Interpreting satellite column observations of formaldehyde over tropical South America

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Space-borne column measurements of formaldehyde (HCHO), a high-yield oxidation product of volatile organic compounds (VOCs), represent important constraints for quantifying net regional fluxes of VOCs. Here, we interpret observed distributions of HCHO columns from the Global Ozone Monitoring Experiment (GOME) over tropical South America during 1997–2001. We present the first comparison of year-long in situ isoprene concentrations and fire-free GOME HCHO columns over a tropical ecosystem. GOME HCHO columns and in situ isoprene concentrations are elevated in the wet and dry seasons, with the highest values in the dry season. Previous analysis of the in situ data highlighted the possible role of drought in determining the elevated concentrations during the dry season, inferring the potential of HCHO columns to provide regional-scale constraints for estimating the role of drought on isoprene emissions. The agreement between the observed annual cycles of GOME HCHO columns and Along-Track Scanning Radiometer firecount data over the Amazon basin (correlations typically greater than 0.75 for a particular year) illustrates the potential of HCHO column to provide quantitative information about biomass burning emissions.

Keywords: formaldehyde; volatile organic compound; biogenic emissions; biomass burning; global ozone monitoring experiment

1. Introduction

The terrestrial biosphere emits a wide range of reactive volatile organic compounds (VOCs; Kesselmeier & Staudt 1999). Biogenic VOCs emitted by the terrestrial biosphere have important implications for tropospheric O3 (Wang & Shallcross 2000), formation of organic aerosol (e.g. Claeys et al. 2004) and climate change (Sanderson et al. 2003). Isoprene is the dominant non-methane VOC with an estimated global annual emission of 440–660 Tg C (Guenther et al. 2006).

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Bottom-up emission models, which describe the magnitude and variability of biogenic VOC fluxes (e.g. Guenther et al. 2006), are derived largely from sparse in situ measurements, representative of less than 1 km, and are at least a factor of 2 uncertain on regional and global scales (Guenther et al. 2006). Temporal variability in these models is driven by a series of empirical relationships relating biogenic emissions to weather and climate (e.g. surface temperature and photosynthetic active radiation; PAR). This approach has worked well for deciduous mid-latitude forests, but it has not been tested extensively for tropical ecosystems where other external factors play a role in determining the seasonal cycle of biogenic emissions, e.g. the hydrological cycle (Kuhn et al. 2002). Current bottom-up models estimate that 75% of biogenic VOCs are emitted from tropical ecosystems (Guenther et al. 2006).

Detailed in situ biogenic VOC data for tropical ecosystems (e.g. Serça et al. 2001; Kesselmeier et al. 2002; Trostdorf et al. 2004; Baker et al. 2005) are invaluable for testing models and evaluating satellite data, but are sparse in time and space. Satellite observations provide information on scales of tens to hundreds of kilometres and therefore represent the ideal tool for extrapolating in situ data to continental scales.

We have shown previously that column measurements of HCHO, a high-yield oxidation product of VOCs, from the Global Ozone Monitoring Experiment (GOME) can be used to quantify net fluxes of VOCs, specifically isoprene over North America during summertime, on spatial scales of hundreds of kilometres (Palmer et al. 2003, 2006). The atmospheric abundance of HCHO is determined by a balance between production from the oxidation of VOCs and losses from oxidation by the hydroxyl radical and photolysis. Oxidation of CH₄ provides a global background of HCHO. In continental boundary layers, oxidation of short-lived VOCs dominates over the source from CH₄, resulting in a major enhancement of the total HCHO column. Anthropogenic sources of VOCs are important in urban environments, but biogenic sources usually dominate elsewhere, at least during the growing season. In the tropics, biomass burning is also an important source of HCHO from both direct emissions (Andreae & Merlet 2001) and the oxidation of co-emitted hydrocarbons. Formaldehyde columns measured from space therefore provide constraints on the underlying VOC emissions. As discussed in §2, correlation of the HCHO column distribution measured by GOME with the emission field of the parent VOCs thus depends on the VOC lifetime, the HCHO yield from VOC oxidation and the HCHO lifetime. Non-zero lifetimes for both the parent VOCs and the HCHO result in smearing and displacement of the correlation.

