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Accessibility
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 the OMI instrument to infer biogenic isoprene emissions at monthly 1 × 1° 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 AA TSR satellite data for persistent small-flame fires (gas flaring). The resulting biogenic HCHO columns (ΩHCHO) from OMI follow closely the distribution of vegetation patterns in Africa. We infer isoprene emission (EISOP) from the local sensitivity \( S = \frac{\Delta \Omega_{HCHO}}{\Delta E_{ISOP}} \) 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 NOx under low-NOx conditions that we fit to a linear function of tropospheric column NO2. We estimate a 40% error in our inferred isoprene emissions under high-NOx conditions and 40–90% under low-NOx conditions. Our results suggest that isoprene emission from the central African rainforest is much lower than estimated by the state-of-the-science MEGAN inventory.

1 Introduction

Isoprene (\( \text{CH}_2 = \text{C} (\text{CH}_3) \text{CH} = \text{CH}_2 \)) 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., 1995; Olivier et al., 1996; Arneth et al., 2008). It is a major precursor of organic aerosol (Claeys et al., 2004; Henze and Seinfeld, 2006; Kroll et al., 2006) and of tropospheric ozone (Trainer et al., 1987; Tao et al., 2003; Fiore et al., 2011), 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-Arnke 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 emissions in Africa are particularly limited, consisting of a few data for tropical rainforests (Klinger et al., 1998; Greenberg et al., 1999; Serça et al., 2001), woodlands (Greenberg et al., 1999, 2003; Otter et al., 2002), savannas (Guenther et al., 1996; Klinger et al., 1998; Otter et al., 2002; Harley et al., 2003; Saxton et al., 2007), and shrublands (Otter et al., 2002).

An alternate “top-down” approach for estimating above-canopy 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 midday lifetime of 1–2 h against photolysis and oxidation by OH. This adds to the HCHO background originating 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), although care is needed to screen biomass burning and large anthropogenic influences (Fu et al., 2007; Barkley et al., 2008). Inference of isoprene emissions from HCHO column measurements by the GOME (1995 launch), SCIAMACHY (2002), and OMI (2004) satellite instruments has been reported in a number of studies for North America (Abbot et al., 2003; Palmer et al., 2003, 2005; Millet et al., 2007), Asia (Fu et al., 2007), Europe (Dufour et al., 2009; Ceruti et al., 2010), South America (Barkley et al., 2008), and globally (Shim et al., 2005; Stavrakou et al., 2009a).

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 (NOx = NO + NO2) that originate in the atmosphere from combustion sources and soil emissions. Under these high-NOx conditions (> 1 ppb NOx) the organic peroxy radicals (RO2) 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 (Palmer et al., 2003; Millet et al., 2006). Under low-NOx conditions more typical of Africa, the RO2 radicals may instead react with HO2 or isomerize (Peeters et al., 2009), modifying and delaying HCHO yields (Palmer et al., 2003, 2006; Mao et al., 2010). 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 account-
Fig. 1. HCHO columns and land cover types over Africa. The first three panels are annual mean HCHO columns for 2005–2009 at 1 × 1° 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).

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

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 Eq. (1) from the OMI measurement of \( \Omega_s \) and refer to the residual as \( \Omega_s \) in what follows.

We thus compile 8-day average values for \( \Omega_s \) on a 1 × 1° (lat × lon) grid for 2005–2009 (Fig. 1a). The slant column fitting uncertainty for a single observation is 8 × 10\(^{15}\) molecules cm\(^{-2}\) on average. 8-day and 1 × 1° averaging reduces the uncertainty to 1–2 × 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 (Jaeglé et al., 2005; Barkley et al., 2008). 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 × 1 km² (Giglio et al., 2003) and we average them for 8 days on the same 1 × 1° grid as Ω. 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-Arnek 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 NO₂, and Barkley et al. (2008) previously used NO₂ as an additional filter to screen against biomass burning in tropical South America. However, we find that this filter is insufficient because the atmospheric lifetime of NOₓ emitted from biomass burning is only a few hours, whereas the influence of fires on HCHO is sustained downwind by oxidation of emitted NMVOCs (Hobbs et al., 1996; Trentmann et al., 2003; Alvarado et al., 2010).

