The CU Airborne MAX-DOAS instrument: ground based validation, and vertical profiling of aerosol extinction and trace gases

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Received: 2 August 2012 – Accepted: 13 September 2012 – Published: 26 September 2012

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Published by Copernicus Publications on behalf of the European Geosciences Union.

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Abstract

The University of Colorado Airborne Multi Axis Differential Optical Absorption Spectroscopy (CU AMAX-DOAS) instrument uses solar stray light remote sensing to detect and quantify multiple trace gases, including nitrogen dioxide (NO$_2$), glyoxal (CHOCHO), formaldehyde (HCHO), water vapor (H$_2$O), nitrous acid (HONO), iodine monoxide (IO), bromine monoxide (BrO), and oxygen dimers (O$_4$) at multiple wavelengths (360 nm, 477 nm, 577 nm and 632 nm) simultaneously, and sensitively in the open atmosphere. The instrument is unique, in that it presents the first systematic implementation of MAX-DOAS on research aircraft, i.e. (1) includes measurements of solar stray light photons from nadir, zenith, and multiple elevation angles forward and below the plane by the same spectrometer/detector system, and (2) features a motion compensation system that decouples the telescope field of view (FOV) from aircraft movements in real-time (< 0.35° accuracy). Sets of solar stray light spectra collected from nadir to zenith scans provide some vertical profile information within 2 km above and below the aircraft altitude, and the vertical column density (VCD) below the aircraft is measured in nadir view. Maximum information about vertical profiles is derived simultaneously for trace gas concentrations and aerosol extinction coefficients over similar spatial scales and with a vertical resolution of typically 250 m during aircraft ascent/descent.

The instrument is described, and data from flights over California during the CalNex and CARES air quality field campaigns is presented. Horizontal distributions of NO$_2$ VCDs (below the aircraft) maps are sampled with typically 1 km resolution, and show good agreement with two ground based CU MAX-DOAS instruments (slope 0.95±0.09, $R^2 = 0.86$). As a case study vertical profiles of NO$_2$, CHOCHO, HCHO, and H$_2$O mixing ratios and aerosol extinction coefficients, $\varepsilon$, at 477 nm calculated from O$_4$ measurements from a low approach at Brackett airfield inside the South Coast Air Basin (SCAB) are presented. These profiles contain ~ 12 degrees of freedom (DOF) over a 3.5 km altitude range, independent of signal-to-noise at which the trace gas is detected. The boundary layer NO$_2$ concentration, and the integral aerosol extinction over
height (aerosol optical depth, AOD) agrees well with nearby ground-based in-situ NO$_2$ measurement, and AERONET station. The detection limits of NO$_2$, CHOCHO, HCHO, $\varepsilon_{360}$, $\varepsilon_{477}$ from 30 s integration time spectra recorded forward of the plane are 5 ppt, 3 ppt, 100 ppt, 0.004 km$^{-1}$, 0.002 km$^{-1}$ in the free troposphere (FT), and 30 ppt, 16 ppt, 540 ppt, 0.012 km$^{-1}$, 0.006 km$^{-1}$ inside the boundary layer (BL), respectively. Mobile column observations of trace gases and aerosols are complimentary to in-situ observations, and help bridge the spatial scales probed by ground-based observations, satellites, and predicted by atmospheric models.

1 Introduction

Airborne differential optical absorption spectroscopy (DOAS) measurements of different trace gases in the atmosphere by solar stray light started in late 1980s and has come a long way since then. Early studies were focused on obtaining column integrals of stratospheric trace gases like nitrogen dioxide, NO$_2$ (Wahner et al., 1990a), chlorine dioxide, OClO (Schiller et al., 1990), and bromine oxide, BrO (Wahner et al., 1990b) from zenith measurements. First retrievals of trace gas concentrations close to the aircraft altitude were reported by Petritoli et al. (2002) for stratospheric ozone. These studies were followed by the application of the AMAX-DOAS technique to obtain tropospheric columns for NO$_2$ (Melamed et al., 2003; Heue et al., 2005; Wang et al., 2005) and sulfur dioxide, SO$_2$ (Wang et al., 2006; Melamed et al., 2008) over polluted regions. These instruments used multiple telescopes, most notably zenith and nadir to collect scattered sunlight. The focus has shifted towards retrievals of vertical distribution of trace gases from the aircraft using several limb viewing telescopes over the past few years. Figure 1 shows the conceptual viewing geometry of the so-called Airborne Multi-Axis DOAS (AMAX-DOAS) technique. Individual elevation angles (EAs) contain different amounts of information from different layers in the atmosphere and hence can be used to infer vertical distributions of trace gases. Bruns et al. (2006) first reported profiles of NO$_2$ over the Po valley from an airborne MAX-DOAS instrument with four...
telescopes, pointing at fixed EAs. A boundary layer NO$_2$ profile was obtained by Dix et al. (2009) using multiple lines of sight (LOS) and a descent of an aircraft. Prados-Roman et al. (2011) used only one LOS parallel to the plane and the aircraft descent to retrieve vertical profiles of bromine oxide, BrO in the Arctic. Most recently, a limb scanning airborne DOAS instrument was developed at Belgium Institute for Space Aeronomy (BIRA) to obtain vertical distribution of trace gases like NO$_2$ (Merlaud et al., 2011). Most airborne DOAS instruments use either a single or multiple fixed LOS and use a spectrum collected from the same EA as the reference spectrum for DOAS analysis. The DOAS technique yields relative differences in absorber amounts between a measured spectrum and a reference spectrum. These instruments also lack control of the viewing geometry of the telescope during the flight. Pitch and roll information from the aircraft is used during post-processing to calculate the true viewing angle at the time of measurement during the flight. This often leads to an average EA assigned to a measurement and results in a larger uncertainty since MAX-DOAS instruments rely on exactly assigned viewing angles to retrieve vertical profile information of trace gases.

Here, we describe the University of Colorado Airborne MAX-DOAS (CU AMAX-DOAS) instrument, which to our knowledge presents the first true MAX-DOAS implementation from research aircraft. The CU AMAX-DOAS instrument has the capability to access zenith, nadir and limb viewing geometry by means of a single, rotatable prism telescope which is coupled to a motion compensation system. The motion compensation system includes angle sensors to measure pitch and roll angles of the aircraft and feedback loop to correct for it in real-time the pointing angle of the telescope to maintain a constant EA during spectra acquisition in flight. This isolates the telescope from aircraft movements, and enables us to systematically probe the atmosphere with desired sets of EAs to retrieve vertical profiles of trace gases and aerosol extinction simultaneously, and with the highest possible information content. The use of a single telescope to collect spectra from zenith, and other EAs (nadir, and forward of the plane) further enables the zenith spectra to be used as the Fraunhofer reference spectrum in
the DOAS analysis. Zenith spectra usually contain the least amount of tropospheric absorbers, and the ability to record zenith spectra close in time to other EA spectra assures that absorbers above the plane are characterized with minimum difference in radiation fields, and makes the instrument inherently more sensitive to absorbers near and below the aircraft altitude (Volkamer et al., 2009a).

The CU AMAX-DOAS instrument was successfully deployed from 19 May–19 July 2010 as part of two air quality studies in California, namely the California Research at the Nexus of Air Quality and Climate Change (CalNex) (see overview paper by Ryerson et al., 2012) and the Carbonaceous Aerosols and Radiative Effects Study (CARES) (see overview paper by Zaveri et al., 2012). A total of 52 research flights were performed during this deployment and here we focus on results from one flight on 16 July 2010 to describe the technique, and characterize instrument performance. In Sect. 2 the CU AMAX-DOAS instrument is described, and the instrument configuration is introduced. Section 3 describes the DOAS analysis procedures, radiative transfer model (RTM) calculations, and algorithms to retrieve VCDs and vertical profiles of the trace gas concentrations and aerosol extinction coefficients. Section 4 demonstrates the capability of the new instrument. As a case study, vertical profiles of NO$_2$, CHOCHO, HCHO, H$_2$O and aerosol extinction coefficients at 477 nm are retrieved from a low approach at Brackett airfield in the South Coast Air Basin (SCAB). Finally, as a validation, CU AMAX-DOAS NO$_2$ VCDs are compared with VCDs measured by two CU ground based MAX-DOAS instruments that were regularly over-passed during flights; the boundary layer NO$_2$ concentration retrieved from the vertical profile is compared to a ground-based in-situ sensor concentration, and the integral aerosol extinction over height, i.e. AOD is compared with data from an AERONET station.

