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What drives the observed variability of HCN in the troposphere and lower stratosphere?

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Abstract

We use the GEOS-Chem global 3-D chemistry transport model to investigate the relative importance of chemical and physical processes that determine observed variability of hydrogen cyanide (HCN) in the troposphere and lower stratosphere. Consequently, we reconcile ground-based FTIR column measurements of HCN, which show annual and semi-annual variations, with recent space-borne measurements of HCN mixing ratio in the tropical lower stratosphere, which show a large two-year variation. We find that the observed column variability over the ground-based stations is determined by a superposition of HCN from several regional burning sources, with GEOS-Chem reproducing these column data with a positive bias of 5%. GEOS-Chem reproduces the observed tropical HCN variability from the Microwave Limb Sounder and the Atmospheric Chemistry Experiment satellite instruments with a negative bias of 7%. We show the tropical biomass burning emissions explain mostly the observed HCN variations in the upper troposphere and lower stratosphere (UTLS), with the remainder due to atmospheric transport and HCN chemistry. In the mid and upper stratosphere, atmospheric dynamics progressively exerts more influences on HCN variations. The extent of temporal overlap between African and other continental burning seasons is key in establishing the apparent bienniel cycle in the UTLS. Similar analysis of other, shorter-lived trace gases have not observed the transition between annual and bienniel cycles in the UTLS probably because the signal of inter-annual variations from surface emission has vanished before arriving at the lower stratosphere (LS), due to shorter atmospheric lifetimes.

1 Introduction

Hydrogen cyanide (HCN) is a tracer of biomass burning (BB; Lobert et al., 1990; Holzinger et al., 1999) and could play a non-negligible role in the nitrogen cycle (Li et al., 2000, 2003). Before we can confidently use HCN to infer surface sources and

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sinks of trace gases we must first develop a robust understanding of the chemical and physical processes that determine observed variability.

Laboratory and field measurements support that BB is the major source for atmospheric HCN but the magnitude is still uncertain (0.1–3.2 Tg N/year) (Li et al., 2003 and references therein). Automobile exhaust and industrial processes represent additional minor tropospheric sources of HCN (Lobert et al., 1991; Bange and Williams, 2000; Holzinger et al., 2001). The HCN source from burning domestic biofuel is still unclear with studies reporting values from zero, based on laboratory fire measurements in Africa (Bertschi et al, 2003), to 0.2 Tg N/year based on analysis of aircraft concentration measurements over the western Pacific downwind of eastern Asia (Li et al., 2003), which probably reflects regional differences in the nitrogen content of domestic biofuels. Ocean uptake has been hypothesized as the dominant tropospheric sink with values ranging from 0.73 to 1.0 Tg N/year, where it is biologically consumed (Singh et al., 2003), leading to a lifetime of 5 months in the troposphere (Hamm and Warneck 1990; Li et al., 2003). Additional minor sinks of HCN include atmospheric oxidation by the hydroxyl radical (OH) and $O(^1D)$, photolysis, and scavenging by precipitation, yielding a stratospheric lifetime of a few years (Cicerone and Zellner, 1983; Brasseur et al., 1985). Li et al. (2000, 2003) showed using the GEOS-Chem global 3-D model that the observed seasonal variation of the HCN tropospheric column in different regions of the world was consistent with a scenario where BB provides the main source and ocean uptake provides the main sink. Recently Lupu et al. (2009) reproduced similar seasonal variations of the HCN tropospheric column using the GEM-AQ tropospheric global 3-D model.

