Isoprene emissions in Africa inferred from OMI observations of formaldehyde columns

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Abstract

We use 2005-2009 satellite observations of formaldehyde (HCHO) columns from OMI to infer biogenic isoprene emissions at monthly $1^\circ \times 1^\circ$ resolution over the African continent. Our work includes new approaches to remove biomass burning influences using OMI absorbing aerosol optical depth data (to account for transport of fire plumes) and anthropogenic influences using AATSR satellite data for persistent small-flame fires (gas flaring). The resulting biogenic HCHO columns ($\Omega_{\text{HCHO}}$) follow closely the distribution of vegetation patterns in Africa. We infer isoprene emission ($E_{\text{ISOP}}$) from the local sensitivity $S = \Delta \Omega_{\text{HCHO}} / \Delta E_{\text{ISOP}}$ derived with the GEOS-Chem chemical transport model using two alternate isoprene oxidation mechanisms, and verify the validity of this approach using AMMA aircraft observations over West Africa and a longitudinal transect across central Africa. Displacement error (smearing) is diagnosed by anomalously high values of $S$ and the corresponding data are removed. We find significant sensitivity of $S$ to NO$_x$ under low-NO$_x$ conditions that we fit to a linear function of tropospheric column NO$_2$ from OMI. We estimate a 40% error in our inferred isoprene emissions under high-NO$_x$ conditions and 40-90% under low-NO$_x$ conditions. Comparison to the state-of-science MEGAN inventory indicates a large overestimate of central African rainforest emissions in that inventory.
1. Introduction

Isoprene (CH$_2$=C(CH$_3$)CH=CH$_2$) is the dominant non-methane volatile organic compound (NMVOC) emitted by vegetation, accounting for about 50% of global NMVOC emissions according to current inventories (Guenther et al., 2006). It is a major precursor of organic aerosol (Claeys et al., 2004; Henze and Seinfeld, 2006; Kroll et al., 2006) and of tropospheric ozone (Fiore et al., 2011; Tao et al., 2003; Trainer et al., 1987), thus impacting air quality, climate, and human health. Isoprene also affects the abundance of OH, the main atmospheric oxidant (Lelieveld et al., 2008; Ren et al., 2008). Satellite observations of formaldehyde (HCHO), a high-yield product of isoprene oxidation, can provide useful constraints on isoprene emissions (Palmer et al., 2003). Here we use HCHO satellite observations from the Ozone Monitoring Instrument (OMI) to better quantify isoprene emissions from the African continent. Africa appears as a major isoprene source region in global HCHO satellite data (Meyer-Arnek et al., 2005; de Smedt et al., 2008), yet it has thus far received little attention.

Isoprene emission inventories in atmospheric chemistry models generally follow the Guenther et al. (1995) framework, which uses base emissions for different ecosystem types modulated by local environmental factors. These inventories are constructed by extrapolation of limited ecosystem data and best understanding of processes, and are commonly called “bottom-up”. Arneth et al. (2008) point out that there is considerable uncertainty in bottom-up isoprene emission inventories, more than is apparent from the spread of values in the literature, as all tend to rely on the same limited data and algorithm framework. Direct isoprene emission measurements in Africa are particularly limited, consisting of a few data for tropical rainforests (Greenberg et al., 1999; Klinger et al., 1998; Serça et al., 2001), woodlands (Greenberg et al.,
2003, 1999; Otter et al., 2002), savannas (Guenther et al., 1996; Harley et al., 2003; Klinger et al., 1998; Otter et al., 2002; Saxton et al., 2007), and shrublands (Otter et al., 2002).

An alternate “top-down” approach for estimating isoprene emissions is to use HCHO column measurements made by satellites from solar backscatter in the 330-360 nm absorption bands (Chance et al., 2000). Isoprene has an atmospheric lifetime of typically less than 1 h against oxidation by OH, producing HCHO which has a lifetime of 1-2 h against photolysis and oxidation by OH. This adds to the HCHO background originating mainly from the oxidation of methane. Thus the HCHO columns measured from space can be related to the underlying isoprene emission (Palmer et al., 2003). Contributions from other biogenic or anthropogenic NMVOCs are generally much weaker because emissions are lower and/or HCHO production is slower (Palmer et al., 2003). Inference of isoprene emissions from HCHO column measurements by the GOME (1995 launch), SCIAMACHY (2002 launch), and OMI (2004 launch) satellite instruments has been reported in a number of studies for North America (Abbot et al., 2003; Millet et al., 2008; Palmer et al., 2006, 2003), Asia (Fu et al., 2007), Europe (Curci et al., 2010; Dufour et al., 2009), South America (Barkley et al., 2008), and globally (Shim et al., 2005; Stavrakou et al., 2009a). Biomass burning makes a major seasonal contribution to HCHO in the tropics, and was screened by Barkley et al. (2008) using satellite fire count and NO$_2$ data.

Relating HCHO columns to isoprene emission requires a quantitative relationship between the two obtained with a chemical transport model (CTM). Most of our current understanding of isoprene chemistry has been developed for high concentrations of nitrogen oxide radicals (NO$_x$ $\equiv$ NO+NO$_2$) that originate in the atmosphere from combustion sources and soil emissions. Under these high-NO$_x$ conditions (>1 ppb NO$_x$) the organic peroxy radicals (RO$_2$) produced from isoprene oxidation react preferentially with NO. The resulting HCHO yield is relatively well
quantified and is mostly realized in the first stage of isoprene oxidation (Millet et al., 2006; Palmer et al., 2003). Under low-NO\textsubscript{x} conditions more typical of Africa, the RO\textsubscript{2} radicals may instead react with HO\textsubscript{2} or isomerize (Peeters et al., 2009), modifying and delaying HCHO yields (Mao et al., 2010; Palmer et al., 2006, 2003). Delay in HCHO production causes smearing in the local relationship between isoprene emission and the HCHO column (Palmer et al., 2003). This smearing can in principle be resolved in a formal inversion accounting for CTM transport (Shim et al., 2005; Stavrakou et al., 2009a), but this requires more confidence than is probably warranted in the coupling between chemical and transport timescales.

Here we use a 5-year record of OMI HCHO data (2005-2009) to constrain isoprene emissions from the African continent. We convert HCHO columns to isoprene emissions by using the GEOS-Chem CTM with updated isoprene chemistry (Paulot et al., 2009a, 2009b). We introduce a new method to screen biomass burning influence based on OMI observations of aerosol absorption optical depth (AAOD) (Torres et al., 2007) and also screen urban and gas flaring influences. We use aircraft observations from the African Monsoon Multidisciplinary Analysis (AMMA) campaign in West Africa during July-August 2006 (Murphy et al., 2010; Reeves et al., 2010; Stone et al., 2010) to test the GEOS-Chem simulation of isoprene chemistry and estimate the smearing in the isoprene-HCHO relationship. We also derive a new approach to account for the NO\textsubscript{x} dependence of the isoprene-HCHO relationship using OMI NO\textsubscript{2} data.

