the top of atmosphere is equal to 1. (b) Normalized radiance from the numerical model (c) Measurements of normalized radiance from CLARS instrument on 13 March 2013 (clear) and 23 March 2013 (hazy) at 4:30 pm.

Figure 4. One-line spectra simulated by the analytic model for a CO₂ absorption line. (a) Absolute reflectance with different AOD and ω₀ in the PBL. (b) Normalized reflectance with different AOD in the PBL, ω₀=0.99. (c) Normalized reflectance with different AOD in the PBL, ω₀=0.2. (d) Normalized reflectance with different CO₂ concentrations, AOD = 0. The central wavenumber ν₀ = 6243.9 cm⁻¹ has been
subtracted.

**Figure 5.** Retrieval of CO₂ concentrations in the free troposphere and the PBL with increasing AOD. The red lines indicate retrievals with SZA = 60°. The blue lines indicate retrievals with SZA = 0°. The solid lines indicate retrievals in the free troposphere and the dashed lines indicate retrievals in the PBL.

**Figure 6.** Simulated 'U shape' of the SCD daily variations, assuming AOD increases linearly from 0 to 0.1 in the PBL and SZA varies linearly from -60° to 60° for absorption lines of (a) CO₂ with $\omega_0=0.99$ (b) CO₂ with $\omega_0=0.2$ (c) O₂ with $\omega_0=0.99$ (d) O₂ with $\omega_0=0.2$. Units for CO₂ and O₂ SCDs are scaled as in Figure 2. The red lines indicate 1:1 correspondence between measured and geometric SCDs.

**Figure 7.** Simulated spectra of (a) CO₂ absorption band 6220-6245 cm⁻¹ (b) O₂ absorption band 7910-7935 cm⁻¹.

**Figure 8.** Retrieval of (a) CO₂ concentrations in the free troposphere and the PBL with increasing AOD (b) O₂ concentrations and (c) $X_{CO_2}$. The Black dotted lines show the true or the *a priori* values. The red star corresponds to the left-bottom corner in Figure 9(c).

**Figure 9.** Retrieval biases caused by different kinds of aerosols in the SSA-g
parameter space with AOD = 0.1 for (a) CO₂ SCD (b) O₂ SCD and (c) X_{CO₂}. SCD biases are displayed in percentage with respect to the value with AOD = 0. The true value of X_{CO₂} with AOD = 0 is 400.8 ppm. The bottom-left corner of panel (c) corresponds to the value marked with a red star '*' in Figure 8(c).

**Figure 10.** Comparison between the simulated and measured SCD daily variations on 23 March 2013 in West Pasadena for (a) CO₂ SCD and (b) O₂ SCD. Units for the CO₂ and O₂ SCDs are scaled as in Figure 2. The red lines indicate 1:1 correspondence between measured and geometric SCDs.
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Figure 7. Simulated spectra of (a) CO$_2$ absorption band 6220-6245 cm$^{-1}$ (b) O$_2$ absorption band 7910-7935 cm$^{-1}$.
Figure 8. Retrieval of (a) CO$_2$ concentrations in the free troposphere and the PBL with increasing AOD (b) O$_2$ concentrations and (c) $X_{\text{CO}_2}$. The Black dotted lines show the true or the a priori values. The red star corresponds to the left-bottom corner in Figure 9(c).
Figure 9. Retrieval biases caused by different kinds of aerosols in the SSA-g parameter space with AOD = 0.1 for (a) CO$_2$ SCD (b) O$_2$ SCD and (c) $X_{CO_2}$ SCD. Biases are displayed in percentage with respect to the value with AOD = 0. The true value of $X_{CO_2}$ with AOD = 0 is 400.8 ppm. The bottom-left corner of panel (c) corresponds to the value marked with a red star '*' in Figure 8(c).
Figure 10. Comparison between the simulated and measured SCD daily variations on 23 March 2013 in West Pasadena for (a) CO\(_2\) SCD and (b) O\(_2\) SCD. Units for the CO\(_2\) and O\(_2\) SCDs are scaled as in Figure 2. The red lines indicate 1:1 correspondence between measured and geometric SCDs.