Figure 1 shows the August 2000 monthly mean distribution of GOME HCHO columns. The global distribution shows elevated HCHO columns over several continental regions, reflecting land-surface sources, above a global background due to the oxidation of CH₄. The feature over the southeast USA is from the oxidation of isoprene emitted from broadleaf trees (Palmer et al. 2003, 2006). The elevated columns over eastern Asia are from a mixture of anthropogenic, biogenic and pyrogenic VOCs (Fu et al. 2007). As we discuss in this paper, over the tropics the main features are due to VOC emissions from biomass burning, with a smaller source from biogenic VOC emissions. Noisy, elevated columns over eastern South America and the South Atlantic are due to the South Atlantic Anomaly, a region where the magnetic field of the Earth is at a minimum allowing high-energy particles from space to hit the satellite detector.

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In §2, we describe the GOME HCHO columns and how they can be used to estimate VOC emissions. In §3, we present the first comparison between seasonal cycles of GOME HCHO, and ground-based measurements of isoprene concentration and satellite measurements of firecount over tropical South America. We conclude the paper in §4.

2. Satellite observations of HCHO columns and their relationship to VOC emissions

(a) Retrieval of vertical HCHO columns

GOME is a nadir-viewing UV/vis solar backscatter instrument aboard the European Remote-Sensing-2 satellite, launched in 1995 (Burrows et al. 1999). The satellite is in a sun-synchronous orbit, crossing the equator at approximately 10.30 local solar time in the descending node. Spectra are collected for three forward scans of the Earth: east, centre and west, each with a pixel size (‘footprint’) of 40×320 km². Full mapping of the globe is achieved in 3 days. HCHO columns from GOME are useful until the end of 2001 (Palmer et al. 2006), after which instrument degradation hampers quantitative analysis of observed spectra.

For brevity, we include here only a short description of the retrieval of HCHO columns from the measured radiances. For further details, we refer the reader to Chance et al. (2000), Palmer et al. (2001, 2003, 2006) and Martin et al. (2002). Vertical columns of HCHO derived from measurements of backscattered UV absorption are determined using a two-step procedure: (i) slant columns are fitted in the 336–356 nm wavelength region, with a mean column fitting uncertainty of $4\times10^{15}$ mol cm$^{-2}$, and (ii) vertical columns are calculated from fitted slant

![GOME HCHO slant columns](image-url)

Figure 1. Monthly mean HCHO slant columns observed by the GOME during August 2000. The data are for a 10.30 local equator crossing time, averaged on a $2^\circ\times2.5^\circ$ grid, and cloud cover 40% or less.
columns using an air-mass factor (AMF) formulation that accounts for the HCHO vertical profiles and scattering processes from aerosols and clouds, in addition to Rayleigh scattering.

The two major sources of error in the retrieval of vertical HCHO columns are from slant column fitting and the AMF calculation (Palmer et al. 2006). For a typical scene over North America with a vertical column of $2 \times 10^{16}$ mol cm$^{-2}$ and an AMF of 0.7, the overall uncertainty of the vertical column is $9 \times 10^{15}$ mol cm$^{-2}$. For the work shown here, we use only GOME data with an associated cloud fraction of less than 40%. A more restrictive cloud filter does not affect the HCHO slant column statistics (Palmer et al. 2001).

(b) Relating observed HCHO columns to VOC emissions

VOCs emitted to the atmosphere are oxidized photochemically by a succession of steps leading eventually to the formation of CO$_2$ and H$_2$O. Formaldehyde is a high-yield intermediate of this oxidation chain. Laboratory chamber data are available for the HCHO yield from oxidation of many VOCs in atmospheres with high concentrations of nitrogen oxides (NO$_x$=NO+NO$_2$). In the general case of the oxidation of a hydrocarbon (RH) by OH, the organic peroxy radical (RO$_2$) produced in the first stage of oxidation reacts with NO, producing HCHO or higher carboxylic acids that subsequently react to eventually yield HCHO (Atkinson 1994). In this manner, one obtains ultimate HCHO yields per unit carbon of 1 for methane and typically 0.3–1 for C$_2$–C$_6$ VOCs (Altshuller 1991). Yields less than unity reflect mainly the formation of peroxyacyl radicals (RC(O)OO), which on further reaction with NO, followed by cleavage, converts the $\alpha$ carbon to CO$_2$.