2. Constructing a data set of OMI biogenic HCHO columns

2.1 Slant columns

The Ozone Monitoring Instrument (OMI) (Levelt et al., 2006) was launched onboard the Aura satellite in 2004. It has spatial resolution of 13×24 km\textsuperscript{2} at nadir, an equator crossing time of
HCHO slant columns (\(\Omega_s\)) are a standard product from the OMI instrument, obtained by spectral fitting of backscattered solar radiation in the 327.5 – 356.5 nm window (http://www.cfa.harvard.edu/atmosphere/Instruments/OMI/PGEReleases/READMEs/OMHCHO_README.pdf). We use OMHCHO Version 2.0 (Collection 3) retrievals for 2005-2009 from the NASA Data and Information Services Center (http://disc.sci.gsfc.nasa.gov/Aura/dataholdings/OMI/omhcho_v003.shtml). We exclude observations that (1) do not pass all fitting and statistical quality checks specified in the standard product (i.e. \(\text{MainDataQualityFlag} = 0\)), (2) have a cloud fraction > 0.4 determined from the OMI O\(_2\)-O\(_2\) cloud product (Stammes et al., 2008), or (3) are affected by the OMI row anomaly (http://www.knmi.nl/omi/research/product/rowanomaly-background.php).

The OMI data feature a slow increase in the baseline \(\Omega_s\) with time over 2005-2009 that likely reflects degradation of the instrument. We correct for this using observations over the remote Pacific (40-50\(^\circ\)S, 150-160\(^\circ\)W) where the OMI data are essentially noise. Following the methodology of Kim et al. (2011) we fit a 4\(^{th}\) order polynomial function to the baseline slant column \(\Omega_{s,b}\) over that region as a function of time \(t\):

\[
\Omega_{s,b} = -2.0 \times 10^3 t^4 + 9.6 \times 10^6 t^3 - 1.3 \times 10^{10} t^2 + 7.5 \times 10^{12} t + 2.5 \times 10^{15} \tag{1}
\]

where \(\Omega_{s,b}\) is in molecules cm\(^{-2}\) and \(t\) is in days (\(t = 1\) on 1 January 2005). We remove \(\Omega_{s,b}\) calculated with (1) from the OMI measurement of \(\Omega_s\) and will refer to the residual as \(\Omega_s\) in what follows.
We thus compile 8-day average values for $\Omega_s$ on a $1^\circ \times 1^\circ$ (lat×lon) grid for 2005-2009 (Fig. 1a). The slant column fitting uncertainty for a single observation is $8 \times 10^{15}$ molecules cm$^{-2}$ on average. 8-day and $1^\circ \times 1^\circ$ averaging reduces the uncertainty to $1-2 \times 10^{15}$ molecules cm$^{-2}$.

### 2.2 Removing biomass burning and anthropogenic influences

We remove biomass burning and anthropogenic influences from the $\Omega_s$ data in order to isolate the biogenic component. The standard procedure for removing biomass burning is to use space-based observations of fire counts (Barkley et al., 2008; Jaéglé et al., 2005). We begin with this approach by using MODIS day and night fire counts from the Terra satellite. The data are provided daily at a resolution of $1\times1$ km$^2$ (Giglio et al., 2003) and we average them for 8 days on the same $1^\circ \times 1^\circ$ grid as $\Omega_s$. We exclude persistent fires associated with large industrial and urban areas of Cairo (Egypt), the Mpumalanga Highveld region (South Africa), and the Niger Delta (Nigeria). We then remove as contaminated by biomass burning all grid-squares with non-zero fire counts for the concurrent and preceding 8-day periods.

Screening only on the basis of fire counts is insufficient as it does not account for the long-range transport of HCHO in biomass burning plumes. Plume influences on HCHO far downwind of fires in Africa are evident from Lagrangian analyses of satellite data (Meyer-Arnèk et al., 2005) and AMMA aircraft data (Janicot et al., 2008; Mari et al., 2008; Murphy et al., 2010; Reeves et al., 2010). Solar backscatter satellite instruments retrieve both HCHO and NO$_2$, and Barkley et al. (2008) previously used NO$_2$ as an additional filter to screen against biomass burning in tropical South America. We find that this filter is inadequate for Africa because the atmospheric lifetime of NO$_x$ emitted from biomass burning is only a few hours whereas the
influence of fires on HCHO is more sustained owing to continued oxidation of precursor NMVOCs (Alvarado et al., 2010; Hobbs et al., 1996; Trentmann et al., 2003).

Our method to diagnose biomass burning plumes is to use the AAOD product from OMI for the same scenes as HCHO (Torres et al., 2007). Absorbing aerosol is conserved in the plume in the absence of precipitation. We use the level 2 version 3 gridded OMI AAOD product (http://disc.sci.gsfc.nasa.gov/Aura/data-holdings/OMI/omaeruvg_v003.shtml), provided at 0.25°×0.25° horizontal resolution, and average it over 8-day periods on the same 1°×1° grid as ω. The product includes separate contributions from dust and smoke aerosol but separation between the two can be difficult (Ahn et al., 2008) and we find that smoke AAOD is elevated in dusty regions. To address this problem, we subdivide the continent latitudinally into the Mediterranean strip (north of 20°N), northern Africa (4°N-19°N), equatorial Africa (5°S-4°N), and southern Africa (south of 5°S). For each region we plot the 5-year frequency distribution of OMI smoke AAOD, as shown in Fig. 2 for southern Africa. This separates biomass burning and non-biomass burning scenes into two populations, and we remove the biomass burning scenes. The smoke AAOD thresholds are 0.02, 0.07, 0.05, and 0.04 for the Mediterranean strip, northern Africa, equatorial Africa, and southern Africa, respectively.

Large dust influence is also problematic in the interpretation of HCHO slant columns because of scattering and absorption by the dust. Northern and equatorial Africa can be very dusty. We filter out high dust scenes with the OMI dust AAOD product previously described using a threshold value of 0.1, above which the radiative interference would be of concern.

The OMI HCHO data show high values over Nigeria (Fig. 1a) that may reflect urban NMVOC emissions in Lagos (Hopkins et al., 2009; Oketola and Osibanjo, 2007; Reeves et al., 2010), biofuel use that is particularly dense in rural Nigeria (Yevich and Logan, 2003), and gas
flaring in the Niger Delta (Casadio et al., 2011). Other African countries that practice gas flaring related to the oil and gas industry include Libya, Algeria, Angola, Egypt, Gabon, Sudan, Congo and Tunisia (Casadio et al., 2011). We remove HCHO associated with gas flaring by using gas flare hotspots retrieved in the 1.6 μm band (Algorithm3 or ALGO3) from the Advanced Along Track Scanning Radiometer (AATSR) satellite instrument (Casadio et al., 2011). We average the AATSR fire counts over the same 1°×1° grid and 8-day averaging period as OMI and remove gridsquares with non-zero gas flares. Over Nigeria the enhancements in HCHO occur beyond the region of flaring, which may reflect pollution transport as well as Lagos emissions and intense biofuel use. We therefore remove a more extensive 3°×3° area around the gridsquares affected by flaring in Nigeria. The AATSR data do not extend over South Africa due to noise from the South Atlantic Anomaly (Casadio et al., 2011), but we find that the six oil refineries in South Africa [SAPIA, 2008] are not associated with elevated HCHO in the OMI data of Fig. 1a. We therefore see no need for additional screening.

Our filtering scheme to remove biomass burning, dust, and anthropogenic contributions from the OMI Ωs observations is summarized in Fig. 3. It removes 40% of observations over Africa on average and 70-80% in the southern hemisphere during the dry season. Figure 1 shows the mean OMI Ωs observations for 2005-2009 before (a) and after (b) application of the filtering scheme. The filtered observations are taken to represent biogenic HCHO in what follows.