2 The CU AMAX-DOAS Instrument

The CU-AMAX-DOAS instrument collects spectra of scattered sunlight between 330 and 720 nm at different EAs. The scattered sunlight spectra are analyzed for the
presence of absorbers, using the DOAS method (Platt and Stutz, 2008), like \( \text{NO}_2 \), \( \text{CHOCHO} \), \( \text{HCHO} \), \( \text{H}_2\text{O} \), \( \text{HONO} \), \( \text{IO} \), \( \text{BrO} \), \( \text{O}_4 \). \( \text{NO}_2 \), \( \text{CHOCHO} \), \( \text{HCHO} \), \( \text{H}_2\text{O} \) and \( \text{O}_4 \) data will exemplarily be presented in this paper. The instrument consists of a telescope pylon mounted on the outside of a window plate on a NOAA Twin Otter Remote Sensing research aircraft. The collected photons are transferred via optical fibers to two synchronized spectrometer-detector systems that are housed inside the aircraft fuselage. An optical fiber switch box is placed in between the light sources (telescopes and Hg calibration lamp) and the spectrometer-detector systems to select between different light sources at a given time. The Hg calibration lamp is used to characterize the optical resolution of the spectrometer-detector systems. The instrumental setup is shown in Fig. 2.

### 2.1 Telescope system

The telescope is designed for high light throughput and a very narrow vertical field of view (0.3° × 5.89°). It comprises a 1/2” rotating prism, a 1/2” lens tube with a 1/2” f/4 lens and a stepper motor. All the telescope components are housed in a telescope pylon, an aluminum housing with quartz windows, which is mounted on the outside of a window plate on a NOAA Twin Otter research aircraft. The rotating prism is installed with 0° EA parallel to the aircraft heading and is driven by a stepper motor with an internal encoder to rotate vertically. The prism is capable of making a complete 360° rotation and hence allows characterization of the air masses above, below and in front of the aircraft using the same telescope. Viewing directions behind the aircraft are not accessible due to the structural design of the pylon including the placement of viewing ports. An additional telescope with a fixed EA is therefore present in the pylon to reach some of the inaccessible viewing geometries of the rotating prism. This telescope was rarely used during CalNex and CARES campaigns and data from this telescope is not presented in this paper. The viewing ports on the pylon are heated to prevent formation of ice at higher altitudes. The pylon also includes two webcams; a downward and a forward looking one, to capture atmospheric conditions during the flight. The
light collected by the rotatable prism is focused via a lens tube onto a 12 m long fiber bundle consisting of $72 \times 145 \, \mu m$ fibers. The fiber bundle is configured into two rows of 36 fibers at the telescope end and a circular arrangement at the other. The ends of the fibers away from the telescope are connected to a custom-made optical fiber switch box.

### 2.2 Optical fiber switch box

The optical fiber switch box is used to select between different incoming light sources. It consists of a translational stage mounted to a stepper motor linear actuator. The fibers from the telescopes and Hg calibration lamp are connected to one end of the box. A 10 m long 1.7 mm diameter silica mono-fiber, which is used as a mixing fiber to minimize polarization effects, is mounted on the translational stage opposite the incoming fibers from the light sources. The motor of the linear actuator drives the platform to place the mono-fiber directly in front of the desired fiber with the incoming light at a given time. The other end of the mono-fiber is connected to a bifurcated fiber bundle ($72 \times 145 \, \mu m$) to deliver light to two spectrometers simultaneously. The bifurcated ends are aligned in a single row of 36 fibers to connect to the spectrograph entrance slits.

### 2.3 Spectrometer and detector system

Two spectrometers and their respective detectors are housed in a standard 19″ aluminum instrument rack (19″ × 22″ × 10 1/2″) with modifications to the bottom and top plates for added stability. The spectrometers are Princeton Instrument Acton SP2150 Imaging Czerny-Turner spectrometers with PIXIS 400 back illuminated CCD detectors. The first spectrometer (later referred to as the O$_4$ spectrometer) is equipped with a 500 grooves mm$^{-1}$ grating, blazed at 330 nm. It covers 350–720 nm and is used to measure all four major O$_4$ bands at 360, 477, 577 and 632 nm. The second spectrometer (later referred to as trace gas (TG) spectrometer) covers a wavelength range from 330–470 nm with a custom 1000 grooves mm$^{-1}$ (250 nm blaze wavelength) grating. It
is used to measure all other trace gases. The optical resolution of the O₄ and TG spectrometers were ~2.2 and ~0.7 nm, respectively, inferred from the full-width at half-maximum (FWHM) of a representative Hg line. The CCDs are cooled to −30°C to reduce dark current. The temperatures of the spectrometers are actively controlled with heaters while the instrument rack box temperature is actively cooled using peltier cooling units assuring a constant temperature over a range of varying ambient temperatures. Please refer to Coburn et al. (2011) for additional information on temperature stability, data acquisition and electronic and dark current correction for a comparable instrument. To reduce stray light and higher order diffraction in the TG spectrometer, two filters, a BG3 and a BG38, were placed immediately after the shutter.

2.4 Motion compensation system

The motion compensation system is used to correct the viewing geometry of the telescope for the aircraft pitch and roll effects during the flight. It consists of a PC104 computer connected to the prism motor and two angle sensors, a Systron Donner Inertial MMQ-G, and an electronic clinometer. The MMQ-G is a small robust Global Positioning System (GPS) based Inertial Navigation System (INS). It provides accurate 3-dimensional position, time, velocity, and attitude. It is primarily used to measure the pitch and roll angles of the aircraft for our application and has an angle accuracy of 5 mrad (≈ 0.29°). The information from the sensor is processed by custom LabVIEW software into the coordinate system along the horizon. It is then used to drive the stepper motor of the prism to a new position such that it corrects for the aircraft’s movement and keeps the telescope at the desired EA. The software has capability for 100 Hz loop rate, and was typically operated at 10 Hz. The stepper motor has a precision of 0.01° but is limited by the resolution of the internal encoder (0.2°) to precisely read back the position of the motor. The MMQ-G, clinometer and the telescope prism are mounted on planes parallel to the ground such that the elevation angle of the telescope and the pitch of the aircraft read zero simultaneously. The clinometer is used as a backup during flights for situations when the GPS signal required for the MMQ-G is lost. The
theoretical angle accuracy of the motion compensation system is 0.35° considering the MMQ-G accuracy of ∼ 0.29° (1σ) and motor internal encoder resolution of 0.2°. The system is configured to reset the motor when it does not reach a given position within a desired tolerance level by a fixed time interval. The same motion compensation system has also been integrated as part of another telescope pylon designed for adaptation of the CU AMAX-DOAS instrument aboard the NSF/NCAR GV HIAPER aircraft.

2.5 Performance of the motion compensation system

Figure 3 shows the performance of the system during research flights aboard the GV HIAPER and Twin Otter aircrafts. GV HIAPER flights provide an excellent opportunity to test the system as the aircraft pitch and roll angles measured by the aircraft avionics system during the flight are recorded, while avionics data for the Twin Otter flights are not available. The histogram of differences in aircraft pitch angle recorded at 1 Hz frequency measured by NSF/NCAR GV HIAPER aircraft avionics and our MMQ-G recording during a research flight (∼ 8 h) on 24 February 2012 is plotted as a probability density function in Fig. 3a. A Gaussian fit (black line) to the histogram has a 1σ deviation of 0.16° which is less than the 1σ accuracy (yellow line in Fig. 3a) of the MMQ-G pitch measurement. This shows that the MMQ-G measures the aircraft pitch and roll angles with sufficient accuracy, which are then being used for real-time pointing corrections. Figure 3b shows the difference in desired elevation angle and the real-time elevation angle read back from the motor internal encoder as a probability density for the same flight. The 1σ of the Gaussian fit to the histogram (0.12°) is smaller than the resolution of the motor internal encoder confirming that the telescope position was corrected for the aircraft movements within our ability to read back the motor position.