The theory for relating HCHO column to emissions of reactive VOCs is described in Palmer et al. (2003). In the absence of horizontal transport, the HCHO column $Q$ at steady state is linearly related to the sum of the underlying VOC emissions $E_i$ scaled by their HCHO yields $Y_i$ as follows:

$$Q = \frac{1}{k_{\text{HCHO}}} \sum_i Y_i E_i,$$  \hspace{1cm} (2.1)

where $k_{\text{HCHO}}$ is the loss rate constant for HCHO (reaction rate with OH, photolysis) applied to $Q$; reaction with O$_3$ and NO$_3$ represents minor losses during the day when GOME passes overhead. Horizontal transport smears this local relationship to a degree that depends on wind speed and the time lag between VOC emission and HCHO production.

In practice, a chemistry transport model (CTM) is used to quantify the local relationship between VOC emissions and HCHO columns as a linear transfer function to infer local VOC emissions from the GOME HCHO columns,

$$Q = SE_{\text{VOC}} + B,$$  \hspace{1cm} (2.2)

where $S$ denotes the linear slope determined by the chemistry; $E_{\text{VOC}}$ is the local VOC emissions; and $B$ is the background HCHO determined by the oxidation of VOCs that produce $(1-1/e)$ of the ultimate HCHO yield on timescales greater than a day (Palmer et al. 2003).

Palmer et al. (2003) showed using equation (2.1) that over North America during summertime, only isoprene contributes significantly to the observed variability in GOME HCHO column data. They used the GEOS-Chem CTM.
chemical mechanism to relate isoprene emissions to HCHO columns over North America and showed that even in low NO\textsubscript{x} conditions (0.1 ppb), isoprene can rapidly produce significant HCHO concentrations. This conclusion is supported in Palmer et al. (2006) by calculations from the fully explicit Master Chemical Mechanism (MCM; Saunders et al. 2003), in which the GEOS-Chem mechanism was found to be within 20–30\% of the time-dependent HCHO yield predicted by the MCM.

Palmer et al. (2006) evaluated subsequent isoprene emissions derived from GOME against in situ data and showed that GOME tracked the seasonal variation with a −30\% bias over North America. The MEGAN isoprene emission dependence on surface air temperature (Guenther et al. 2006) explained 75\% of the month-to-month variability in GOME-derived isoprene emissions over the southeast USA during May–September 1996–2001. Palmer et al. (2006) used the MCM to parametrize the time-dependent HCHO yield from the oxidation of alpha- and beta-pinenes for use in GEOS-Chem. Alpha- and beta-pinenes have atmospheric lifetimes of a few hours against OH and O\textsubscript{3}, with initial products including HCHO (with a smaller per carbon yield than isoprene), other aldehydes and acetone. Long-lived intermediates such as acetone delay HCHO production, leading to a diffuse contribution to observed HCHO columns comparable to the slant column fitting uncertainty (Palmer et al. 2006).

Tropical ecosystems emit a large number of VOCs for many of which we have an incomplete knowledge of their oxidation chemistry, limiting our current ability to infer speciated VOC emissions from observed HCHO columns over these regions. Over Amazônia, Kuhn et al. (2004) showed that a number of monoterpene compounds, including sabinene, alpha- and beta-pinenes, camphene and limonene, had a similar diurnal pattern. Recent observations over western tropical Africa show similar results. Figure 2 shows the mean diurnal cycles of isoprene, alpha- and beta-pinenes and limonene during 1–13 June 2006, at a surface field station in northern Benin (sampling and methods are described in Saxton et al. (2007)). All VOCs measured were present in significant quantities during the day. There was also significant daily variation in the concentrations, owing to changes in local weather. As discussed above, we already have some quantitative understanding of the time-dependent HCHO yield from alpha- and beta-pinenes. The contribution of limonene to the observed variability in HCHO columns has not previously been considered, owing to lack of data and an incomplete knowledge of its oxidation chemistry. Limonene has an atmospheric lifetime of less than 1 h against OH and O\textsubscript{3}. Similar to beta-pinene, HCHO is a primary product. Further production of HCHO from subsequent oxidation of intermediates from limonene is likely to occur faster than the other monoterpenes because all oxidation products are reasonably reactive (cf. acetone for alpha- and beta-pinenes). Based on its chemical structure, it is probable that approximately three HCHO molecules can ultimately be produced from one molecule of limonene, but in practice, the precise yield is influenced by the extent to which intermediate radicals undergo isomerization reactions (M. Jenkin 2006, personal communication, Imperial College, UK). In future work, we will estimate the time-dependent production of HCHO from limonene using the MCM, which currently includes only a small subset of biogenic VOCs isoprene, alpha- and beta-pinenes and methylbutenol (Palmer et al. 2006).
Figure 3 shows the seasonal variation of observed HCHO columns over northwestern South America (20°S–10°N, 60°S–80°W) during the period 1997–2001. We have minimized the influence of fires in our analysis of this region by excluding scenes where an active fire has been identified by monthly mean Along-Track Scanning Radiometer (ATSR) firecounts taken from the European Space Agency World Fire Atlas (WFA, dup.esrin.esa.int/ionia/wfa/index.asp). The ability of WFA firecount data to observe active fires is discussed in §3b.