2.3 Conversion to vertical columns

The slant column Ωs obtained by spectral fitting is related to the true vertical column ΩHCHO by an air mass factor (AMF = Ωs/ΩHCHO) obtained with a radiative transfer model. We use the formulation of Palmer et al. (2001), which calculates the AMF as the vertical integral of the
relative vertical distribution of HCHO (shape factor) weighted by altitude-dependent coefficients (scattering weights). The scattering weights are functions of viewing geometry, surface albedo, and atmospheric scattering by air molecules, aerosols, and clouds. Cloud fraction and cloud top pressure are from the OMI O$_2$-O$_2$ cloud product (Stammes et al., 2008). The LIDORT radiative transfer model (Spurr et al., 2001) is used to calculate scattering weights for individual scenes. Clouds are represented by Lambertian surfaces with an albedo of 0.8, as recommended by Koelemeijer and Stammes (1999), and consistent with the O$_2$-O$_2$ cloud algorithm. Surface albedo for the African continent is from the OMI reflectance climatology at 345 nm (Kleipool et al., 2008). HCHO and aerosol vertical distributions are monthly mean values from the GEOS-Chem CTM, described in Sect. 3.

We find that 62% of the spatial variability in the annual average AMFs over Africa is driven by OMI surface albedo. The AMF is close to unity for much of the continent (average 1.2), with larger values over the Sahara and Namib Deserts (high albedo) and lower values over central Africa (low albedo). Figure 1c shows the resulting annual mean distribution of HCHO vertical columns $\Omega_{\text{HCHO}}$. We see that most of the variability in $\Omega_{\text{HCHO}}$ is present in the slant column data and thus is not driven by the AMF. The $\Omega_{\text{HCHO}}$ patterns match closely the distribution of major land types in Africa (Fig. 1d), supporting the interpretation of HCHO as a proxy for isoprene emission. Maximum values are found over evergreen broadleaf forests in the tropics. Low values occur over barren, shrub, herbaceous, and cultivated vegetation. Small-scale biogenic features are apparent such as the forested belt along the east coast of South Africa, crops along the Nile River, and the coastal vegetated Mediterranean strip.
3. GEOS-Chem model

3.1 General description

We use the GEOS-Chem global 3D CTM (version 8-03-01, http://geos-chem.org) to (1) estimate the vertical distribution of HCHO for use in the AMF calculation and (2) quantify the relationship between isoprene emissions and HCHO column abundance. GEOS-Chem is driven by Goddard Earth Observing System (GEOS-5) assimilated meteorological data from the NASA Global Modeling and Assimilation Office (GMAO). The GEOS-5 meteorological data have a native horizontal resolution of 0.5°×0.67° with 72 vertical pressure levels and 6-h temporal frequency (3-h for surface variables and mixing depths). We use data for year 2006 and degrade the horizontal resolution to 2°×2.5° for input to GEOS-Chem. The model results presented here are from one year of simulation (2006) following one year of spinup for chemical initialization.

Biogenic emission of isoprene is calculated locally in GEOS-Chem using the MEGAN v2.1 inventory (Guenther et al., 2006), with modifications described below. Anthropogenic emissions of NO\textsubscript{x} in Africa are from the EDGAR v2.0 inventory (Olivier et al., 1996). Biomass burning NMVOC and NO\textsubscript{x} emissions are from the Global Fire Emissions Database v2 (Van der Werf et al., 2006). NO\textsubscript{x} emissions from soils and fertilizer use are from the algorithm of Yienger and Levy (1995) as implemented by Wang et al. (1998).

Dry deposition in GEOS-Chem follows the standard resistance-in-series scheme of Wesely (1989). In that scheme, gases are deposited as determined by their Henry’s law solubility and their surface reactivity (referenced to ozone). Here we have updated the dry deposition of HCHO and other oxygenated products of isoprene oxidation including methyl vinyl ketone (MVK), methacrolein (MACR), glycolaldehyde, and dicarbonyls to have the same surface reactivity as ozone, based on observational evidence of rapid deposition (Karl et al., 2009, 2004;
Misztal et al., 2010; Pugh et al., 2010; Sumner et al., 2001) and following the recommendation of Karl et al. (2010). We also include in the model wet and dry deposition of isoprene peroxides and epoxydiols using respective Henry’s law constants of $1.7 \times 10^6$ M atm$^{-1}$ (US EPA, 2011) and $1.3 \times 10^8$ M atm$^{-1}$ (Eddingsaas et al., 2010).

We account in this GEOS-Chem version for the grid-scale transport of isoprene peroxides produced from oxidation of isoprene under low-NO$_x$ conditions. Previous versions of GEOS-Chem did not include this transport, leading to an underestimate in the spatial displacement (smearing) between isoprene emission and the resulting HCHO columns.

### 3.2 Improved treatment of isoprene chemistry

GEOS-Chem includes detailed ozone-NO$_x$-VOC-aerosol coupled chemistry originally described by Bey et al. (2001) and Park et al. (2004), with recent updates described by Mao et al. (2010). We have updated the rate coefficients for the reactions of HO$_2$ with $> C_2$ peroxy radicals to Eq. (iv) of Saunders et al. (2003). At 298 K the rate coefficient doubles from $0.8$ to $1.6 \times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ relative to previous versions of GEOS-Chem, increasing the relative importance of the low-NO$_x$ isoprene oxidation pathway.

The standard isoprene oxidation scheme used in GEOS-Chem is largely based on Horowitz et al. (1998). As with all conventional schemes, it leads to OH titration by isoprene under low-NO$_x$ conditions, but this titration is not seen in observations (Lelieveld et al., 2008; Ren et al., 2008). We implement as alternate isoprene oxidation scheme in GEOS-Chem the Paulot et al. (2009b) mechanism, where regeneration of OH under low-NO$_x$ conditions takes place via oxidation of epoxydiol species produced from oxidation of isoprene hydroperoxides. Isomerization of the isoprene peroxy radicals leading to the formation of hydroperoxyaldehydes,
described in Peeters et al. (2009) and Peeters and Müller (2010), is not included in our mechanism as experimental evidence indicates that it is too slow to compete with reaction with HO$_2$ (Crounse et al., 2011). We compare below results from the “standard” and “Paulot” schemes to assess the degree of uncertainty in simulating HCHO yields. The “standard” chemistry scheme is that in version 8-03-01 of GEOS-Chem with updated RO$_2$ + HO$_2$ kinetics as described above.

Figure 4 shows the time-dependent yields of HCHO from isoprene oxidation calculated in the DSMACC box model (Emmerson and Evans, 2009) for the standard and Paulot schemes as implemented in GEOS-Chem with different NO$_x$ levels. Each simulation uses fixed concentrations of O$_3$ (28 ppbv), CO (150 ppbv), and NO$_x$ (0.01, 0.1, and 1 ppbv). Isoprene is initially 1 ppbv and allowed to decay. The temperature is 298 K. Diurnally varying photolysis frequencies are calculated for clear sky at the Equator with surface albedo of 0.1 and an ozone column of 260 Dobson units. Under high-NO$_x$ conditions (1 ppbv), we find that the ultimate HCHO yield is approached within a few hours and is similar for both schemes. Under low-NO$_x$ conditions (0.1 ppbv), the ultimate yield is 10-20% lower and takes 1-2 days to achieve, again with similar values for both schemes. The largest difference is under very low NO$_x$ conditions (0.01 ppbv) where the ultimate yield is 30-40% lower than under high-NO$_x$ conditions and the timescale for reaching that yield is 5-6 days. The Paulot scheme does not show a shorter timescale for reaching the ultimate yield than the standard scheme, despite higher OH, because it generates more HCHO from later-generation isoprene oxidation products. The implications of these results for the isoprene-HCHO relationship will be discussed further in Sect. 4 in the context of GEOS-Chem results and using OMI NO$_2$ columns to identify NO$_x$ regimes.
3.3 MEGAN Bottom-Up Isoprene Emission Inventory