Ground-based HCN column measurements from Fourier transform infrared (FTIR) spectrometers, available at several sites around the world (Mahieu et al., 1995, 1997; Rinsland et al., 1999, 2000, 2001, 2007; Zhao et al., 2000, 2002), represent important but sparse constraints to our quantitative understanding of HCN spatial and temporal distributions. As we show later these data show large variations on intra-seasonal to yearly timescales. Recent analysis of satellite HCN measurements from the NASA

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Aura Microwave Limb Sounder (MLS) (Waters, 2006) and the Atmospheric Chemistry Experiment Fourier Transform Spectrometer (ACE-FTS) (Boone et al., 2005) show an approximate 2-year cycle of HCN anomalies in the tropical upper troposphere and lower stratosphere (UTLS) (Pumphrey et al., 2008), hypothesized to be due to year-to-year variations in surface burning over Indonesia and Australia. These satellite measurements potentially provide invaluable global constraints on BB but first we have to reconcile the observed annual cycle from ground-based and 2-year cycle from MLS and ACE-FTS measurements. We use the GEOS-Chem global 3-D chemistry transport model (CTM) (Bey et al., 2001; Li et al., 2003) to understand the role of surface emissions, and atmospheric chemistry and transport in determining the observed variations of HCN from ground-based and space-borne measurements.

In the next section we describe the GEOS-Chem HCN simulation and evaluate model concentrations using ground-based FTIR and space-borne measurements. In Sect. 3 we examine the model ability to reproduce observed tropical HCN anomalies and in Sect. 4 we determine the importance of surface biomass burning emissions, atmospheric chemistry and transport in reproducing this tropical signal. We conclude the paper in Sect. 5.

2 Description and evaluation of GEOS-Chem HCN simulation

2.1 Model description

We use the GEOS-Chem global 3-D CTM (version 7.4.11) to simulate the atmospheric distribution of HCN from 2001 to 2006. Our calculations use assimilated meteorological analyses from the Goddard Earth Observing System v4 (GEOS4) of the NASA GMAO (Global Modeling and Assimilation Office), at 6-h temporal resolution (3-h for surface variables and mixed layer depths), updated until 2006. We use the model with a horizontal resolution of $2^{\circ}\times2.5^{\circ}$ (Lat.×Lon.) and 30 levels (derived from the native 48 levels) ranging from the surface to the mesosphere, 20 of which are below 12 km.

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Here we focus on model details pertinent to the HCN simulation; for a more detailed description of the GEOS-Chem model we refer the reader to Bey et al. (2001), Martin et al. (2002), and Park et al. (2004).

The HCN simulations are conducted for a 6-year period (January 2001–December 2006), using the previous 24 months to remove initial conditions. Correspondingly, we study the ground-based observation from January 2001 to December 2006 and space-borne observations from September 2004 to December 2006. The time domain of our analysis is limited by the availability of GEOS-4 meteorology, which runs to January 2007. We use fixed 3-D monthly mean OH fields (see below) that linearize the HCN simulation, allowing us to describe total HCN concentrations as a linear sum of contributions from individual source regions/types. For our experiments, we include two continental sources: BB and domestic biofuel burning. Figure 1 shows the ten source regions we study in this paper: North America (NA), South America (SA), Europe (EU), northern Africa (NAF), southern Africa (SAF), boreal Asia (BA), Southeast Asia (SE AS), and Indonesia and Australia (IND+AUS). Table 1 shows the latitude and longitude definitions of each geographical region.

We use monthly mean BB emission estimate of HCN, based on CO estimates from the Global Fire Emission Database version 2 (GFEDv2) (van der Werf et al., 2006), using an observed HCN:CO emission ratio of 0.27% over the western Pacific (Li et al., 2003). Figure 2 shows that global HCN BB emissions peak in August and to a lesser extend in January, with global annual values ranging from 0.63 to 0.77 Tg N/year over 2001–2006. The largest emissions originate from Africa, SA, IND+AUS, SE AS and BA, with only small emissions from NA and EU. Figure 2 also shows that the zonal mean of BB over 2001–2006 is generally larger in the tropics, as expected, with northern tropical regions (NAF) leading the southern tropics (SAF, SA) by approximately 8 months. Monthly mean emissions of domestic biofuel burning have a small seasonal cycle related to the heating source and are based on CO emission estimates from Streets et al (2003), scaled by an HCN emission factor of 1.6% (Li et al., 2003). We estimate a global domestic biofuel burning HCN source of 0.22 Tg N/year, with