A similar plot from a research flight (∼ 4 h) on 16 July 2010 aboard the NOAA Twin Otter is shown in Fig. 3c and the 1σ of the Gaussian fit is 0.2°. This slightly larger distribution is within the resolution of the motor internal encoder. The fact that the 1σ for both platforms is less than or equal to the ability with which we can accurately...
read the position of the motor demonstrates that this motion compensation system is suitable for a wide range of moving platforms. Since the precision of the stepper motor is 0.01°, it is very likely that the difference between the real-time and desired elevation angle is smaller than what is being read back from the internal encoder and the overall angle accuracy (1σ) of the motion compensation system is better than 0.35°. The offset of 0.17° for the Gaussian fit in Fig. 3c is probably due to some remaining misalignment between the angle sensor and the motor but is smaller than the accuracy of the angle sensor.

The tolerance level (brown dashed lines in Fig. 3b, c) above which the motor performs an automatic reset was set to 0.7° (2σ theoretical accuracy) for the campaigns described here. The statistical distribution of the elevation angle difference indicates that the desired position of the motor was achieved after the reset.

### 2.6 Field deployment and operation during CalNex and CARES

The CU AMAX-DOAS instrument was deployed aboard the NOAA Twin Otter remote sensing research aircraft during the CalNex and CARES field campaigns from 19 May–19 July 2010 in California after test flights in 2008 and 2009. The pylon was modified significantly after 2009. The aircraft is an unpressurized twin engine turboprop with an altitude ceiling of ~4 km above sea level (without supplemental cabin oxygen). It has a normal cruising speed of ~65 m s⁻¹ and ascent rate of ~10 m s⁻¹ making it particularly suitable for surveying vertical and horizontal distributions of trace gases in a polluted urban environment. During CalNex, the NOAA Twin Otter aircraft was stationed at Ontario, CA, and joined the CARES campaign from 16–29 June 2010 at Sacramento, CA. The plane was equipped with a suite of remote sensing instruments: the University of Colorado deployed (1) CU AMAX-DOAS instrument, (2) two 4-channel radiometers (zenith and nadir viewing) to measure surface albedo; further, NOAA/ESRL/CSD deployed (3) a nadir-pointing Tunable Ozone Profiler for Aerosol and oZone (TOPAZ) lidar (Alvarez II et al., 2011), which measures vertical distribution of O₃, and the (4) University of Leeds HALO Doppler lidar (Pearson et al., 2009), which
measures 3-dimensional wind fields, as well as (5) a nadir pointing infrared pyrometer, and (6) an in-situ O$_3$ monitor.

The purpose of the CU AMAX-DOAS deployment was to measure horizontal and vertical distributions of NO$_2$, HCHO, CHOCHO and aerosol extinction over California, particularly over the SCAB, characterize boundary conditions for comparison with atmospheric models, and probe for pollutant concentrations above the boundary layer. A total of 52 research flights, each lasting up to ~4 h, were carried out over the two months period (206 flight hours). Flight plans were developed with the scientific objectives of mapping out horizontal and vertical distribution as well as characterizing transport of pollutants and validation of satellite retrievals. As this was the first deployment of this specific instrument pylon, different integration times and EA sequences were explored as well as the LabVIEW acquisition software was updated during the early portion of the campaign for optimization. Spectra were collected with 2 s integration time during the second half of the campaign and all the data presented in this paper are 2 s data unless otherwise noted. The most commonly used EA sequence included EAs 90° (zenith), 20°, 10°, 5°, 2°, 0°, –2°, –5°, –10°, –20° and –90° (nadir) with 0° corresponding to a view parallel to the horizon. The FOV of the telescope at nadir viewing geometry gives a footprint of ~0.55 km while flying at 4 km altitude. Typically, nadir spectra were recorded every 12–15 s, corresponding to a horizontal resolution of ~1 km.

3 Data analysis

3.1 DOAS analysis

The measured spectra were analyzed for NO$_2$, CHOCHO, HCHO, H$_2$O and O$_4$ using the DOAS method (Platt and Stutz, 2008) implemented by the WinDOAS software (Fayt and Van Roozendael, 2001). In DOAS, measured spectra are analyzed against a Fraunhofer reference spectrum, and absorption cross-sections of different absorbers
in the atmosphere are fitted simultaneously in a selected wavelength interval applying
a non-linear least-square fitting routine. A low order polynomial to account for scattering
processes and broadband absorption in the atmosphere as well as broadband instru-
mental features, a Ring reference spectrum to account for the filling in of Fraunhofer
lines due to rotational Raman scattering (Grainger and Ring, 1962), and an additional
intensity offset to account for instrumental stray light were also included in the fitting
procedure. The Ring spectrum is calculated from the Fraunhofer reference spectrum
with the DOASIS software (Kraus, 2006). A high altitude (∼ 4 km) zenith spectrum from
a clean, cloud free region of the same flight was included for the analysis of the indi-
vidual flight data. The choice of the zenith spectrum as Fraunhofer reference spectrum
minimizes the amount of tropospheric absorbers in the reference spectrum, allowing
for the detection of trace gases more sensitively. Since measured spectra are analyzed
with respect to a reference spectrum, the quantity retrieved from the DOAS analysis
is a differential slant column density (dSCD), which is the integrated excess concen-
tration of the absorber along the light path length with respect to the reference. The
trace gas absorption cross sections and analysis settings for the retrievals of the dif-
ferent trace gases are listed in Tables 1 and 2, respectively. Examples for spectral fits
of NO₂, CHOCHO, HCHO, O₃, and H₂O from the data measured during CalNex and
CARES campaigns are shown in Fig. 4. Detection limit for CU AMAX-DOAS instrument
in clean FT and polluted urban BL such as the SCAB for 30 and 2 s integration time
is listed in Table 3. It is roughly equivalent to the 3σ DOAS fit error for typical clean
FT (near Rayleigh atmosphere) and polluted urban BL atmospheric conditions (see
Fig. 10b for aerosol extinction profile). Note that detection limit highly depends upon
the atmospheric conditions during the time of measurement. The quantity retrieved
from a DOAS analysis, the dSCD is converted to VCD by using an air mass factor
(AMF). The VCD is the integral absorber concentration per unit area.

\[
VCD = \frac{dSCD}{dAMF} \tag{1}
\]
dAMF is usually calculated with the help of a radiative transfer program to convert the measured dSCD to a VCD. It requires a-priori knowledge of trace gas vertical concentrations and aerosol extinction coefficients along with other input parameters such as pressure, temperature, surface albedo (SA), aerosol asymmetry parameter, g, and aerosol single scattering albedo (SSA). NO$_2$ concentrations, profile shapes and aerosol scenarios are highly variable in the SCAB because of the variable sources and hence the probability of introducing a significant amount of error in radiative transfer calculations of AMFs is very high. Instead, we applied a simple geometric approximation for the nadir viewing geometry to convert dSCDs to VCDs. The geometric approach, its validity and error associated with this approximation are further discussed in Sect. 3.3.

### 3.2 Radiative transfer modeling

Since the AMAX-DOAS measurements are carried out in the open atmosphere using scattered sun light as the light source, the solar radiative transfer during the time of measurement needs to be modeled to interpret the retrieved data. The radiative transfer program McArtim (Monte Carlo atmospheric radiative transfer inversion model) (Deutschmann et al., 2011) used here is a fully spherical model and simulates radiative transfer in the atmosphere in the UV/vis/NIR spectral range using a Monte Carlo approach. In McArtim, the 3-D atmosphere is simulated as a 1-D modeled atmosphere divided in concentric spherical shells. The atmospheric conditions during the time of measurement in each vertical layer are assumed to be horizontally and vertically homogeneous. McArtim has the capability to simulate SCDs and AMFs of trace gases and aerosols needed for the interpretation of AMAX-DOAS data. Auxiliary input parameters used in the radiative transfer program were either measured aboard the aircraft (i.e. surface albedo), on the ground at CalNex ground site (Ryerson et al., 2012) (i.e. aerosol single scattering albedo), California Air Resources Board (CARB) (http://www.arb.ca.gov/homepage.htm) monitoring stations or typical values for urban environments based on previous studies (e.g. Dubovik et al., 2002).
3.3 Geometric approximation for conversion of dSCDs to VCDs

Under the geometric approximation, it is assumed that all the photons get scattered only once very close to the ground or are reflected from the surface before entering the telescope in nadir geometry. The geometric air mass factor (geoAMF) is then only a function of the solar zenith angle (SZA) and is given by

$$\text{geoAMF} = 1 + \frac{1}{\cos(SZA)}$$ (2)

The schematic of the geometric approximation is shown in the Fig. 1 inset.