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 (4–19° N), equatorial Africa (5° S–4° N), and southern Africa (south of 5° S). For each region we plot the 5-yr 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 (Oketola and Osibanjo, 2007; Hopkins et al., 2009; Reeves et al., 2010), biofuel use that is particularly intense in rural Nigeria (Yevich and Logan, 2003), and gas flaring in the Niger Delta (Casadio et al., 2012). 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., 2012). 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., 2012). We average the AATSR fire counts over the same 1 × 1° grid and 8-day averaging period as OMI and remove grid squares 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 biofuel use. We therefore remove a more extensive 3 × 3° area around the grid squares 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., 2012), 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. These excluded areas account...
for 27% of African isoprene emissions in the MEGAN inventory (Sect. 3.3). Figure 1 shows the mean OMI $\Omega_s$ 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 $\Omega_s$ obtained by spectral fitting is related to the true vertical column $\Omega_{\text{HCHO}}$ by an air mass factor (AMF = $\Omega_s / \Omega_{\text{HCHO}}$) 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.

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**Fig. 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 $1 \times 1^\circ$ grid. The MODIS fire counts filter uses MODIS data for the 8-day periods preceding and concurrent with the OMI HCHO observation.
3 GEOS-Chem model

3.1 General description

We use the GEOS-Chem global 3-D 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 $0.5 \times 0.67^\circ$ 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 $2 \times 2.5^\circ$ 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 NOx in Africa are from the EDGAR v2.0 inventory (Olivier et al., 1996). Biomass burning NMVOC and NOx emissions are from the Global Fire Emissions Database v2 (van der Werf et al., 2006). NOx 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 (Sumner et al., 2001; Karl et al., 2004, 2009) and following the recommendation of Karl et al. (2010).

We also include in the model wet and dry deposition of isoprene hydroperoxides and epoxides using respective Henry’s law constants of $1.7 \times 10^6$ M atm$^{-1}$ (US EPA, 2011) and $1.3 \times 10^6$ M atm$^{-1}$ (Eddingsaas et al., 2010). We account for the grid-scale transport of isoprene hydroperoxides, which have a sufficiently long lifetime against oxidation by OH (3–5 h; Paulot et al., 2009b) to contribute to spatial displacement (smearing) between isoprene emission and the resulting HCHO columns. Previous inversions of HCHO using GEOS-Chem did not include this transport and would therefore underestimate the smearing under low-NOx conditions.

3.2 Improved treatment of isoprene chemistry

GEOS-Chem includes detailed ozone-NOx-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 HO2 with >C2 peroxo 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-NOx 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-NOx conditions when the isoprene peroxy radicals (ISOPOO) produced from the isoprene + OH reaction react with HO2 rather than NO to form isoprene hydroperoxides (ISOPOOH). This titration is not seen in observations (Lelieveld et al., 2008; Ren et al., 2008). We implement as an alternate isoprene oxidation scheme in GEOS-Chem the Paulot et al. (2009b) mechanism, where regeneration of OH under low-NOx conditions takes place via oxidation of epoxioxydol species produced from oxidation of ISOPOOH. Isomerization of ISOPOO leading to formation of hydroperoxylaldehydes is another pathway for OH regeneration (Peeters et al., 2009; Peeters and Müller, 2010), but the kinetics are highly uncertain (Crounse et al., 2011; Taraborrelli et al., 2012). 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 RO2 + HO2 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 NOx levels. Each simulation uses fixed concentrations of O3 (28 ppbv), CO (150 ppbv), and NOx (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 conditions at the Equator with surface albedo of 0.1 and an ozone column of 260 Dobson units. Under high-NOx conditions (1 ppbv), we find that the ultimate HCHO yield is approached within a few hours and is similar for both schemes. Under low-NOx 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 NOx conditions (0.01 ppbv) where the ultimate yield is 30–40 % lower than under high-NOx 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 isoprene-HCHO relationship will be discussed further in Sect. 4 in the context of GEOS-Chem results and using OMI isoprene-HCHO relationship will be discussed further in Sect. 4 in the context of GEOS-Chem results and using OMI