We use the MEGAN algorithm of Guenther et al. (2006) as our best prior emission estimate for isoprene to which the constraints from the OMI HCHO data can be compared. This inventory is widely used in global CTMs. Isoprene accounts for 80% of biogenic NMVOC emissions on a per-carbon basis in Africa according to MEGAN. The canopy-scale isoprene emission flux, \( E_{\text{ISOP}} \), per unit area of Earth surface (atoms C cm\(^{-2}\) s\(^{-1}\)) is computed as:

\[
E_{\text{ISOP}} = E_0 \gamma_T \gamma_{\text{AGE}} \gamma_{\text{SM}} \gamma_{\text{CE}}
\]

Here \( E_0 \) is the emission at baseline conditions of air temperature (303 K), leaf age (80% mature, 10% growing, and 10% old), soil moisture (0.3 m\(^3\) water m\(^{-3}\) soil), light (1500 \( \mu \)mol photons m\(^{-2}\) s\(^{-1}\)), and leaf area index (LAI = 5). The unitless environmental scaling factors (\( \gamma \)) describe the effects of temperature (\( T \)), leaf age (\( \text{AGE} \)), soil moisture (\( \text{SM} \)), and canopy radiative environment (\( \text{CE} \)) on \( E_0 \). \( \gamma_{\text{CE}} \) includes the effects of both LAI and light. Values of \( E_0 \) are specified for five plant functional types (PFTs): broadleaf trees, needleleaf trees, grasses, crops, and shrubs. The global distribution of PFTs is taken from the biome database of Olson et al. (2001), and the distribution of trees in Africa south of the Equator is overwritten by the regional database of Otter et al. (2003). In GEOS-Chem \( E_0 \) is input at 1\(^\circ\)×1\(^\circ\) and regridded to 2\(^\circ\)×2.5\(^\circ\) resolution prior to estimating \( E_{\text{ISOP}} \).

Our GEOS-Chem simulation uses the environmental scaling factors \( \gamma \) as given by Guenther et al. (2006) and applied to the local GEOS-5 surface data, except for soil moisture. Stavrakou et al. (2009b) found in their analysis of GOME and SCIAMACHY HCHO satellite data that water stress is an important contributor to variability of isoprene emissions over
southern Africa and is not well represented in MEGAN. We use here the soil moisture parameterization developed by Müller et al. (2008) and found by Ferreira et al. (2010) to achieve a good simulation of isoprene emission over West Africa during AMMA:

\[
\gamma_{SM} = \sum_{i=1}^{n} f_i \times \max \left(0, \min \left(1, \frac{\theta_i - \theta_{i,w}}{0.06} \right) \right) \tag{3},
\]

where the summation is over \( n \) vertical soil layers, \( f_i \) is the root fraction within soil layer \( i \) such that \( \sum_{i=1}^{n} f_i = 1 \), \( \theta_i \) is the degree of saturation or volumetric ratio of soil moisture to the porosity of the soil (m\(^3\) water m\(^3\) air), and \( \theta_{i,w} \) is the degree of saturation at the wilting point. The GEOS-5 meteorological data provide \( \theta_i \) for two layers \( (n = 2) \): a top soil layer (2 cm) and a root zone layer (1 m). Müller et al. (2008) used a fixed wilting point value of 0.171, but here we use gridded monthly average wilting points, ranging from 0.05 to 0.6 in Africa, from the GEOS-5 catchment land surface model (Koster et al., 2000). We determine \( f_i \) within each layer using the parameterization of Zeng (2001) for dominant IGBP landcover types at 1°×1° from the MODIS landcover data set (Friedl et al., 2002).

Our resulting global emission of isoprene in GEOS-Chem for 2006 is 470 Tg C a\(^{-1}\), within the 440-660 Tg C a\(^{-1}\) range given by Guenther et al. (2006). Africa accounts for 20% of global isoprene emissions. Implementation of the soil moisture scaling factor \( \gamma_{SM} \) as described above reduces annual isoprene emissions by about 10% globally and 15% over Africa. The global reduction in isoprene emissions is less than the 30% reduction obtained by Müller et al. (2008), likely due to the spatially variable wilting points used here.
4. **HCHO-isoprene relationship**

Previous interpretation of the HCHO column $\Omega_{\text{HCHO}}$ in terms of isoprene emission using GEOS-Chem has relied on a local linear regression between the two quantities in the model (Palmer et al., 2003):

$$\Omega_{\text{HCHO}} = SE_{\text{ISOP}} + B$$  \hspace{1cm} (4)

where $S$ is the slope of the reduced-major-axis regression line and $B$ is the intercept representing the background HCHO column. The value of $S$ is determined by the HCHO yield from isoprene oxidation and by the HCHO lifetime. Millet et al. (2008) presented estimates of $S$ for North America in summer by performing either a single regression for the ensemble of GEOS-Chem gridsquares covering North America or local regressions for individual $2^\circ \times 2.5^\circ$ gridsquares. The first method yielded $S = 2.4 \times 10^3$ s with high correlation ($R^2 = 0.82$), while the second yielded variable slopes with an interquartile range of $2.0-3.0 \times 10^3$ s. These values were consistent with observation-based estimates for the PROPHET forest site in Michigan ($2.1 \times 10^3$ s) and INTEX-A aircraft observations over the eastern US ($2.3 \times 10^3$ s) (Millet et al., 2006; Palmer et al., 2003).

Over tropical South America where NO$_x$ levels are much lower, Barkley et al. (2008) found a strong spatial correlation ($R^2 > 0.7$) between $E_{\text{ISOP}}$ and $\Omega_{\text{HCHO}}$ in GEOS-Chem but with large seasonal variability in $S$ – ranging from $1 \times 10^3$ s in January-March to $2 \times 10^3$ s in May-July.

Here we use our updated version of GEOS-Chem, together with observational constraints from AMMA and OMI, to examine the local $E_{\text{ISOP}}$-$\Omega_{\text{HCHO}}$ relationships over Africa and their suitability for inferring isoprene emissions from the HCHO column data. We quantify the smearing of the relationship caused by delay in HCHO production from isoprene, develop a
parameterization for the dependence of the $E_{\text{ISOP}}-\Omega_{\text{HCHO}}$ relationship on NO$_x$, and estimate the errors in the resulting isoprene emission estimates.

### 4.1 Smearing

We first examine the extent of smearing in the HCHO-isoprene relationship over Africa using aircraft measurements of isoprene, the sum of MVK and MACR (MVK+MACR), and HCHO concentrations obtained during AMMA in West Africa in July-August 2006 (Murphy et al., 2010; Reeves et al., 2010). The AMMA wet season aircraft campaign (Redelsperger et al., 2006), based in Niamey, Niger, made latitudinal transects across sharp vegetation gradients from ocean to dense woodland to desert (Fig. 5). 19 flights were made from 20 July to 17 August, 2006, mainly during daytime hours. Boundary layer winds were prevailingly from the south (West African monsoon) (Janicot et al., 2008). We exclude biomass burning plumes as diagnosed by $>250$ pptv acetonitrile (Commane et al., 2010; Murphy et al., 2010) as well as the flights of August 8 (Lagos urban plume) and August 15 (mesoscale convective system).