In our DOAS analysis, a high altitude zenith spectrum from a clean background area is used as reference spectrum. Assuming this background zenith spectrum has no tropospheric NO$_2$, the nadir dSCDs can be considered as tropospheric SCDs for most flight performed at low SZA. At high SZA, stratospheric NO$_2$ contribution changes with SZA and hence requires independent removal. For such flights (18 out of 52), stratospheric NO$_2$ contribution was corrected by fitting a polynomial through all the zenith dSCDs above 1.8 km flight altitude and subtracting the polynomial from the nadir measurements. The resulting quantity is defined as the tropospheric SCDs. This quantity is then converted to VCD (VCD = SCD/geoAMF), and is defined as VCD below the aircraft.

Sensitivity studies using the radiative transfer model (RTM), McArtim were performed to estimate uncertainties associated with the geometric approximation. A range of conditions that could potentially occur during the time of measurements were explored for this study. A representative sample of the results is summarized in Table 4, as the relative error in the geoAMF assumption compared to AMFs calculated using the RTM for different scenarios specified in the table. The results for the most likely atmospheric state in the SCAB (surface albedo, SA = 0.1; single scattering albedo, SSA = 0.94; asymmetry parameter, g = 0.68; AOD = 0.4, boundary layer height BLH = 1.0 km; NO$_2$ = 10 ppb) is also shown in Table 4; it is based on ancillary measurements aboard the aircraft, CalNex ground site at Pasadena, CA and CARB 7256.
ground monitoring stations. Thomson et al. (2012) reported an average value for SSA
of 0.92 at 532 nm during the entire CalNex campaign at Pasadena. They find SSA
values to be slightly higher during the day time, when our measurements were taken.
AOD measured at the AERONET station at Pasadena, CA showed AOD values to be
lower than 0.4 at 440 nm for almost all of summer 2010, and the AOD of 0.4 likely rep-
5
resents an upper limit to provide a conservative estimate of relative error. It should be
noted that these quantities are wavelength dependent. The largest source of error was
found to be surface albedo (see Table 4), which is constrained using the measurement
aboard the aircraft. Notably, our SA measurements also provide means to filter data
for conditions where the error may exceed 10 %. The error from using the geoAMF
compared to AMF calculated for the most likely atmospheric state in SCAB is plotted
as a function of SZA in Fig. 5. Based on this, a SZA cutoff of 65° was used to constrain
10
the error in the NO$_2$ vertical columns (85 % of flight time with SZA < 65°). With these
filters, the error in geoAMF is < 7 % for most conditions, and slightly larger (error < 25 %
in all cases) for SZA ~ 65° or during high altitude flights over low surface albedo. The
error associated with the geoAMF is consistent with previous airborne DOAS studies
which used the geometric approximation. Melamed et al. (2003) estimated the error in
NO$_2$ VCD from the geometric approximation to be ~ 20 % based on the discrepancies
between measured and modeled O$_2$ AMF. To the best of our knowledge, there have
been no previous deployments of AMAX-DOAS with simultaneous SA measurements
by independent sensors. The higher SA (~ 10 % at 479 nm) is found widespread in the
SCAB, and has the favorable effect to reduce errors from the geoAMF assumption due
to compensating effects in the radiative transfer calculations.

3.4 Aerosol extinction profile retrieval

In the near-UV and visible wavelength range, the change in photon path length com-
25 pared to a Rayleigh atmosphere and hence the measured dSCDs of a trace gas de-
pends mainly on the aerosol extinction profile. Thus, if the vertical distribution of an ab-
sorber is well known, the dSCD measurements of such species can be exploited to infer
aerosol properties. The collisional complex of oxygen, O$_4$ is one such species (Honninger et al., 2004; Wagner et al., 2004; Wittrock et al., 2004; Clemer et al., 2010). The O$_4$ concentration varies with pressure, temperature and square of the concentration of O$_2$. Hence, the dSCD measurements of O$_4$ can be used to calculate aerosol extinction profiles. O$_4$ dSCD measurements from ground-based and airborne MAX-DOAS have previously been used for aerosol extinction profile and aerosol optical depth (AOD) retrievals (Clemer et al., 2010; Merlaud et al., 2011 and references within). We used an iterative forward model approach to obtain the aerosol extinction profile. Under this approach a set of measured O$_4$ SCDs, $y$, is related to the aerosol extinction vertical profile, $x$, by forward model $F$ such that

$$ y = F(x, b) + \epsilon $$

where $b$ are forward model parameters that are not retrieved and $\epsilon$ is the sum of measurement and model errors. For $0^\circ$ EA, i.e. parallel to the horizon, the measurement is almost entirely sensitive to the altitude of measurement and almost all of the information contained in the SCD comes from that particular altitude. We exploit this property and retrieve the aerosol extinction profile by using a modified onion peeling algorithm using $0^\circ$ EA O$_4$ SCD measurements. First the extinction above the highest altitude is constrained using upward EA scans performed at that altitude. Then the aerosol extinction values at the subsequent altitudes during the descent are determined using the set of $0^\circ$ EA O$_4$ SCD measurements at those altitudes. Aerosol extinction below the lowest aircraft altitude is obtained using downward EA scans performed at the lowest altitude. The process is iterated to account for any information on O$_4$ SCDs for $0^\circ$ EA at a given altitude from O$_4$ column below the measurement altitude, until measured and modeled O$_4$ SCDs agree. The profile is then verified using other angles in the EA scans during the descent/ascent. It should be noted that this approach is feasible only due to the ability to maintain the desired EAs within narrow error bound also during descent/ascent of the aircraft, as discussed in Sect. 2.5.
The relative error in $O_4$ SCDs at different altitudes in the atmosphere for different pointing uncertainties for a $0^\circ$ EA is illustrated in Fig. 6. An uncertainty of 1–2$^\circ$, which can easily happen on an airborne platform, could result in 20–80% error above 10 km. Considering a non-linear relationship between $O_4$ SCD and aerosol extinction, this could result in even larger errors when $O_4$ SCDs are used to retrieve the aerosol extinction profile. This highlights the need for a motion compensation system to maintain pointing accuracy of the telescope.

Sensitivity studies were performed to estimate the error in the retrieved aerosol extinction profile due to uncertainties in model parameters and angle accuracy. We studied the effects of SA, SSA, asymmetry parameter, temperature, and angle uncertainty of the telescope on aerosol extinction coefficients at 477 nm. Results from the study are summarized in Table 5. The asymmetry parameter uncertainty ($g = 0.68$ to 0.75) could result in as much as 10% relative error in extinction values. A 5°C temperature uncertainty could also result in similar relative error as the $O_4$ concentration in the atmosphere is temperature dependent (density effect). We used temperature measured aboard the aircraft to minimize this error. Angle accuracy uncertainty was found to result in large extinction errors ($> 0.01 \text{ km}^{-1}$) in the transition layer at the top of the boundary layer and around elevated layers. It points to the possibility of uncertainty in altitude of aerosol layers in the extinction profile. Angle accuracy uncertainties to our knowledge have not previously been considered for error estimates for vertical profiles from airborne DOAS measurements, but it could be the most important and largest source of error in the retrieved profiles, especially for transition layers.

### 3.5 Trace gas vertical profile retrieval

Trace gas vertical profile retrieval algorithm is based on the concept of Optimal Estimation (Rodgers, 2000). The use of this technique for profile retrieval from AMAX-DOAS measurements have been described in detail before (e.g. Bruns et al., 2004) and hence will only be introduced here briefly. A set of measurements $\mathbf{y}$, which in our case are...
trace gas SCDs for different LOS can be related to a vertical distribution, \( x \) by the forward model \( F \) as shown in Eq. (3).