For the northwestern South American region, defined above, there are two peaks in the 1997–2001 mean HCHO columns, one in March and another in September. The March peak is observed by HCHO columns during 1998, 1999 and 2001; this peak is muted in 1997 (an El Nino year), occurring earlier in the year, and does not appear in 2000. The September peak is a feature observed in all years shown, but with some year-to-year variability in magnitude and timing. Formaldehyde columns during May–June are close to background values from CH₄ oxidation. Formaldehyde production from isoprene oxidation is still

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Figure 2. Mean hourly surface VOC data taken during 1–13 June 2006 at a surface field station in northern Benin (Nanganthori, 9°38.84′N, 1°44.46′E), as part of the African Monsoon Multidisciplinary Analyses campaign. Filled circles denote mean values for that period and the vertical lines associated with each mean value denote the range between the minimum and maximum concentrations over the measurement period. Horizontal arrows denote the relevant ordinate axis. Measurement accuracy and precision are estimated to be 20 and 15%, respectively, with a limit of quantification of 0.03 ppb for each species. Further *in situ* measurement details can be found in Saxton *et al.* (2007).
significant even with low NOx concentrations typically found over remote tropical ecosystems away from active fires (e.g. Jacob & Wofsy 1988). Any smearing effect due to time-delayed HCHO production owing to peroxide formation (via HO2–RO2 reactions) will effectively be included as the background HCHO over the defined geographical region.

In situ isoprene data are sparse, but there is almost a complete annual record of isoprene concentration 67 km south of Santharé (2°51.42′ S, 54°57.42′ W) for 2002 (Trostdorf et al. 2004). We acknowledge that the comparison between GOME and in situ data is between a relatively large region of northwestern South America with point measurements over the Amazon basin. Fire-free GOME scenes over the Amazon basin are rare due to its coarse spatial footprint. We anticipate a more detailed comparison of this region with new sensors that have finer spatial resolution. Degradation of the GOME spectral channel used for HCHO compromises the quantitative worth of columns beyond 2001. Instead, we compare the mean 1997–2001 GOME signal (filled black circles) with the in situ concentration data from 2002 to help interpret the observed seasonal variation in HCHO columns.

Figure 3 shows a large seasonal cycle in surface isoprene concentrations ranging from 0.5 to 5 ppb, with largest values in October and a smaller peak in concentration during March, in agreement with GOME HCHO columns. The timing of the second peak starts earlier in GOME, but could be due to spatial variations in vegetation or year-to-year variability in the second peak. Trostdorf et al. (2004) showed that standard canopy emission models could...
not explain this seasonal cycle, even with increases in ambient levels of surface temperature and PAR during the dry season; a similar conclusion was reached for biogenic emission studies over central Africa (Serça et al. 2001). They used monthly rainfall rates to define three seasons to help explain the seasonal cycle in isoprene concentrations: wet, transition and dry seasons. The dry season, spanning August–December, shows the lowest level of precipitation; the wet season typically spans January–May; and the transition season occurs during June and July, characterized by irregular rains with lower frequency and intensity than during the wet season. This study concluded that leaf-level isoprene emission rates had increased from the wet to dry season, related to water availability, in accordance with branch enclosure measurements from another site (Kesselmeier et al. 2002); as noted by Kesselmeier (2004), it is also possible that these changes in emission rates are also partly due to phenological variation.

(b) Biomass burning

In § 3a, we used ATSR firecounts to remove the influence of fires in our interpretation of observed HCHO columns from GOME in terms of biogenic emissions. Here, we argue that this biomass burning signal in HCHO has quantitative worth that can be used to estimate emissions of trace gases from fires. The general approach encapsulated by equations (2.1) and (2.2) can be readily applied to VOC emissions from biomass burning, provided there is accurate information to estimate the time-dependent HCHO production from VOC oxidation. Such a detailed study is outside the scope of this paper. Figure 4 illustrates the potential of GOME HCHO column data to provide quantitative information on biomass burning emissions by comparing the annual cycles of HCHO columns and ATSR firecounts over the Amazon basin (20°S–0° N, 50–65° W), where much of the seasonal fire activity occurs.