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the largest contributions from Asia (0.19 Tg N/year) and EU (0.02 Tg N/year). Table 1 shows the estimates of HCN emission over 2001–2006 (BB+domestic biofuel burning) from each region. Emissions over the study regions are comparable in magnitude, except over NA and EU, where they are an order of magnitude smaller; we do not investigate further NA and EU. We include the ocean uptake of HCN by air-to-sea HCN transfer flux, following Li et al. (2003). We estimate an ocean sink of 0.73 Tg N/year, peaking in September–December due to the higher surface sea temperature (SST) in the southern hemisphere, reflecting the correlation between HCN deposition velocity over oceans and SST (Singh et al., 2003; Li et al., 2000, 2003).

The largest atmospheric sink of HCN is due to chemical reaction with OH. We use monthly mean tropospheric OH fields from a full-chemistry GEOS-Chem (version 5.07.08) simulation, and use monthly mean stratospheric OH fields from Aura MLS v2.2 data from September 2004 to December 2007, distinguishing between day/night (for each calendar month, fields were produced for day time and night time, respectively) values (Pickett et al., 2006, 2008). The HCN+OH reaction rate coefficient is taken from recent analysis (Kleinboehl et al., 2006) that recommends using a value that is 40% smaller than values used in previous modelling studies (Li et al., 2003). This HCN sink represents a loss of approximately 0.12 Tg N/year. The sink of HCN due to reaction with $O(^1D)$, the rate constant taken from Kleinboehl et al. (2006), represents a minor sink for HCN and we do not discuss this further. We also include a source of HCN from the oxidation of CH_3CN by OH, using a 30% molar yield (Kleinboehl et al., 2006). We acknowledge this molar yield is extremely uncertain and later we present a sensitivity calculation that does not include this HCN source.

2.2 Model evaluation

2.2.1 Ground-based FTIR observations

Ground-based FTIR observations of HCN vertical columns are available at Mauna Loa, Hawaii (19.5° N, 155.6° W, altitude 3.4 km), Kitt Peak, Arizona (31.9° N, 116° W,

altitude 2.09 km), and the Jungfraujoch research station, Switzerland (46.6° N, 8.0° E, altitude 3.58 km), from the Network for Detection of Atmospheric Composition Change (NDACC, http://www.ndacc.org). GEOS-Chem is sampled at the location of each station and convolved with the instrument-specific averaging kernel (Mahieu et al., 1995, 1997; Rinsland et al., 1999, 2000, 2001, 2007).

Figure 3 shows the observed and model HCN total columns at the three stations between 2001 and 2006. In general, we find reasonable agreement (typically bias less than 10%) between the model and observed HCN columns, acknowledging that over some stations the measurement coverage is sparse. Observed and model total columns of HCN at Jungfraujoch show a strong seasonal cycle that peaks in during mid-summer and troughs during mid-winter, with model values typically within +3%. Using our linearly decomposed HCN simulation over Jungfraujoch we show that the seasonal cycle is determined by NAF and BA BB. In particular, the large 2002 and 2003 fire seasons (van der Werf et al., 2006) over BA are captured at this location. At the lower latitude stations, Mauna Loa and Kitt Peak, the seasonal cycle is less pronounced due to the superposition of many regional burning signatures. Model discrepancy is typically less than +5% but can reach +25% (e.g., Summer/Autumn 2003 over Mauna Loa). Model HCN columns over Mauna Loa and Kitt Peak have a strong intraseasonal variation, peaking in March and September. Early in the calendar year, total HCN column variations are determined by NAF, SE AS and IND+AUS. Southern hemisphere burning peaks over SAF and SA during September–October. Elevated burning during 2001 over SE AS is captured by the model and measurements over Mauna Loa.