Equation (3) can be rewritten in a linearized form as:

\[
y = Kx + \varepsilon
\]  

(4)

where \( K \) defined as \( \frac{\partial SCD}{\partial x} \) is the weighting function matrix which expresses the sensitivity of a measurement, \( y \) to \( x \). We used the maximum a posterior solution as described in Rodgers (2000) to solve Eq. (4):

\[
x = x_a + \left( K^T S_{\varepsilon}^{-1} K + S_a \right)^{-1} K^T S_{\varepsilon}^{-1} (y - Kx_a)
\]  

(5)

where \( x_a \) is the a priori profile and \( S_a \) and \( S_{\varepsilon} \) are the a priori error and measurement error covariance matrices, respectively. The a priori profile is used to constrain the above described problem as it is generally ill-posed.

The solution given by Eq. (5) is a weighted mean of the a priori profile and the information from the measurement. This weight is given by the averaging kernel matrix \( A \),

\[
A = \left( K^T S_{\varepsilon}^{-1} K + S_a \right)^{-1} K^T S_{\varepsilon}^{-1} K
\]  

(6)

The retrieval at any layer is an average of the whole profile weighted by the row of the averaging kernel matrix corresponding to that layer. The averaging kernel matrix also contains information about the number of independent pieces of information retrieved, and an estimate of the vertical resolution of the retrieved profile at a given level. The trace of the averaging kernel matrix, \( A \), gives the degrees of freedom (DOF), i.e. number of independent pieces of information retrieved. The FWHM of the main peak of an averaging kernel at any layer gives the estimate of the vertical resolution of the retrieved profile at that layer. For an ideal retrieval scenario, \( A \) is the identity matrix, the DOF equal the number of retrieved profile layers and the averaging kernels peak at their corresponding altitudes. In reality, the retrieved profile is a smoothed version of the true profile.
4 Results and discussion

4.1 Horizontal distribution of NO$_2$

As an example, a map of NO$_2$ VCD distribution in the SCAB from RF# 46 on 16 July 2010 (10:30–14:10 PDT) is shown in Fig. 7. The small footprint (∼ 1 km along the flight track) of the measurement allows us to clearly identify local hotspots and pollution sources. The NO$_2$ map in Fig. 7 reflects our understanding of the NO$_x$ sources and its relatively short life time (∼ 4 h). Clear NO$_2$ hotspots can be observed around downtown Los Angeles and Ontario, along the major highway, State Route 210 and at intersections of major highways. In contrast, very little NO$_2$ is seen in the eastern part of the basin, and over the High Desert to the northeast, where there are no significant local sources of NO$_x$. The footprint of CU AMAX-DOAS is comparable to air quality models, and smaller than that of current solar stray light satellite observations, which also measure VCDs of trace gases; this makes this data set an excellent opportunity to evaluate emissions in air quality models and validate satellite observations. A first application of CU AMAX-DOAS to test NASA NO$_2$ VCD retrievals from the OMI/AURA satellite instrument is currently in preparation (Oetjen et al., 2012).

4.2 Validation of NO$_2$ vertical column

To validate the retrieval of our NO$_2$ VCDs by CU AMAX-DOAS using the geometric approximation, we compare our observations with NO$_2$ VCDs from ground based MAX-DOAS instruments. Two CU GMAX-DOAS instruments (Sinreich et al., 2010; Coburn et al., 2011) were deployed at the CalNex ground site (Ryerson et al., 2012) in Pasadena, CA, the Fontana Arrows CARB monitoring network station and the CARES T1 (Zaveri et al., 2012) site in Cool, CA at various times of the campaign. GMAX-DOAS operates in the same principle as AMAX-DOAS. Spectra measured at off-axis angles were analyzed for NO$_2$ using a closest zenith reference spectrum in time. The retrieved NO$_2$ dSCDs for 20° EA were converted to VCDs using a dAMF calculated by McArtim.
This EA was chosen to minimize the effect of uncertainties in model parameters, especially NO₂ profile shape and magnitude and aerosols. Sensitivity studies were performed to estimate the error in calculated dAMF due to model parameter uncertainties. We estimate the error in GMAX-DOAS VCDs to be around 10%. Further details about GMAX-DOAS measurements during the CalNex and CARES campaigns can be found in (Ortega et al., 2012). GMAX-DOAS instruments at Pasadena and Fontana Arrows were both pointing in east and west directions while the one at the CARES T1 site was looking north and south. Those GMAX-DOAS instruments are capable of making a full 180° EA scan.

The NOAA Twin Otter was frequently routed over these ground sites. The correlation plot between the CU AMAX-DOAS and GMAX-DOAS instruments is shown in Fig. 8. Correlations showed sensitivity to filtering data by criteria such as the distance of the plane and ground site, the relative azimuth angle between plane heading and ground viewing, and inhomogeneous air mass. The inhomogeneity of air mass was measured by GMAX-DOAS, which observed differences in NO₂ VCDs in the east and west view of up to $2.5 \times 10^{16}$ molecules cm$^{-2}$. Figure 7 gives an idea of the NO₂ VCD variability as mapped by CU AMAX-DOAS. Filtering for data within 5 km radius of the ground site, clouds, SZA < 65°, aircraft altitude < 4 km, and < $1.5 \times 10^{16}$ molecules cm$^{-2}$ NO₂ VCD difference in east/west view of GMAX-DOAS instruments in SCAB, as well as coincident measurements within a 10 min of the aircraft overpass, resulted in a correlation with slope $0.86 \pm 0.03$, and offset in VCD of $-0.8 \pm 3.7 \times 10^{14}$ molecules cm$^{-2}$ ($R^2 = 0.96$) (grey dots in Fig. 8). The slope of the linear fit line is skewed by the measurements at CARES T1 site which are near or below the detection limit of both the instruments but nevertheless still a very good agreement between the two instruments. If only measurements in SCAB are considered, and filtering is further constrained (relative azimuth angle between plane heading and ground viewing < ±15°, and variability in NO₂ VCD for both instruments < $8 \times 10^{15}$ molecules cm$^{-2}$), the slope increases to $0.95 \pm 0.09$, offset in VCD of $2.5 \pm 1.4 \times 10^{15}$ molecules cm$^{-2}$ ($R^2 = 0.86$)(Fig. 8). This sensitivity to filtering criteria reflects upon the inhomogeneity of the SCAB air mass.
4.3 Determination of $O_4$ SCD in the reference spectrum

The scale height of $O_4$ in the atmosphere is $\sim 4$ km and as our measurements were usually performed below 4 km altitude, it is important to quantify the $O_4$ SCD contained in the reference spectrum ($SCD_{\text{ref}}$) in order to accurately retrieve the aerosol extinction profile. Merlaud et al. (2011) used a linear regression between measured dSCD and calculated SCD using RTM for airborne measurements above 5.5 km in the Arctic to determine $SCD_{\text{ref}}$ and the dSCD correction factor, $\alpha$:

$$SCD = \alpha \times dSCD + SCD_{\text{ref}}$$

A dSCD correction factor ($\alpha$) for $O_4$ dSCD measurements has been used to retrieve aerosol extinction from MAX-DOAS measurements. The value for the correction factor is different between different environments and research groups, and wavelength, and ranges from 0.75 to 0.89 (Wagner et al., 2009; Clemer et al., 2010; Merlaud et al., 2011; Zieger et al., 2011). The source for a need of $\alpha$ is currently not well understood. It has been speculated that the need for $\alpha$ could be due to the temperature dependence of the $O_4$ absorption cross-section (Wagner et al., 2009; Clemer et al., 2010). Indeed, a temperature uncertainty in the $O_4$ absorption cross-section has been reported (Wagner et al., 2002).