Figure 5 shows the AMMA flight tracks superimposed on a map of MODIS LAI for July-August 2006 (Yang et al., 2006), together with latitudinal profiles of observed and simulated isoprene, MVK+MACR, and HCHO concentrations below 900 hPa. The model is sampled along the flight tracks and at the flight times. Also included in Fig. 5 is the HCHO concentration below 900 hPa inferred from OMI observations for July-August 2005-2009 averaged over the AMMA longitudinal domain (1-4°E) into 1° latitude bins (multi-year temporal averaging is needed to reduce measurement noise). The HCHO concentration below 900 hPa is inferred from OMI HCHO columns by using the mean HCHO vertical profile measured during AMMA (340 pptv
above 750 hPa and linear increase from 750 hPa to the surface. The break in the OMI data at 5-7°N reflects systematic exclusion of anthropogenic influence from Nigeria (Sect. 2.2).

The sharp vegetation gradients sampled in AMMA along the direction of the prevailing southerly monsoon winds make the data of great value for understanding smearing in the HCHO-isoprene relationship. We see from Fig. 5 that observed isoprene and MVK+MACR tightly follow the vegetation gradients, and this is well captured by the model. Model values are much higher than observed at 11-13°N and 7-8°N, reflecting a local overestimate of $E_{\text{ISOP}}$ in MEGAN (Ferreira et al., 2010; Murphy et al., 2010). MVK and MACR are first-stage C$_4$ isoprene oxidation products with HCHO produced from the additional carbon atom (Paulson et al., 1992).

The tightness of the isoprene-(MVK+MACR) relationship in Fig. 5, both in the observations and the model, demonstrates that there is no significant smearing and provides an important test of the isoprene oxidation scheme. Model isoprene concentrations are lower in the Paulot scheme because of OH regeneration from the RO$_2$ + HO$_2$ reaction pathway, as described in Sect. 3.2, but this has negligible impact on the simulation of (MVK+MACR).

The right panel of Fig. 5 shows that observed and simulated HCHO are also strongly correlated with the vegetation gradients. The AMMA observations for HCHO are much lower than the model or inferred from OMI, and we do not have an explanation for this beyond the possibility of large bias in the Hantzsch-fluorometric instrument used on the aircraft (Grossmann et al., 2003; Hak et al., 2005; Klemp et al., 2003; Still et al., 2006). Because HCHO is produced together with MVK+MACR it would be difficult to account for a model bias in HCHO but not in MVK+MACR. Tests with the model indicate little sensitivity to the assumed deposition velocities. In any case, comparison of the HCHO and isoprene latitudinal gradients shows no significant northward smearing either in the observations or the model. The strongest correlation
between observed isoprene and HCHO ($R^2 = 0.86$) occurs for an offset of $0.5^\circ$ north of the peak in observed isoprene ($8$-$12^\circ$N). Smearing of $\sim 0.5^\circ$, combined with a mean observed southerly wind speed of $17$ km h$^{-1}$ south of $12^\circ$N, implies a timescale of less than a day for production of HCHO from isoprene.

The negligible smearing in the AMMA observations may reflect the relatively high NO$_x$ conditions. Boundary layer (i.e. below $900$ hPa) NO$_x$ concentrations in the region of isoprene emission ($7$-$13^\circ$N) averaged $360$ pptv in the observations and $310$ pptv in the model, due to a mix of influences from soil, anthropogenic, and distant biomass burning sources (Hopkins et al., 2009; Reeves et al., 2010; Stewart et al., 2008). We find in GEOS-Chem that such a NO$_x$ concentration places the AMMA conditions at the threshold between the high-NO$_x$ regime (where isoprene RO$_2$ reacts mainly with NO) and the low-NO$_x$ regime (where isoprene RO$_2$ reacts mainly with HO$_2$). Stone et al. (2010) found a $70\%$ mean contribution of the high-NO$_x$ pathway during AMMA using the DSMACC box model.

The OMI NO$_2$ data offer a broader perspective on NO$_x$ regimes across Africa. Figure 6 shows annual average tropospheric columns of NO$_2$ ($\Omega_{NO2}$) from OMI (Boersma et al., 2007) for 2005-2009 and compares to the GEOS-Chem simulation for 2006. Biomass burning influence has been removed in the observations using MODIS fire counts and OMI AAOD (Sect. 2.2) and in GEOS-Chem with black carbon AOD from the model, for consistency with the removal of biomass burning influence in the OMI HCHO column product. We find from the AMMA observations (Stewart et al., 2008) that, similar to HCHO, NO$_2$ increases linearly from $750$ hPa to the surface. Mean NO$_2$ observations above $750$ hPa are below the limit of detection of the aircraft instrument. Thus $1$ ppbv of boundary layer NO$_x$ corresponds roughly to a tropospheric NO$_2$ column of $2.2 \times 10^{15}$ molecules cm$^{-2}$. The fitting precision of $7$-$8 \times 10^{14}$
molecules cm\(^{-2}\) for individual OMI NO\(_2\) pixels (Boersma et al., 2007) is reduced to $3 - 4 \times 10^{13}$ molecules cm\(^{-2}\) for monthly mean data at 1°×1° resolution, so that levels as low as ~0.02 ppb NO\(_x\) are detectable. We see in Fig. 6 that much of Africa is in an intermediate NO\(_x\) regime (0.1-1 ppb). Even in the absence of continental biomass burning influences, significant boundary layer NO\(_x\) levels are maintained in Africa by soil emissions (Jaeglé et al., 2005) and by decomposition of peroxyacetyl nitrate (PAN) originating from outside the continent (Moore and Remedios, 2010; Singh and Hanst, 1981).

We further examined the effect of high isoprene emissions on smearing as a result of OH titration. For this we consider the equatorial forest of central Africa (3°S-3°N) in July where NO\(_x\) levels are moderate (average tropospheric NO\(_2\) columns of 8.4 and $5.7 \times 10^{14}$ molecules cm\(^{-2}\) for OMI and GEOS-Chem, respectively), and ventilation is by a steady easterly wind. Figure 7 shows the longitudinal gradients of MEGAN $E_{\text{ISOP}}$, OMI $\Omega_{\text{HCHO}}$, and model column HCHO (standard and Paulot schemes) across the region. Immediately downwind (to the west) of the rainforest is a shadow region where elevated HCHO does not correspond to collocated isoprene emission but instead reflects transport from the forest. Assuming that MEGAN correctly represents the location of isoprene emission (mainly determined by the location of the equatorial rainforest), enhancements in OMI $\Omega_{\text{HCHO}}$ are sustained ~2-3° west of that location. The smearing is well reproduced by the model using either the standard or Paulot scheme and the extent of smearing is not reduced in the Paulot scheme as a result of OH regeneration. Combined with a mean easterly wind speed of 5 km h\(^{-1}\) for the region, it implies a timescale of ~2-3 days for production of HCHO from isoprene. We will see below how we can screen such shadow regions from the dataset.
4.2 NO\textsubscript{x} dependence

We now examine the variability of the $\Omega_{\text{HCHO}}$-$E_{\text{ISOP}}$ relationship over Africa in GEOS-Chem measured by the local slope $S$ in Eq. (4). This variability reflects differences in the chemical environment as well as the effect of smearing in an inhomogeneous isoprene emission field. Millet et al. (2008) previously examined the spatial variability of $S$ over North America by constructing local $\Omega_{\text{HCHO}}$-$E_{\text{ISOP}}$ regressions at the $2^\circ \times 2.5^\circ$ grid resolution of GEOS-Chem, relying on the temperature-driven day-to-day variation of $E_{\text{ISOP}}$ in a given gridsquare to define a dynamic range for the regression. We find that this is not an effective approach in Africa as day-to-day variability in isoprene emission is often small. We derive instead the $\Omega_{\text{HCHO}}$-$E_{\text{ISOP}}$ relationship in GEOS-Chem by conducting a sensitivity simulation with isoprene emissions reduced by a factor of 2 from the MEGAN values. We then infer $S = \Delta \Omega_{\text{HCHO}} / \Delta E_{\text{ISOP}}$ for individual gridsquares and months (gridsquare-months) where $\Delta$ is the monthly mean change relative to the standard simulation, excluding periods of biomass burning influence (diagnosed with black carbon AOD in the model). Values of $S$ over the southeast US ($75^\circ$-$100^\circ$W, $27^\circ$-$40^\circ$N) for June-August 2006 using this approach are $1.9$ and $2.0 \times 10^3$ s for the standard and Paulot schemes, respectively, similar to values reported by Millet et al. (2008, 2006) and Palmer et al. (2006).