Figure 3 also shows partial (7–20 km) HCN vertical columns over Jungfraujoch, which exhibit a similar but weaker seasonal cycle evident in the total columns. The model captures the broad seasonal cycle of HCN over this altitude range (discrepancies are typically less than 1%), but cannot capture observed values at the peaks and troughs. Space-borne HCN data from the ACE-FTS satellite instrument (Boone et al., 2005) provides additional information over Jungfraujoch. ACE is a Canadian-led solar occultation mission launched in August 2003 into a circular orbit inclined at 74° to the

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equator (Bernath et al., 2005), measuring up to 30 occultations per day that mainly sample mid- and high latitudes. The vertical resolution of ACE-FTS is 3 to 4 km, limited by the instrument field of view. Comparing to ground-based FTIR spectrometers, the ACE-FTS instrument has lower time resolution (crosses the equator 8 times per year). We use ACE-FTS data that fall within 41–51° N. The interannual variations of ACE-FTS HCN are in a good qualitative agreement with the ground-based measurements with a positive bias of 17%. The model generally reproduces the ground-based observations with a positive bias of 5%.

2.2.2 Space-borne observations

Satellite measurements have the major advantage of obtaining global coverage and therefore putting observed variations at fixed stations into a broader context. For our study we use HCN retrievals from the ACE-FTS instrument (described above) and the Aura Microwave Limb Sounder (MLS). The MLS instrument (Waters, 2006) was launched in July 2004 aboard the Aura spacecraft. MLS is an emission limb sounder, operating in the millimetre and sub-millimetre spectral regions. A single day of observations consists of 3495 scans across the Earth's limb and covers all latitudes between 82° S and 82° N with a resolution of about 1.5° of latitude. Successive orbits are separated by 25° of longitude. MLS makes daily, global measurements of 14 trace species using 32 spectrometers distributed across five different regions of the spectrum. The HCN mixing ratio is retrieved from a spectrometer centred on the 177.26 GHz spectral line. Further details can be found in Pumphrey et al. (2006, 2008), who note that the standard HCN product is very noisy and has large biases in the lower stratosphere. As a result, an alternative HCN product was developed which has reduced noise at the cost of being available as a weekly zonal mean (Pumphrey 2006, 2008). Although the zonal mean values of standard HCN product are generally not recommended for use in the lower stratosphere, we find that MLS HCN anomalies agree with other measurements over the equatorial regions. The restriction to equatorial regions is necessary because one of the largest sources of error for HCN retrieval is interference from HNO_3,

which has a small mixing ratio and a small seasonal cycle in the tropical lower stratosphere. We focus on the variation of equatorial HCN, and take the benefit of daily time resolution, by using the standard version 2.2 daily product.

Figure 4 shows tropical (10° S–10° N) zonal mean of ACE-FTS HCN concentration from September 2004 to December 2006 and the sample of the global 3-D model fields at the time and location of ACE-FTS data, taking into account the ACE-FTS field-of-view. The model only captures the very broad features of the zonal mean distribution and generally has a negative bias (typically ∼15%) in the UTLS compared with ACE-FTS. This bias is consistent with our previous comparison with ground-based FTS data that showed ACE-FTS data had a positive bias of 17% relative to ground-based column data. Both ACE-FTS and GEOS-chem HCN show a strong hemispherical asymmetry in the upper troposphere, with a very low HCN mixing ratio in southern high latitudes, implying the large ocean sink of HCN as suggested by Li et al. (2000, 2003). Figure 4 also shows tropical zonal mean of MLS v2.2 HCN daily data from September 2004 to December 2006 and the relative model sample. As discussed previously, the zonal mean of MLS HCN shows larger biases in the lower stratosphere, especially away from tropics (10° S–10° N). In the tropics, MLS HCN concentrations have a negative bias (typically 20%) at altitudes of 50 hPa–20 hPa and a positive bias at higher (∼10%) and lower (∼25%) altitudes, relative to ACE-FTS measurements. However, as we show below, of more importance in this study is the ability of MLS and ACE-FTS to accurately observe the temporal variability in HCN.