We employed the same approach as Merlaud et al. (2011) to determine $SCD_{\text{ref}}$ and $\alpha$. Temperature and pressure as measured on the plane were used to prescribe the vertical distribution of $O_4$ in the model. Temperature and pressure profiles were extrapolated to the ground using the lapse rate and scale height determined from the measurements, respectively. The temperature at the ground was 36.7 °C and the pressure was 966 mbar at the ground. Comparison of extrapolated temperature and pressure values at the ground with measurements at the nearest CARB monitoring stations showed good agreement within ±2 °C and ±10 mbar, respectively. Profiles above the aircraft were extrapolated based on the mean temperature and pressure profiles measured at Joshua Tree, CA. The $O_3$ profile was also constructed similarly and was measured by the NOAA TOPAZ lidar aboard the plane. Based on the regression analysis,
\( \alpha = 0.99 \pm 0.01 \) for 477 nm and hence it was concluded that a scaling factor was not needed to explain our measurements. Figure 9 shows a correlation analysis between simulated \( \text{O}_4 \) SCDs with our retrieved aerosol profile (see Fig. 10a) and measured \( \text{O}_4 \) SCDs at 477 nm for a low approach at Brackett airfield during RF#46 (see more details below). Low approach is a maneuver over an airport in which the pilot intentionally does not make a contact with the runway. An \( \text{O}_4 \) reference SCD of \( 9 \times 10^{42} \text{ molecule}^2 \text{cm}^{-5} \) based on the regression has been added to the measured dSCDs to convert them to SCDs.

### 4.4 Examples of retrieved vertical profiles

Figures 10 and 11 show retrieved vertical profiles of aerosol extinction coefficient and trace gas mixing ratio for the above mentioned low approach during RF#46. The aircraft was flying at \( \sim 3.1 \) km above ground level (AGL), made a slow descent to an altitude of \( \sim 0.6 \) km AGL at the airport, and then ascended again. The telescope was scanning a set of EAs (\(-90^\circ, -5^\circ, -2^\circ, 0^\circ, 2^\circ, 5^\circ, 90^\circ\)) during the low approach. A complete set of EAs was also measured at the highest altitude just before the descent and at the lowest point before starting to ascent in order to characterize the air mass above and below the aircraft. The descent portion of the low approach took \( \sim 8 \) min.

#### 4.4.1 Aerosol extinction coefficient profiles

Aerosol extinction coefficient vertical distribution retrieved at 477 nm is shown in Fig. 10b. The extinction profile was retrieved by iteratively minimizing the residual between measured and simulated \( \text{O}_4 \) SCDs, see Sect. 3.4. Figure 10a illustrates the agreement between the measured and modeled \( \text{O}_4 \) SCDs at 477 nm for EA 0°. The corresponding aerosol extinction profile is presented in Fig. 10b. The aerosol extinction profile in Fig. 10b indicates that most of the aerosols are located inside the boundary layer (up to 0.9 km, indicated by the decrease in \( \text{NO}_2 \) and aerosol) with a 500 m thick elevated layer at \( \sim 2.5 \) km. Error contribution in retrieved extinction due EA uncertainty
of 0.35° is shown Fig. 10c and illustrates that pointing accuracy is needed especially to minimize error in transition layers and elevated layers.

Integration of the extinction coefficient profile over altitude gives AOD, the total load of aerosols in the atmosphere. AOD at 477 nm from the profile in Fig. 10b is 0.16±0.03, and agrees well with 0.18±0.02 at 500 nm measured by AERONET station located at Pasadena. The AOD values for the Aerionet station reported here are hourly averages and standard deviations for the hour of the low approach. Pasadena is located 30 km west of the Brackett airfield; the telescope was pointing towards the west during our low approach, and measurements inherently average over spatial scales of typically few 10 km. The excellent agreement between the AOD calculated from our profiles and AERONET station adds confidence to our retrieval approach and accuracy of the retrieved profile. To our knowledge this is the first demonstration of quantitative retrieval of aerosol extinction from O_4 dSCD observations that does not require a correction factor.

4.4.2 Trace gas vertical profiles

Figure 11 shows the retrieved NO_2, CHOCHO, HCHO and H_2O mixing ratio profiles from the same low approach. NO_2, CHOCHO, and HCHO vertical profiles have a very similar shape, with most of the trace gases located inside the boundary layer. This is not surprising since most of the sources for these gases are close to the surface. On the other hand, the H_2O profile is almost linearly decreasing with altitude. The retrieved NO_2 profile shows an average urban boundary layer value of 14.2±1.5 ppb (at the surface: 1 ppb ≈ 2.46 × 10^{10} molecules cm^{-2} at sea level, and 298 K temperature). The hourly NO_2 data recorded at the nearest CARB monitoring station at Pomona is 13 ppb. Pomona station is located ~ 3 km south of the Brackett airfield. Our retrieved NO_2 surface mixing ratio agrees well with the measurement at the ground station. The CHOCHO profile shows a BL value of 274 ± 48 ppt. It also exhibits an elevated layer of glyoxal with ~ 33 ± 8 ppt at around 2.5 km (Fig. 11b). The lower error bars in the free troposphere compared to the BL is due to two reasons: (1) the dSCD retrieval
error is slightly smaller in the FT, where aerosol extinction presents less of a limitation, and (2) in our low approach, the aircraft only descended down to an altitude of \( \sim 600 \) m AGL and a set of downward EAs at that altitude was used to probe the lower altitudes. Hence, the measurement has lower sensitivity below 600 m, and results in a larger smoothing error in the retrieved profile. The observation of 33 ppt glyoxal in a layer aloft that is decoupled from the boundary layer coincides with the altitude where a layer of enhanced aerosol is observed in the aerosol extinction profile (Fig. 10b). The coexistence of glyoxal and aerosol aloft could indicate the in-situ production of glyoxal from oxidation of volatile organic carbons (VOCs) that have been transported along with the aerosols. Laboratory studies show consistent evidence of glyoxal uptake by aerosols forms secondary organic aerosol (SOA) (Liggio et al., 2005; Volkamer et al., 2009b; Trainic et al., 2011). However, if this process is partly reversible, the collocation of glyoxal and aerosol could also point to aerosols as a source of glyoxal aloft. It should be noted that while glyoxal dSCDs at the elevated layers are close to the detection limit for our 2 s data, this detection limit can be improved by longer averaging times. An elevated layer of \( \text{O}_3 \) is also observed in the NOAA TOPAZ lidar data at the same altitude (C. Senff, personal communication, CIRES and NOAA, 2012). The water vapor mixing ratio inside the BL corresponds to a relative humidity, \( \text{RH} = 23 \pm 5 \% \). Coincident measurements of RH at nearby CARB monitoring stations varied from \( \text{RH} = 23 \% \) (Ontario International Airport) to \( \text{RH} = 34 \% \) (Upland). The good agreement of RH demonstrates control of radiation fields in the inversion.

A 250 m altitude grid was chosen for the retrieval of trace gases. This grid height was chosen based on the FOV of the telescope, rate of aircraft descent and time it took to complete one EA scan cycle during the descent. The averaging kernels for all the trace gases indicate a constant sensitivity for the whole low approach except the lowest layer at the surface. The DOF are 12.5, 11.5, 11.6, and 11.8 for \( \text{NO}_2 \), CHOCHO, HCHO, and \( \text{H}_2\text{O} \), respectively. This shows that the instrument has similar capability to resolve the vertical distribution of weak and strong absorbers, i.e. is essentially independent of the signal-to-noise at which the gases are detected (see Fig. 4). The sensitivity of
the retrieved profile to different a priori profiles was also tested, and resulted in small changes, inside the BL, which were always within the error bars shown. The lower averaging kernels below 600 m are explained from the observing geometry of the low approach (see above). While this decrease in sensitivity for other EAs compared to $0^\circ$ for a given atmospheric layer does not appear to limit our ability to infer meaningful information near the surface (see this section above), it highlights the benefit of capabilities to maintain $EA = 0^\circ$ during aircraft ascent/descent to systematically probe the atmosphere with maximum sensitivity, and vertical resolution.

5 Conclusions

An Airborne MAX-DOAS instrument equipped with a motion-stabilized scanning telescope to collect solar stray light photons provides accurate means to probe atmospheric composition in terms of the horizontal and vertical distributions of multiple trace gases and aerosols simultaneously and sensitively by means of a single, portable, instrument.