Also shown in Fig. 4 are box model results for the standard scheme including artificial OH generation from oxidation of ISOPOOH to prevent OH titration (Lelieveld et al., 2008). We find that this has almost no effect on the HCHO time-dependent yield. The reason is that HCHO formation by the low-NOx channel involving ISOPOOH is limited in the standard scheme by the slow rate of ISOPOOH photolysis (lifetime of 8 days during daylight hours under box model conditions). Attack of ISOPOOH by OH in the standard scheme is assumed to take place mainly at the peroxide H and thus regenerate the peroxy radical ISOPOO. In the Paulot scheme, this attack results instead in the formation of epoxideols, with a different HCHO yield as shown in Fig. 4.

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, \( E_{ISOP} \), per unit area of Earth surface (atoms C cm\(^{-2}\) s\(^{-1}\)) is computed as:

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

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 dimensionless environmental scaling factors \( \gamma \) describe the effects of temperature \( (T) \), leaf age \( (AGE) \), soil moisture \( (SM) \), and canopy radiative environment \( (CE) \) on \( E_0 \). \( \gamma_{SM} \) 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).

We apply the environmental scaling factors \( \gamma \) as given by Guenther et al. (2006) to the local GEOS-5 environment, except for soil moisture. Stavrakou et al. (2009b) found in their analysis of GOME and SCIAMACHY HCHO satellite data that water stress has a major effect on isoprene emissions over southern Africa and is not well represented in MEGAN. We use here the soil moisture parameterization from Guenther et al. (2006) modified 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:

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

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 soil \( (m^3\text{ water m}^{-3}\text{ air}) \), 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 \( (2\, \text{cm}) \) and a root zone layer \( (1\, \text{m}) \). Müller et al. (2008) used a fixed wilting point value of 0.171, but here we use grid-ded 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) applied to MODIS IGBP landcover (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 20 % 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 \( \Omega_{HCHO} \) in terms of above-canopy isoprene emission using GEOS-Chem has relied on a local linear regression between the two
\[ \Omega_{\text{HCHO}} = SE_{\text{ISOP}} + B \]  

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 x 2.5° gridsquares. The first method yielded \( S = 2.4 \times 10^3 \text{ s} \) with high correlation \( (R^2 = 0.82) \), while the second yielded variable slopes with an interquartile range of 2.0–3.0 \( \times 10^3 \text{ s} \). These values were consistent with observation-based estimates for the PROPHET forest site in Michigan \( (2.1 \times 10^3 \text{ s}) \) and INTEX-A aircraft observations over the eastern US \( (2.3 \times 10^3 \text{ s}) \) (Palmer et al., 2003; Millet et al., 2006). 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 1.2 \( \times 10^3 \text{ s} \) in January–March to 2.2 \( \times 10^3 \text{ s} \) 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 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 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 conducted, mainly during daytime hours. Boundary layer winds were prevailing 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 8 August (Lagos urban plume) and 15 August (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 mean profiles of observed and simulated isoprene, MVK + MACR, and HCHO concentrations below 1 km altitude. The model is sampled along the flight tracks and at the flight times. Also included in Fig. 5 is the HCHO concentration below 1 km inferred from OMI observations for July–August 2005–2009 averaged over the AMMA longitudinal domain \( (1–4° \text{ E}) \) into 1° latitude bins (multi-year temporal averaging is needed to reduce measurement noise). The HCHO concentration below 1 km is inferred from OMI HCHO columns by using the mean HCHO vertical profile measured during AMMA (340 pptv above 2 km and linear increase from 2 km down to the surface).
The break in the OMI data at 5–7° N reflects the exclusion of anthropogenic influence from Nigeria (Sect. 2.2). Boundary layer (<1 km) NO\textsubscript{x} concentrations in the region of isoprene emission (7–13° N) averaged 360 pptv in the observations and 310 pptv in the model, reflecting a mix of influences from soil, anthropogenic, and distant biomass burning sources (Stewart et al., 2008; Hopkins et al., 2009; Reeves et al., 2010).