Gridsquare-months affected by smearing can be diagnosed in this analysis by anomalously high values of $S$. We find that 41\% of gridsquare–months in GEOS-Chem over Africa have $S > 4 \times 10^3$ s, which is higher than the HCHO yields from isoprene emission would allow and reflects the effect of smearing mainly in regions where isoprene emissions are close to zero (such as the vast desert expanses as well as coastal gridsquares). Although this may seem like a large population to exclude, the corresponding area accounts for only 2\% of isoprene
emission over Africa in MEGAN and thus is largely irrelevant for our purpose. We remove all gridsquare-months in GEOS-Chem with $S > 4 \times 10^3$ s in what follows.

For the remainder of the data we find a significant dependence of $S$ on the local NO$_x$ concentration, as would be expected from our box model results in Fig. 4. We choose to define this relationship in the model in terms of $S$ vs. $\Omega_{NO2}$ so that the OMI $\Omega_{NO2}$ data can be applied to remove the effects of model errors in NO$_x$. Figure 8 shows the $S$ values calculated for individual $2^\circ \times 2.5^\circ$ gridsquare-months over the African continent in 2006 as a function of local model $\Omega_{NO2}$. The data are averaged into $1 \times 10^{14}$ molecules NO$_2$ cm$^{-2}$ bins. For $\Omega_{NO2} \leq 1 \times 10^{15}$ molecules cm$^{-2}$ (equivalent to 0.6 ppbv surface NO$_x$ using our conversion factor) we find a linear relationship between $S$ and $\Omega_{NO2}$ ($R^2 > 0.9$) reflecting the increasing importance of the RO$_2$ + NO pathway with increasing NO$_x$. For $\Omega_{NO2} > 1 \times 10^{15}$ molecules cm$^{-2}$ we find that $S$ levels off as the RO$_2$ + NO pathway becomes dominant. 10-20% higher HCHO yields in the Paulot scheme compared with the standard scheme are consistent with the box model results of Fig. 4. The average $\Omega_{NO2}$ from OMI during AMMA (July-August 2006) is included in Fig. 8 for reference; we see that the AMMA conditions are at the threshold between high-NO$_x$ and low-NO$_x$ conditions, consistent with Stone et al. (2010) and our earlier discussion.

4.3 Error analysis

Inference of isoprene emission from OMI column HCHO involves a number of steps, all of which are prone to error. Here we estimate these different error terms and their contributions to the overall error.

The spectral fitting uncertainty for $\Omega_\epsilon$ observations averaged over $1^\circ \times 1^\circ$ gridsquares and 8-day periods is $1-2 \times 10^{15}$ molecules cm$^{-2}$ (Sect. 2.1). We find (not shown) that the model can
reproduce the shape of the mean HCHO vertical profile observed in AMMA (linear decrease from the surface to 750 hPa, low values above 750 hPa), suggesting that there is no particular problem in simulating the HCHO vertical shape factor under African conditions. In the absence of better information, we adopt the AMF error estimate of Millet et al. (2006) derived from aircraft observations in North America: 15% for clear sky increasing to 24% for 50% cloud cover (Millet et al., 2006). Taking a fitting error of $2 \times 10^{15}$ molecules cm$^{-2}$ and an AMF error of 20% (since we exclude scenes with >40% cloud cover), and applying these errors in quadrature to a vertical HCHO column of $1 \times 10^{16}$ molecules cm$^{-2}$ with AMF of 1.2, we estimate an overall error on the OMI HCHO retrieval of $2 \times 10^{15}$ molecules cm$^{-2}$ or 20%.

Conversion of HCHO columns to isoprene emission using Eq. (4) involves errors in the slope $S$ due both to the chemical mechanism and to smearing. Figure 8 shows that the standard and Paulot mechanisms differ by only 15% in their calculations of $S$, which is similar to the error estimates from Palmer et al. (2006) and Millet et al. (2008) in comparing $S$ values from GEOS-Chem to aircraft and surface observations over the US. The error is certainly larger under low-NO$_x$ conditions where better understanding of isoprene chemistry is needed. Still, it appears that the error bars on $S$ shown in Fig. 8 (which we attribute mainly to smearing) are larger than the errors induced by the chemical mechanism. From these error bars we derive an uncertainty in $S$ from smearing of 750 s for the low-NO$_x$ regime ($\Omega_{NO2} = 0.2 - 1 \times 10^{15}$ molecules cm$^{-2}$) and 690 s for the high-NO$_x$ regime ($\Omega_{NO2} > 1 \times 10^{15}$ molecules cm$^{-2}$).

Error in the OMI tropospheric NO$_2$ column (standard deviation ($\sigma_{NO2}$) also propagates to error in the linear regression equation $S = (1600 \pm 160) \Omega_{NO2} + (721 \pm 114)$ for the low-NO$_x$ regime (Paulot scheme in Figure 8). We use the expression from Boersma et al. [2008] to estimate $\sigma_{NO2}$ for 8-day average $\Omega_{NO2}$ observations:
\[ \sigma_{\text{NO}_2} = \frac{1.0 \times 10^{15} + 0.3 \times \Omega_{\text{NO}_2}}{\sqrt{8 \times \sqrt{3.5}}} \]  

and propagate this with the linear regression errors in the slope \( m (\sigma_m = 160) \) and intercept \( c (\sigma_c = 114) \). The resulting error standard deviation \( \sigma_S \) in \( S \) is determined as

\[ \sigma_S = \sqrt{\left( m \times \sigma_{\text{NO}_2} \right)^2 + \left( \Omega_{\text{NO}_2} \times \sigma_m \right)^2 + \sigma_c^2} \]

and is in the range 340-440 s for \( \Omega_{\text{NO}_2} \) of 0.2-1.0 \( \times 10^{15} \) molecules cm\(^{-2}\); smaller than the estimated smearing error of 750 s. The error in \( S \) at low \( \text{NO}_x \), adding in quadrature the contributions from smearing and from the linear regression of \( S \) against \( \Omega_{\text{NO}_2} \), is 823-870 s (35-84%).

The overall error in inferring isoprene emission from OMI HCHO columns, adding in quadrature the errors on the OMI retrieval of HCHO columns and the conversion of HCHO columns to isoprene emission, is 40% in the high-\( \text{NO}_x \) regime and 40-90% in the low-\( \text{NO}_x \) regime. These errors apply to 8-day average 1°×1° OMI HCHO data and could be reduced by further temporal averaging to the extent that they are random, which is difficult to assess given the uncertainties associated with the isoprene oxidation mechanism at low levels of \( \text{NO}_x \).