The CU AMAX-DOAS instrument is validated by comparison with NO$_2$ VCDs measured by ground-based MAX-DOAS. A sensitivity study using radiative transfer modeling reveals that the geometric approximation is a viable option to convert NO$_2$ dSCD to VCD for measurements below the plane. This approximation is found to be accurate over Southern California, where elevated surface albedo ($\sim 10\%$ at 479 nm, measured aboard the plane) compensates for reduced sensitivity due to aerosols. We estimate the error in the NO$_2$ vertical columns due to the geometric approximation to be less than 7\% under most conditions for $SZA < 65^\circ$; a slightly larger error ($< 25\%$ in all cases) is found for $SZA \sim 65^\circ$ or during high altitude flights over low surface albedo. These results emphasize benefits of measuring surface albedo and AOD by independent sensors.

For a case study, vertical profiles of NO$_2$, CHOCHO, HCHO, H$_2$O, and aerosol extinction coefficient at 477 nm showed that trace gases and aerosols are located mostly
inside the BL, though the presence of elevated layer was observed as well. Sensitivity studies show that the main error source in the retrieved vertical profiles of aerosol extinction coefficient is the uncertainty in the asymmetry parameter of aerosol scattering. Further, sensitivity studies highlight the need of pointing accuracy of the telescope on moving platforms like an aircraft to accurately retrieve vertical distributions of trace gases and aerosol extinction coefficients. The accuracy of our motion compensation system is found to be < 0.35° by comparison with an independent inertial system.

An ~ 500 m thick layer at around 2.5 km altitude AGL was observed that was decoupled from the BL, and contained 33 ± 8 ppt CHOCHO, NO₂ below the detection limit (30 ppt, for 2 s integration time), 545 ± 114 ppt HCHO, 0.029 ± 0.004 km⁻¹ ε₄₇₇, corresponding to a partial vertical columns of 4.14 ± 1.12 × 10¹³ molecules cm⁻² CHOCHO, 7.10 ± 1.75 × 10¹⁴ molecules cm⁻² HCHO, and partial AOD of 0.047 ± 0.007 at 477 nm. This elevated layer contained ratios of CHOCHO/HCHO of 0.06 ± 0.02, compared to 0.027 ± 0.006 inside the BL. The concurrent location of elevated aerosol extinction at the same altitude indicates either collocated glyoxal sources from VOC oxidation, or the release of glyoxal that was initially taken up as SOA back to the gas-phase. The increase in the CHOCHO/HCHO ratio with altitude appears to be outside error bars, and the cause for this altitude dependence deserves further investigation.

The capabilities of CU AMAX-DOAS are not limited to the parameters presented here, and also include measurements of reactive species, like halogen oxide radicals, and aerosols extinction coefficients at other wavelengths. The absence of sampling lines, and inherent averaging over extended spatial scales enable the AMAX-DOAS technique to bridge between ground-based networks, atmospheric models, and satellites, and holds as yet unexplored potential to advance airborne atmospheric observations, and improve our understanding of the processes taking place in the atmosphere. The CU AMAX-DOAS deployment during the CalNex and CARES field campaigns makes a 10 week long data set available that we plan to apply for such studies.
Appendix A

List of frequently used abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AGL</td>
<td>above ground level</td>
</tr>
<tr>
<td>AMAX-DOAS</td>
<td>airborne multi-axis differential optical absorption spectroscopy</td>
</tr>
<tr>
<td>AMF</td>
<td>air mass factor</td>
</tr>
<tr>
<td>AOD</td>
<td>aerosol optical depth</td>
</tr>
<tr>
<td>BL</td>
<td>boundary layer</td>
</tr>
<tr>
<td>BLH</td>
<td>boundary layer height</td>
</tr>
<tr>
<td>CalNex</td>
<td>California Research at the Nexus of Air Quality and Climate Change</td>
</tr>
<tr>
<td>CARB</td>
<td>California Air Resources Board</td>
</tr>
<tr>
<td>CARES</td>
<td>Carbonaceous Aerosols and Radiative Effects Study</td>
</tr>
<tr>
<td>dAMF</td>
<td>differential air mass factor</td>
</tr>
<tr>
<td>dSCD</td>
<td>differential slant column density</td>
</tr>
<tr>
<td>DOF</td>
<td>degrees of freedom</td>
</tr>
<tr>
<td>EA</td>
<td>elevation angle</td>
</tr>
<tr>
<td>FOV</td>
<td>field of view</td>
</tr>
<tr>
<td>FT</td>
<td>free troposphere</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>geoAMF</td>
<td>geometric air mass factor</td>
</tr>
<tr>
<td>LOS</td>
<td>lines of sight</td>
</tr>
<tr>
<td>MAX-DOAS</td>
<td>multi-axis differential optical absorption spectroscopy</td>
</tr>
<tr>
<td>RF</td>
<td>research flight</td>
</tr>
<tr>
<td>RTM</td>
<td>radiative transfer model</td>
</tr>
<tr>
<td>SA</td>
<td>surface albedo</td>
</tr>
<tr>
<td>SCD</td>
<td>slant column density</td>
</tr>
<tr>
<td>SCAB</td>
<td>South Coast Air Basin</td>
</tr>
</tbody>
</table>
SOA secondary organic aerosol
SSA single scattering albedo
SZA solar zenith angle
VCD vertical column density

Acknowledgements. This work was supported by the California Air Resource Board (CARB) contract 09-317, the National Science Foundation CAREER award ATM-847793, CU startup-funds (RV) and an ESRL-CIRES Graduate Fellowship (SB). The authors like to thank Tim Deutschmann, University of Heidelberg for the radiative transfer code, McArtim, David Thomson for the software support, Caroline Fayt and Michel van Roozendael for the WINDOAS software and the NOAA Twin Otter research flight crew.

References


Table 1. List of trace gas references used for DOAS analysis.

<table>
<thead>
<tr>
<th>No.</th>
<th>Molecule</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>NO$_2$ (220 K)</td>
<td>Vandaele et al. (1997)</td>
</tr>
<tr>
<td>2</td>
<td>NO$_2$ (294 K)</td>
<td>Vandaele et al. (1997)</td>
</tr>
<tr>
<td>3</td>
<td>O$_3$ (223 K)</td>
<td>Bogumil et al. (2003)</td>
</tr>
<tr>
<td>4</td>
<td>O$_3$ (243 K)</td>
<td>Bogumil et al. (2003)</td>
</tr>
<tr>
<td>6</td>
<td>CHOCHO (298 K)</td>
<td>Volkamer et al. (2005)</td>
</tr>
<tr>
<td>7</td>
<td>HCHO (298 K)</td>
<td>Meller and Moortgat (2000)</td>
</tr>
<tr>
<td>8</td>
<td>H$_2$O</td>
<td>Rothman et al. (2005)</td>
</tr>
<tr>
<td>9</td>
<td>O$_4$</td>
<td>Greenblatt et al. (1990)</td>
</tr>
</tbody>
</table>
Table 2. Summary of DOAS analysis settings for different trace gases. 2 Rings (warm and cold) were fitted for HCHO retrievals, and spectra collected for SZA $<\sim 65^\circ$ were only analyzed and hence BrO was not included in the fit.

<table>
<thead>
<tr>
<th>Trace gas</th>
<th>Wavelength range (nm)</th>
<th>Fitted absorber</th>
<th>Polynomial order</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO$_2$</td>
<td>433–460</td>
<td>1, 2, 3, 6, 8, 9</td>
<td>3</td>
</tr>
<tr>
<td>CHOCHO</td>
<td>433–460</td>
<td>1, 2, 3, 6, 8, 9</td>
<td>3</td>
</tr>
<tr>
<td>HCHO</td>
<td>335–357</td>
<td>1, 2, 3, 4, 5, 7</td>
<td>3</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>435–455</td>
<td>1, 2, 4, 5, 6, 8</td>
<td>3</td>
</tr>
<tr>
<td>O$_3$</td>
<td>350–386</td>
<td>1, 2, 3, 4, 5</td>
<td>3</td>
</tr>
<tr>
<td>O$_4$</td>
<td>440–490</td>
<td>1, 2, 4, 5, 8</td>
<td>5</td>
</tr>
</tbody>
</table>


Table 3. Detection limits of CU AMAX-DOAS instrument in the clean free troposphere and the boundary layer in polluted urban conditions like SCAB for different integration times.