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 \(E\textsubscript{ISOP}\) in MEGAN (Ferreira et al., 2010; Murphy et al., 2010). MVK and MACR are first-stage C\textsubscript{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 of these species 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 ISOPOO + HO\textsubscript{2} reaction pathway, as described in Sect. 3.2, but this has negligible impact on the simulation of (MVK + MACR).

The far 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 (Hak et al., 2005, and references therein). Because HCHO is produced together with MVK + MACR and the first-stage production accounts for 80–90% of the ultimate HCHO yield under the AMMA conditions (see below), 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. Correlation between observed isoprene and HCHO is strongest (\(R^2 = 0.86\)) for a 0.5° northward shift of HCHO relative to isoprene. Smearing of \(\sim 0.5°\), combined with a mean observed southerly wind speed of 17 km h\(^{-1}\) south of 12° 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\textsubscript{x} conditions and low levels of isoprene, promoting loss of the ISOPOO radicals by reaction with NO which results in fast HCHO production (high-NO\textsubscript{x} pathway). Figure 6 shows the simulated fraction of ISOPOO radicals reacting with NO across Africa in July 2006 (Paulot scheme). For the AMMA region that fraction is \(\sim 50\%\). Stone et al. (2010) previously found a 70% mean fraction during AMMA using the DSMACC box model constrained by the NO observations.

The OMI NO\textsubscript{2} data offer a broad perspective on NO\textsubscript{x} regimes across Africa. Figure 7 shows annual average tropospheric columns of NO\textsubscript{2} (\(\Omega\textsubscript{NO_2}\)) 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. Assuming a linear decrease of NO\textsubscript{2} mixing ratio from the surface to 3 km with negligible NO\textsubscript{2} above, based on the AMMA observations (Stewart et al., 2008), we can make a rough estimate of the boundary layer (<1 km) NO\textsubscript{x} concentration from the OMI NO\textsubscript{2} data and this is also shown in Figure 7. Thus 1 ppbv of boundary layer NO\textsubscript{x} corresponds roughly to a tropospheric NO\textsubscript{2} column of \(2 \times 10^{15}\) molecules cm\(^{-2}\). The fitting precision of 7–8 \(\times 10^{14}\) molecules cm\(^{-2}\) for individual OMI NO\textsubscript{2} pixels (Boersma et al., 2007) is reduced to 3–4 \(\times 10^{13}\) molecules cm\(^{-2}\) for monthly mean data at 1° \(\times 1°\) resolution, so that levels as low as \(\sim 0.02\) ppbv NO\textsubscript{x} are
detectable. We see in Fig. 7 that much of Africa is in an intermediate NOx regime (0.1–1 ppbv). Even in the absence of continental biomass burning influences, significant boundary layer NOx levels are maintained in Africa by soil emissions (Jaeglé et al., 2005) and by decomposition of peroxyacetyl-nitrate (PAN) originating from outside the continent (Singh and Hanst, 1981; Moore and Remedios, 2010).

Inspection of Fig. 6 suggests that the equatorial rainforest, where isoprene emissions are very high, could be particularly sensitive to the expected smearing of the HCHO-isoprene relationship. There the model fraction of ISOPOO radicals reacting with NO is only 15%, even though boundary layer NOx is not particularly low (~300 pptv; Fig. 7). That region is ventilated by a steady easterly wind so that a longitudinal transect can reveal smearing. Figure 8 shows the longitudinal gradients of MEGAN $E_{\text{ISOP}}$, OMI $\Omega_{\text{HCHO}}$, and model column HCHO (standard and Paulot schemes) across the region at 0–3° N for gridsquares not influenced by biomass burning. Immediately downwind (to the west) of the rainforest is a shadow region where elevated HCHO does not correspond to collocated isoprene emission. The shadow region is well reproduced by the model using either the standard or Paulot scheme. 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. Combined with a mean easterly wind speed of 5 km h$^{-1}$ this implies a timescale of ~2–3 days for production of HCHO from isoprene, consistent with Fig. 4. We will see below how we can screen such shadow regions when inferring isoprene emissions from the OMI HCHO data.