3 Model and observed variability of HCN in the troposphere and stratosphere

Atmospheric transport from the troposphere to the stratosphere generally plays an important role in the atmospheric distribution of trace gases. Over the tropics, deep convection via cumulonimbus clouds reaching the UTLS and large-scale ascent via the major upward branch of the Brewer-Dobson (BD) circulation in the stratosphere represent the dominant vertical transport processes. Studies have shown that for trace

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gases over the tropics with an atmospheric lifetime longer than the transit time from the tropopause to the mid-stratosphere, there is a clear upward transport of the signal from annual fluctuations, which has been called the "atmospheric tape recorder" (Mote et al., 1996). For H_2O and CO, there is a clear annual tape recorder effect (Mote et al., 1996; Schoeberl et al., 2006). However, a recent analysis of HCN anomalies from Aura MLS and ACE-FTS instruments showed an approximate 2-year cycle (Pumphrey et al., 2008), and it was suggested that this was partly due to the year-to-year variability in BB emissions over Indonesia and Australia.

We determine HCN anomalies, defined here as the fluctuation from the time mean, from ACE-FTS and MLS data and the GEOS-Chem model. Model HCN anomalies are calculated by sampling the global 3-D HCN field as in the same way as they are sampled by ACE-FTS and MLS. Figure 5 shows that model HCN anomalies in the troposphere alternate between positive and negative on a 12-month cycle, with the positive anomalies occurring from September to January and negative anomalies from February to August. Starting from the UTLS the seasonal anomalies from 2 consecutive years merge to form a 2-year cycle in the stratosphere. Figure 5 shows that there is remarkable agreement at the UTLS between model HCN anomalies in the troposphere and MLS and ACE-FTS HCN anomalies in the UTLS (with a typical bias of only 3%). This suggests that the model and measured HCN anomalies are consistent, and using the GEOS-Chem model as an intermediary suggests that the ground-based FTS data are consistent with MLS and ACE-FTS. However, the contour lines for the GEOS-Chem HCN slope upwards more steeply than those for the observed mixing ratios, implying that vertical transport in the model is more rapid than in the real atmosphere, particularly at altitudes above 30 hPa (Figs. 10 and 11 of Schoeberl et al., 2008). Due to the limited time resolution of ACE-FTS instrument (crosses the equator 8 times per year), we have to smooth the ACE-FTS data in time to retrieve the continuous tape recorder of HCN. We use a kernel smoothing technique (Wand and Jones, 1995) with a bandwidth of 0.2 year. Unsurprisingly, seasonal variations of HCN in the troposphere (peaks in February/September and troughs in June/November), and simi-

lar stratospheric variations but with a month lag, observed by MLS are not well captured by ACE-FTS because of the 0.2 year bandwidth kernel smoothing. The 2-year cycle in the lower stratosphere is still captured by the smoothed ACE data.