<table>
<thead>
<tr>
<th>Trace gas</th>
<th>Free troposphere (FT) (ppt)</th>
<th>Boundary layer (BL) (ppt)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>30 s</td>
<td>2 s</td>
</tr>
<tr>
<td>NO₂</td>
<td>5</td>
<td>30</td>
</tr>
<tr>
<td>CHOCHO</td>
<td>3</td>
<td>16</td>
</tr>
<tr>
<td>HCHO</td>
<td>98</td>
<td>290</td>
</tr>
<tr>
<td>ε₄₇₇nm</td>
<td>0.002</td>
<td>0.002</td>
</tr>
<tr>
<td>ε₃₆₀nm</td>
<td>0.004</td>
<td>0.004</td>
</tr>
</tbody>
</table>
Table 4. Relative error of geometric approximation compared to AMF calculated at 455 nm using radiative transfer program McArtim under different scenarios.

<table>
<thead>
<tr>
<th>Altitude (km)</th>
<th>Solar zenith angle (SZA)</th>
<th>Most probable conditions</th>
<th>Boundary layer height (m)</th>
<th>NO$_2$ concentration (ppb)</th>
<th>Surface albedo (SA)</th>
<th>Single scattering albedo (SSA)</th>
<th>Aerosol optical depth (AOD)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 (low)</td>
<td>20</td>
<td>6.3</td>
<td>3.3</td>
<td>9.0</td>
<td>7.2</td>
<td>5.6</td>
<td>3.0</td>
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<td>5.9</td>
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<td>6.3</td>
<td>6.0</td>
<td>7.0</td>
<td>15.3</td>
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<tr>
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<td>20</td>
<td>3.0</td>
<td>6.3</td>
<td>0.3</td>
<td>2.8</td>
<td>3.2</td>
<td>15.2</td>
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<tr>
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<td>40</td>
<td>5.4</td>
<td>8.6</td>
<td>3.1</td>
<td>4.1</td>
<td>5.1</td>
<td>15.9</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>16.1</td>
<td>16.4</td>
<td>14.0</td>
<td>14.5</td>
<td>16.5</td>
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Table 5. Uncertainty in aerosol extinction coefficient due to uncertainty in model input parameters.

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<thead>
<tr>
<th>Parameter</th>
<th>Uncertainty in parameter</th>
<th>Uncertainty in extinction coefficient</th>
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<tr>
<td>Surface albedo</td>
<td>±0.05</td>
<td>&lt; 2 %</td>
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<tr>
<td>Single scattering albedo</td>
<td>±0.05</td>
<td>&lt; 2 %</td>
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<tr>
<td>Asymmetry parameter</td>
<td>±0.07</td>
<td>Up to 10 %</td>
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<tr>
<td>Temperature</td>
<td>±5 °C</td>
<td>Up to 10 %</td>
</tr>
<tr>
<td>Pointing accuracy</td>
<td>±0.35°</td>
<td>Mostly in transition layer</td>
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Fig. 1. Schematic of the AMAX-DOAS measurement principle. Individual EAs contain different amount of information from different layers in the atmosphere. The inset (green triangle) illustrates the geometric approximation used to convert nadir dSCDs to VCDs.
Fig. 2. CU AMAX-DOAS instrument setup aboard the NOAA Twin Otter during the CalNex and CARES campaigns.
Fig. 3. (A) Distribution of difference in pitch angle of the aircraft measured at real time by the MMQ-G angle sensor of the CU-AMAX-DOAS and aircraft avionics system of NSF/NCAR GV HIAPER aircraft during a research flight on 24 February 2012. 1σ angle accuracy (0.29°) of the MMQ-G sensor is shown in yellow dotted lines. 1σ for the Gaussian fit (black line) is 0.16°. Distribution of elevation angle accuracy of the CU AMAX-DOAS telescope (B) from the above mentioned flight on NSF/NCAR GV HIAPER flight, (C) during RF#46 aboard NOAA Twin Otter on 16 July 2010. 1σ for the Gaussian fits (black lines) are 0.12° and 0.2° for instrument aboard HIAPER and Twin Otter aircraft respectively and are within the resolution of the motor internal encoder (0.2°), shown in blue dotted lines. Brown dashed lines represent the motor tolerance level (0.7°) set in the software before an automatic reset of the motor position takes place. The red lines represent the cumulative densities.
Fig. 4. Spectral proofs for the detection of: (A) CHOCHO, (B) HCHO, (C) O₄ at 360 nm, (D) NO₂, (E) H₂O and (F) O₄ at 477 nm. CHOCHO and NO₂ fits are from 14 July 2010 at 22:08 UTC at ~150 m AGL. HCHO and H₂O fits are from 16 July 2010 at 20:19 UTC at ~600 m AGL. O₄ fits are from the same flight at 20:11 UTC at ~3000 m AGL. The black lines represent the measured spectra and red lines are fitted reference cross sections. Note that for NO₂ and O₄ at 477 nm, the absorptions are so strong that the black lines are not visible. All the fits are for 0° EA.
Fig. 5. (A) Relative error of geometric air mass factor (geoAMF) compared to AMF calculated using RTM, McArtim for flight altitude of 3.5 km (green) and 2 km (blue) AGL, for most likely atmospheric conditions in South Coast Air Basin (SCAB). (B) AMF calculated using McArtim (green and blue) and geoAMF (black). Most likely atmospheric state in SCAB: surface albedo = 0.10, single scattering albedo = 0.94, g parameter = 0.68, aerosol optical depth = 0.4, boundary layer height = 1 km and NO$_2$ mixing ratio = 10.0 ppb.
Fig. 6. (A) Vertical profile of O₄ SCDs calculated for 0° EA at 477 nm using McArtim (US standard atmosphere with exponential aerosol extinction profile with extinction of 0.2 km⁻¹ at the ground and 2.5 km scale height). (B) Relative error in O₄ SCDs for 0.35° (blue), 1° (red) and 2° (green) pointing error of the telescope at 0° EA. The solid and dashed lines represent angles above and below the horizon, respectively.
Fig. 7. (A) Map showing horizontal distribution of NO$_2$ VCDs below the aircraft from RF#46 on 16 July 2010 (10:30–14:10 Pacific Daylight Time, PDT) in the SCAB. GMAX-DOAS instruments deployment sites and the base airport for the Twin Otter are shown as red targets. (B) Time trace of flight altitude (blue), ground altitude (black) and SZA (green) from the same flight.
**Fig. 8.** Correlation plot of NO$_2$ VCDs between CU AMAX-DOAS and two GMAX-DOAS instruments deployed in California during the CalNex and CARES field campaigns. Grey dots represent all data from both CalNex and CARES campaigns (see text for filtering conditions). Data from CalNex further constrained for relative azimuth between plane heading and GMAX-DOAS viewing geometry < ±15° and NO$_2$ VCD variability < 8 × 10$^{15}$ molecules cm$^{-2}$ are shown in red and blue. Black line is the linear fit through the colored points.
Fig. 9. Correlation plot of modeled and measured O₄ SCDs at 477 nm for the case study shown in Fig 10b. SCD of the zenith reference (9 × 10⁴² molecules² cm⁻⁵) has been added to the measured O₄ dSCDs. Forward viewing geometry includes 0°, ±2°, ±5° EAs.
Fig. 10. (A) Measured (green) and simulated (red) vertical profiles of O₄ SCDs for EA 0° at 477 nm from a low approach at Brackett airfield during RF#46 on 16 July 2010 in SCAB. (B) Corresponding aerosol extinction vertical profile retrieved at 477 nm. (C) Error contribution in extinction due to angle uncertainty of ±0.35°. Note that the aircraft only flew down to ~ 600 m AGL during the low approach and a set of downward EAs at that altitude was used to probe the lower altitudes.
Fig. 11. Retrieved vertical profiles and corresponding averaging kernels for (A) NO₂, (B) CHO-CHO, (C) HCHO and (D) H₂O from the low approach at Brackett airfield. NO₂, CHOCHO and HCHO profiles show most of the trace gases are located close to the source region inside the BL. Averaging kernels indicate almost constant sensitivity for all trace gases over the entire altitude range.