4.2 NOx 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. (1). 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 × 2.5° 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 12:00–15:00 LT 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 (75–100° W, 27–40° N) for June–August 2006 using this approach are 1.9 and 2.0 × 10$^3$ s for the standard and Paulot schemes, respectively, similar to values reported by Millet et al. (2006, 2008) and Palmer et al. (2006).

We find that 41% of grid squares–months in GEOS-Chem over Africa have $S > 4 \times 10^3$ s, which is higher than HCHO
yields from isoprene emission would allow. This reflects smearing as diagnosed in the model and mainly affects regions where isoprene emissions are very low (such as the vast desert expanses as well as coastal grid squares). We exclude this population from further analysis; 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.

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. $\Omega_{NOx}$ so that the OMI $\Omega_{NOx}$ data can be applied to remove the effects of model errors in NO$_x$. Figure 9 shows the $S$ values calculated for individual 2 $\times$ 2.5° grid square-months over the African continent in 2006 as a function of local model $\Omega_{NOx}$. The data are averaged into $1 \times 10^{14}$ molecules NO$_2$ cm$^{-2}$ bins. For $\Omega_{NOx} \leq 1 \times 10^{15}$ molecules cm$^{-2}$ (roughly 0.5 ppbv boundary layer NO$_x$ using our conversion factor) we find a linear relationship between $S$ and $\Omega_{NOx}$ ($R^2 > 0.9$) reflecting the increasing importance of the RO$_2$ + NO pathway with increasing NO$_x$. For $\Omega_{NOx} > 1 \times 10^{15}$ 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.

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 $\Omega_{x}$ observations averaged over 1 $\times$ 1° grid squares 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 2 km, low values above 2 km), consistent with previous results for North America (Palmer et al., 2003; Millet et al., 2006), and suggesting that there is no particular problem in simulating the HCHO vertical shape factor under African conditions. 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. (1) involves errors in the slope $S$ due both to the chemical mechanism and to smearing. Figure 9 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 low-NO$_x$ yields of HCHO is needed. The error bars on $S$ shown in Fig. 9 (which we attribute mainly to smearing) are larger than errors induced by the chemical mechanism. From these error bars we derive a smearing uncertainty in $S$ of 750 s for the low-NO$_x$ regime ($\Omega_{NOx} = 0.2–1 \times 10^{15}$ molecules cm$^{-2}$) and 690 s for the high-NO$_x$ regime ($\Omega_{NOx} > 1 \times 10^{15}$ molecules cm$^{-2}$).

Error in the OMI tropospheric NO$_2$ column also propagates to error in the linear regression equation $S = (1600 \pm 160) \Omega_{NOx} + (721 \pm 114)$ for the low-NO$_x$ regime (Paulot scheme in Fig. 9). We use the expression from Boersma et al. (2008) to estimate the error standard deviation of NO$_2$ (molecules cm$^{-2}$) for 8-day average $\Omega_{NOx}$ observations:

$$\sigma_{NO2} = \frac{1.0 \times 10^{15} + 0.3 \times \Omega_{NOx}}{\sqrt{8 \times 3.5}}$$

Fig. 9. Dependence of the HCHO-isoprene relationship on the local tropospheric NO$_2$ column $\Omega_{NOx}$ 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 $\times$ 2.5° grid squares and months in 2006 at 12:00–15:00 LT. Values of $S$ have been sorted by the local value of $\Omega_{NOx}$ in $1 \times 10^{14}$ 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 $\Omega_{NOx} \leq 1 \times 10^{15}$ molecules cm$^{-2}$ show a linear relationship between $S$ and $\Omega_{NOx}$, and reduced-major-axis regression parameters are shown inset with standard deviations determined using jackknife resampling (Manly, 1997). The data for $\Omega_{NOx} > 1 \times 10^{15}$ molecules cm$^{-2}$ show no significant dependence between $S$ and $\Omega_{NOx}$, and the corresponding mean values and standard deviations of $S$ are shown inset.
and propagate this with the linear regression errors in the slope $m$ ($\sigma_m = 160 \times 10^{-15}$ s cm$^{-2}$ molecule$^{-1}$) and intercept $c$ ($\sigma_c = 114$ s). The resulting error standard deviation $\sigma_S$ in $S$ is $\sigma_S = \sqrt{(m \times \sigma_{NO_x})^2 + (\Omega_{NO_x} \times \sigma_m)^2 + \sigma_c^2}$, and is in the range 340–440 s for $\Omega_{NO_x}$ 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 NO$_x$, adding in quadrature the contributions from smearing and from the linear regression, is 823–870 s (35–84 %).