### 5. Implications for OMI-derived isoprene emissions in Africa

We have presented here a new methodology for inferring isoprene emissions from HCHO satellite data and applied it to the African continent using OMI. Detailed discussion of the implications for African isoprene emissions and their dependence on environmental variables is left to a separate paper. We present here some preliminary results. For this purpose we use the 2005-2009 monthly mean OMI HCHO vertical columns at 1°×1° horizontal resolution derived in Sect. 2, monthly mean \( S \) values computed from GEOS-Chem with the Paulot scheme, and 2005-2009 monthly mean \( \text{NO}_2 \) tropospheric column observations from OMI (Boersma et al., 2007).
Figure 9 shows the resulting spatial distribution of annual isoprene emissions at 12-15 local time (LT) and compares to the corresponding values from the MEGAN inventory. Values are means for all 1°×1° gridsquare-months that are not excluded from our analysis because of biomass burning, anthropogenic, dust, or smearing influences. Fully excluded areas are shown in grey. The right panel of Fig. 9 shows the difference between the OMI-derived emissions and values from MEGAN.

From the data in Fig. 9 we find that the annual mean isoprene emissions in Africa inferred from OMI (60 Tg C a⁻¹) are on average 22% lower than the MEGAN values (77 Tg C a⁻¹). Larger regional discrepancies are apparent. For example, OMI is on average 33% lower than MEGAN over the central African rainforest, while 38% higher over the southern deciduous broadleaf forests.

6. Conclusions

We presented a new method for inferring biogenic isoprene emissions from satellite observations of HCHO columns under the particularly challenging conditions of the tropics, and applied this method to 2005-2009 OMI HCHO observations over the African continent. Removing biomass burning influence is critical for isolating the biogenic component of HCHO in the tropics. Previous procedures using satellite fire counts or NO₂ columns are insufficient because they do not account for long-range transport of fire plumes. Here we used OMI observations of absorbing aerosol optical depth (AAOD) as an additional screening tool. We also identified a significant anthropogenic component over Africa associated with gas flaring, particularly in Nigeria, and removed it using small-flame satellite fire data. Our resulting
biogenic HCHO product shows close correspondence with the distribution of vegetation in Africa.

Inferring isoprene emission from HCHO column data requires knowledge of the time-dependent HCHO yield from isoprene oxidation. This is a challenge in the tropics because of the prevailing low-NOx conditions under which the isoprene oxidation mechanism is not well understood and HCHO production may be delayed. Here we used two alternate mechanisms to quantify HCHO-isoprene relationships in GEOS-Chem. The two mechanisms show a similar positive NOx dependence of the HCHO yield under low-NOx conditions, and a delay between isoprene emission and HCHO production ranging from less than a day under high-NOx conditions to several days under low-NOx conditions. This delay smears the local relationship between isoprene emission (\(E_{\text{ISOP}}\)) and HCHO columns (\(\Omega_{\text{HCHO}}\)).

We evaluated the GEOS-Chem simulation of the HCHO-isoprene relationship using aircraft observations from the AMMA campaign along a latitudinal transect of vegetation types in West Africa. Both observations and model show strong spatial correlation between isoprene, MVK+MACR (first-stage products of isoprene oxidation associated with HCHO formation), and HCHO. This implies insignificant (< 100 km) smearing in the HCHO-isoprene relationship.

Inspection of longitudinal gradients across the equatorial forest of central Africa, where NOx is low, indicates smearing of ~200-300 km. This means that large isoprene source regions under low-NOx conditions produce a shadow effect downwind that affects interpretation of the local HCHO-isoprene relationship.

We computed local relationships between HCHO columns and isoprene emission at the 2°×2.5° GEOS-Chem grid resolution and on a monthly basis by conducting a sensitivity simulation with uniformly perturbed isoprene emission and inferring the relationship \(S = \)
ΔΩ_{HCHO}/ΔE_{ISOP}. Smearing was diagnosed by anomalously high $S$ values and the corresponding scenes were excluded from further analysis. We found that $S$ is sensitive to NO$_x$ at levels below 600 pptv (tropospheric NO$_2$ column $\leq 1 \times 10^{15}$ molecules cm$^{-2}$). From there we used the OMI NO$_2$ column observations to diagnose $S$ for the corresponding OMI HCHO data. The error in OMI-derived isoprene emissions is 40% at high NO$_x$ and 40-90% at low NO$_x$ for 8-day 1°×1° OMI HCHO gridsquares. Smearing makes the largest contribution to the error for both NO$_x$ regimes.

We presented a preliminary comparison of the OMI-derived annual mean isoprene emissions over Africa to the values computed from the bottom-up MEGAN inventory used in GEOS-Chem. The total OMI-derived isoprene emission for the African continent is 23% lower than MEGAN. Large regional discrepancies are apparent for the high-emitting evergreen broadleaf trees of central Africa and the adjacent deciduous broadleaf trees. In a follow-up paper we will exploit the OMI HCHO data to develop improved understanding of the environmental, seasonal, and interannual variations in isoprene emission over Africa using the OMI HCHO observations.

The two main uncertainties in using space-based HCHO column data to infer isoprene emission are (1) the isoprene oxidation mechanism as it relates to HCHO production under low-NO$_x$ conditions, (2) the coupling between transport and chemistry determining the displacement between observed HCHO columns and precursor isoprene emissions. The latter could be addressed by using a CTM adjoint inversion (Stavrakou et al., 2009a). This will eventually be necessary if we are to exploit the fine resolution of the satellite observations (13×24 km$^2$ in nadir for OMI) to obtain correspondingly fine constraints on isoprene emission. However, the value of such an approach is hampered at present by inadequate knowledge of the time-dependent HCHO
yields from isoprene oxidation under low-NO\textsubscript{x} conditions, and by the difficulty of representing the coupling between transport and chemistry over timescales relevant to boundary layer mixing and mesoscale motions. Future progress most critically requires an improved understanding of isoprene oxidation chemistry through laboratory and field measurements.
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Figure Captions

Figure 1:
HCHO columns and land cover types over Africa. The first three panels are annual mean HCHO columns for 2005-2009 at $1^\circ \times 1^\circ$ resolution: (a) original slant columns, (b) biogenic slant columns after removing biomass burning, dust, and anthropogenic influences, (c) vertical columns obtained by applying air mass factors (AMFs) to the slant columns. The bottom right panel (d) shows the Global Land Cover (GLC) map for 2000 (Bartholomé and Belward, 2005).

Figure 2:
Cumulative probability distribution of OMI smoke AAOD 8-day average values at $1^\circ \times 1^\circ$ resolution over southern Africa (south of $2^\circ$S) for 2005-2009. The $x$-axis is a probability scale such that a normal distribution would plot as a straight line. This allows us to separate biomass burning from non-biomass burning conditions by plotting separate regression lines fitted to the bottom and top quantiles of the data. Intersection of these regression lines defines a smoke AAOD threshold for diagnosing biomass burning conditions and we remove the corresponding scenes from the OMI data set. Different AAOD thresholds are used for different regions of Africa as discussed in the text.

Figure 3:
Flow chart of the filtering algorithm used to remove biomass burning, dust, and anthropogenic influences in OMI slant HCHO columns ($\Omega_s$). All data are 8-day averages on the same $1^\circ \times 1^\circ$ grid. The MODIS fire counts filter uses MODIS data for the 8-day periods preceding and concurrent with the OMI HCHO observation.
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Figure 4:
Cumulative yields of HCHO per unit carbon from isoprene oxidation as a function of time in the DSMACC chemistry box model using the standard GEOS-Chem chemistry scheme (red) and the Paulot scheme (blue) for different NO\textsubscript{x} levels and initialized at local noon. Details on the box model simulation are given in the text.