The main burning season spans August–October and is shown by elevated monthly mean firecounts and HCHO columns over the Amazon basin. There is also significant year-to-year variability in both datasets, a reflection of both climate and human activity. Correlation between observed HCHO columns and firecounts for a particular year is typically greater than 0.75. Monthly mean HCHO columns during the peak of the burning are greater than $2 \times 10^{16}$ mol cm$^{-2}$, more than a factor of 2 larger than values earlier in the year. HCHO columns at the start of year are noisy and may reflect regions that include both biogenic emissions and biomass burning.

Firecounts represent information about the location and persistence of active fires. Sampling of these fire patterns affects the ability to relate them to surface emission estimates. Instrument issues such as night-time sampling, multi-day repeat times, identifying non-vegetation fires and the coarse spatial resolution all hamper derived emission estimates (Mota et al. 2006). The amount of HCHO produced from a fire will depend on its intensity, i.e. smouldering versus active, a quantity not available from current space-borne sensors. Here, we have shown for the first time that the broad features of the observed HCHO column distribution over the Amazon basin are consistent with what we know about the regional burning season.
4. Future directions

We have presented the first qualitative comparison between GOME HCHO columns and in situ measurements of isoprene concentration and ATSR firecounts over tropical South America. In general, the GOME data reproduce the broad features of biogenic emissions and biomass burning. Here, we outline some of the key challenges necessary to relate the observed HCHO columns to speciated VOC emissions.

A number of VOCs are emitted in large quantities from tropical ecosystems, but our knowledge of their oxidation chemistry is sufficiently poor, particularly at low NO\textsubscript{x} concentrations (0.1 ppb or less); thus, we are currently unable to estimate speciated VOC emissions from observed HCHO columns. This was illustrated in this paper with limonene. We know from structural analysis that it has a short lifetime and can produce HCHO, but the rate at which HCHO is produced, critical for interpreting HCHO column measurements, is unknown. Further dedicated laboratory and field studies are needed to improve the current situation.

A more fundamental approach to estimating net fluxes is to estimate directly the parameters that describe the magnitude and variability of VOC emissions, e.g. the Q10 factor describing the temperature dependence of isoprene emission. This can be achieved by using either an ad hoc inverse model that estimates time-dependent surface emissions, as outlined in this paper, and fits them to Q10 factors or an optimal estimation inverse model that solves for model parameters directly from the weighted difference between model and data.

![Figure 4. Monthly mean GOME HCHO slant columns and monthly mean ATSR firecounts over central Amazonia (20° S–0° N, 50–65° W) for 1997–2001. The number n of slant columns used to calculate the monthly spatial mean is typically greater than 30. Horizontal dashed lines denote the fitting uncertainty scaled by $\sqrt{n}$. Correlations between slant columns and firecounts for a particular year are typically greater than 0.75. The small black dots denote the multi-year mean (1997–2001) of the seasonal HCHO column cycle over this region, and the associated vertical lines denote the standard deviation about each mean value.](http://rsta.royalsocietypublishing.org/)

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New satellite instruments, such as the Ozone Monitoring Instrument, can measure HCHO with a spatial resolution of an order of 250 km$^2$ (cf. 12 800 km$^2$ for GOME) and with daily global coverage (cf. global coverage within 3 days for GOME). These advances in resolution improve the probability of cloud-free scenes and consequently lead to a greater number of useful data points; provide a better opportunity to spatially disaggregate different sources of HCHO, e.g. biomass burning and biogenic emissions; and potentially can provide a more detailed description of land-surface processes. However, care must be taken when relating observed HCHO columns to parent VOC emissions. For example, isoprene takes approximately an hour to produce $(1 - 1/e)$ of the ultimate HCHO yield, corresponding to a smearing length-scale of 100 km (Palmer et al. 2003). Without resorting to more complicated inverse model techniques, 100 km may represent the finest resolution that is useful for estimating VOC emissions. Even at this spatial scale, a top-down VOC emission inventory would significantly reduce uncertainties in chemistry–climate calculations.

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