The overall error in inferring isoprene emission from OMI HCHO columns, adding in quadrature the errors in the OMI retrieval of HCHO columns and the conversion of HCHO columns to isoprene emission, is 40 % in the high-NO$_x$ regime and 40–90 % in the low-NO$_x$ regime. These errors apply to 8-day average 1 $\times$ 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 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 $\times$ 1° horizontal resolution derived in Sect. 2, monthly mean $S$ values computed from GEOS-Chem with the Paulot scheme, and 2005–2009 monthly mean NO$_x$ tropospheric column observations from OMI (Boersma et al., 2007).

Figure 10 shows the resulting spatial distribution of annual above-canopy isoprene emissions at 12:00–15:00 LT and compares with the corresponding values from the MEGAN inventory. Values are means for all 1 $\times$ 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 shows the difference between the OMI-derived emissions and values from MEGAN.

From the data in Fig. 10 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$^{-1}$). Some larger regional discrepancies are apparent. Maximum isoprene emissions in central Africa are displaced north in MEGAN relative to OMI, and OMI is on average 43 % lower than MEGAN over the central African rainforest, and 21 % higher over the southern deciduous broadleaf forests. The discrepancy in central Africa increases to 53 % if scenes with > 40 % cloud cover are excluded from the MEGAN emission inventory for consistency with the OMI screening threshold.

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 NO$_2$ 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 columns data requires knowledge of the time-dependent HCHO yield from isoprene oxidation. This is a challenge in the tropics because of the prevailing low-NO$_x$ 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 NO$_x$ dependence of the HCHO yield under low-NO$_x$ conditions, and a delay between isoprene emission and HCHO production ranging from less than a day under high-NO$_x$ conditions to several days under low-NO$_x$ conditions. This delay smears the local relationship between isoprene emission ($E_{ISOP}$) and HCHO columns ($S_{HCHO}$).

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. The conditions for isoprene oxidation in AMMA are intermediate between the low-NO$_x$ and high-NO$_x$ regimes, with 50 % of isoprene peroxy radicals (ISOPOO) reacting with NO. Inspection of longitudinal gradients across the equatorial forest of central Africa, which is more strongly in the low-NO$_x$ regime (15 % of ISOPOO reacting with NO), indicates a smearing of ~ 200–300 km. This means that large isoprene source regions under low-NO$_x$ 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 $2 \times 2.5^\circ$ GEOS-Chem grid resolution and on a monthly basis by conducting a sensitivity simulation with uniformly perturbed isoprene emission and inferring the relationship $S = \Delta \Omega_{\text{HCHO}} / \Delta E_{\text{ISOP}}$. 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 500 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 estimated error in OMI-derived isoprene emissions is 40% at high NO$_X$ and 40–90% at low NO$_X$ for 8-day averages with $1 \times 1^\circ$ resolution. Smearing makes the largest contribution to the estimated 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. The total OMI-derived isoprene emission for the African continent is 22% lower than MEGAN. Large regional discrepancies are apparent for the high-emitting evergreen broadleaf trees of central Africa and the southern hemisphere 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 ($13 \times 24$ 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$_X$ 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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Fig. 10. Annual average isoprene emissions from Africa at $1 \times 1^\circ$ horizontal resolution at 12:00–15:00 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 $1 \times 1^\circ$ 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.

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