Figure 5:
Mean latitudinal gradients of boundary layer (>900 hPa) isoprene, MVK+MACR, and HCHO concentrations during the AMMA aircraft campaign in July-August 2006. The left panel shows the AMMA flight tracks superimposed on a map of MODIS leaf area index (LAI) (Yang et al., 2006) for the AMMA period. Observations averaged over 0.5\textdegree latitude bins are shown in black. Model results sampled along the flight tracks and at the flight times are shown in red (standard GEOS-Chem isoprene oxidation scheme) and in blue (Paulot scheme). Mean OMI HCHO for July-August 2005-2009 is shown in orange (see text).

Figure 6:
Annual mean tropospheric NO\textsubscript{2} columns over Africa at 12-15 local time (LT). The left panel shows OMI 2005-2009 data at 1\degree×1\degree resolution (Boersma et al., 2007). The right panel shows GEOS-Chem model values for 2006. The colorbar includes boundary layer (i.e. below 900 hPa) NO\textsubscript{x} estimated from column NO\textsubscript{2} (see text for details). Biomass burning influence was removed using MODIS fire counts and OMI smoke AAOD in the observations, and BC AOD in GEOS-Chem. The equator is indicated.
Figure 7: Mean longitudinal gradients of isoprene emission (black) and HCHO columns (color) across central Africa (3°S-3°N) at 12-15 LT in July. HCHO columns are shown for the OMI observations in 2005-2009 (orange) and from the GEOS-Chem simulations using the standard isoprene oxidation scheme (red) and the Paulot scheme (blue) in 2006 at 12-15 LT. Isoprene emissions are from MEGAN. The HCHO columns have been filtered against biomass burning as described in the text.

Figure 8: Dependence of the HCHO-isoprene relationship on the local tropospheric NO₂ column $\Omega_{NO2}$ over Africa in GEOS-Chem. The figure shows statistics of $S = \Delta \Omega_{HCHO}/\Delta E_{ISOP}$ computed as described in the text for individual 2°×2.5° gridsquares and months in 2006 at 12-15 LT. Values of $S$ have been sorted by the local value of $\Omega_{NO2}$ in 1×10¹⁴ molecules cm⁻² bins, and means and standard deviations are shown in each bin for GEOS-Chem using the standard isoprene oxidation scheme (red) and the Paulot scheme (blue). The data for $\Omega_{NO2} \leq 1 \times 10^{15}$ molecules cm⁻² show a linear relationship between $S$ and $\Omega_{NO2}$, and reduced-major-axis regression parameters are shown inset with standard deviations determined using jackknife resampling (Manly, 1997). The data for $\Omega_{NO2} > 1 \times 10^{15}$ molecules cm⁻² show no significant dependence between $S$ and $\Omega_{NO2}$, and the corresponding mean values and standard deviations of $S$ are shown inset. The mean $\Omega_{NO2}$ inferred from AMMA observations is also indicated (orange arrow).

Figure 9:
Annual average isoprene emissions from Africa at 1°×1° horizontal resolution at 12-15 LT.

Values inferred from the OMI HCHO 2005-2009 data (left) are compared to values from the MEGAN bottom-up inventory (center). The right panel shows the difference between the two. Results are for the ensemble of 1°×1° gridsquare-months that are not excluded from our analysis due to biomass burning, anthropogenic, dust, or smearing influences (see text). Completely excluded areas are shown in grey.
Figure 1: HCHO columns and land cover types over Africa. The first three panels are annual mean HCHO columns for 2005-2009 at $1^\circ \times 1^\circ$ resolution: (a) original slant columns, (b) biogenic slant columns after removing biomass burning, dust, and anthropogenic
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Figure 3: Flow chart of the filtering algorithm used to remove biomass burning, dust, and anthropogenic influences in OMI slant HCHO columns ($\Omega_s$). All data are 8-day averages on the same $1^\circ \times 1^\circ$ grid. The MODIS fire counts filter uses MODIS data for the 8-day periods preceding and concurrent with the OMI HCHO observation.
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Figure 5. Mean latitudinal gradients of boundary layer (>900 hPa) isoprene, MVK+MACR, and HCHO concentrations during the AMMA aircraft campaign in July-August 2006. The left panel shows the AMMA flight tracks superimposed on a map of MODIS leaf area index (LAI) (Yang et al., 2006) for the AMMA period. Observations averaged over 0.5° latitudinal bins are shown in black. Model results sampled along the flight tracks and at the flight times are shown in red (standard GEOS-Chem isoprene oxidation scheme) and in blue (Paulot scheme). Mean OMI HCHO for July-August 2005-2009 is shown in orange (see text).
Figure 6. Annual mean tropospheric NO$_2$ columns over Africa at 12-15 local time (LT). The left panel shows OMI 2005-2009 data at 1°×1° resolution (Boersma et al., 2007). The right panel shows GEOS-Chem model values for 2006. The colorbar includes boundary layer NO$_x$ estimated from column NO$_2$ (see text for details). Biomass burning influence was removed using MODIS fire counts and OMI smoke AAOD in the observations, and black carbon AOD in GEOS-Chem. The equator is indicated.
Figure 7. Mean longitudinal gradients of isoprene emission (black) and HCHO columns (color) across central Africa (3°S-3°N) at 12-15 LT in July. HCHO columns are shown for the OMI observations in 2005-2009 (orange) and from the GEOS-Chem simulations using the standard isoprene oxidation scheme (red) and the Paulot scheme (blue) in 2006 at 12-15 LT. Isoprene emissions are from MEGAN. The HCHO columns have been filtered against biomass burning as described in the text.
Figure 8. Dependence of the HCHO-isoprene relationship on the local tropospheric NO\textsubscript{2} column $\Omega$\textsubscript{NO\textsubscript{2}} over Africa in GEOS-Chem. The figure shows statistics of $S = \Delta \Omega_{\text{HCHO}} / \Delta E_{\text{ISOP}}$ computed as described in the text for individual $2^\circ \times 2.5^\circ$ gridsquares and months in 2006 at 12-15 LT. Values of $S$ have been sorted by the local value of $\Omega$\textsubscript{NO\textsubscript{2}} in $1 \times 10^{14}$ molecules cm\textsuperscript{-2} bins, and means and standard deviations are shown in each bin for GEOS-Chem using the standard isoprene oxidation scheme (red) and the Paulot scheme (blue). The data for $\Omega$\textsubscript{NO\textsubscript{2}} $\leq 1 \times 10^{15}$ molecules cm\textsuperscript{-2} show a linear relationship between $S$ and $\Omega$\textsubscript{NO\textsubscript{2}}, and reduced-major-axis regression parameters are shown inset with standard deviations determined using jackknife resampling (Manly, 1997). The data for $\Omega$\textsubscript{NO\textsubscript{2}} $> 1 \times 10^{15}$ molecules cm\textsuperscript{-2} show no significant dependence between $S$ and $\Omega$\textsubscript{NO\textsubscript{2}}, and the corresponding mean values and standard deviations of $S$
are shown inset. The mean and standard deviation of OMI $\Omega_{NO2}$ during AMMA (July-August 2006) is also shown (orange).
Figure 9. Annual average isoprene emissions from Africa at 1°×1° horizontal resolution at 12-15 LT. Values inferred from the OMI HCHO 2005-2009 data (left) are compared to values from the MEGAN bottom-up inventory (center). The right panel shows the difference between the two. Results are for the ensemble of 1°×1° gridsquare-months that are not excluded from our analysis due to biomass burning, anthropogenic, dust, or smearing influences (see text). Completely excluded areas are shown in grey.