We conducted the HCN simulation for a 6-year period (January 2001–December 2006), allowing us to put the relatively short ACE (April 2004) and MLS (September 2004) record in to a broader temporal perspective. Figure 6 shows that our results over the ACE-FTS and Aura MLS time period are consistent with the 6-year model calculation that encompasses approximately three 2-year cycles in the LS. We find that the quasi-biennial oscillation (QBO) of tropical zonal wind in the stratosphere may also have a connection to the 2-year cycle of HCN in the stratosphere over tropics. The QBO, an approximate 2-year oscillation in equatorial zonal winds between easterlies and westerlies in the tropical stratosphere, can influence the upward branch of Brewer-Dobson (BD) circulation and the atmospheric transport of chemical species (Plumb et al., 1995; Baldwin et al., 2001). A secondary circulation, associated with the superposition of the QBO upon the BD circulation, consists of an increase in the upwelling during the easterly shear phase of the QBO and a suppression of the upwelling during the westerly shear phase of the QBO (Plumb and Bell, 1982), and can consequently modify distributions of atmosphere tracers in the tropical stratosphere. The QBO signal has been observed in tropical ozonesonde data (Logan et al., 2003) and satellite measurements of other trace gases such as ozone, methane and water vapor (Randel and Wu, 1996; Randel et al., 1998, 2007; Schoeberl et al., 1998, 2008). However, it is still not clear to us whether the transition between the annual variation of HCN in the UT and the 2-year cycle in the LS is related to the QBO. Recent analysis of variability of MLS HCN measurements suggested the variations of surface burning in Indonesia and Australia might contribute to the inter-annual variability of HCN in the LS (Pumphrey et ao, 2008). In the next section we investigate the role of atmospheric dynamics and regional BB on determining the tropical variation of HCN through a sensitivity analysis of the model results.

Table 2 shows the 2001–2006 mean percentage contribution of regional BB emis-

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sions to the global HCN budget and to the tropical stratospheric HCN budget. We find the largest contributions to the global budget are from IND+AUS, NAF, SAF, SA, and BA, all representing more than 10%; contributions from NA and EU represent less than 3%, as expected. The largest stratospheric contributions are from IND+AUS, NAF, SAF, and SA, again all representing more than 10%. We find the increased stratospheric percentage contributions from individual HCN budget terms compared to the global values are from IND+AUS, NAF and SE AS, corresponding to the active tropical convective regions as found by Liu et al. (2005). BB emissions represent approximately 80% of tropical stratospheric HCN, with the remainder from domestic biofuel and from the oxidation of CH_3CN (Sect. 2).

4 Sensitivity of results to biomass burning, dynamics and atmospheric chemistry

In this section we investigate how sensitive model HCN anomalies are to changes in our assumptions about atmospheric dynamics, biomass burning and atmospheric chemistry.

4.1 Role of atmospheric dynamics and biomass burning sources

Figure 6 showed that the tape recorder effect of model HCN between 2001 and 2006 encompassed approximately three 2-year cycles in the lower stratosphere. To isolate the influence of dynamics and BB emissions on variations in HCN, we calculate HCN anomalies using a single year (2001 in this study) of either meteorology or BB emissions, respectively, eliminating the effect of year-to-year variations in atmospheric transport or BB emissions. Figure 7 shows highest correlations between BB emissions and variability of HCN over the tropical troposphere and lower/mid-troposphere, suggesting that surface BB emissions are the primary driving factor for observed HCN variability in the troposphere and lower stratosphere. Surface emissions from Africa, In-

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donesia and Australia contribute the most to both the magnitude (Table 2) and variability of HCN over this vertical region. Year to year changes in meteorology (e.g., QBO) play a larger role in determining HCN variability in the upper stratosphere (Fig. 7).

So why during some years is HCN anomalously high in the lower stratosphere? Figure 8 suggests that both the magnitude of the emissions and the length of burning seasons play a role. Here, we have identified monthly emissions that are greater than the 2001–2006 mean (denoted by red triangles) as a crude measure of peak burning months that determine the burning season; anomalous burning months (denoted by blue squares) are 2.5 times greater than the mean. The African burning season, according to GFEDv2 (van der Werf et al., 2006) estimates, is more regular in magnitude (peaking in late/early months) and timing than burning seasons from other continents, reflected in the contribution of atmospheric HCN from Africa BB emissions. Based on the small number of complete burning seasons, the only two common characteristics for anomalous high HCN concentrations in the UTLS (2002/03, 2004/05, 2005/06) is 1) larger than normal emissions and 2) longer burning seasons from IND+AUS and/or SA. We acknowledge that the duration of the burning season and the magnitude of emissions may be interrelated. During 2002/03, BB emissions over IND+AUS are particularly high (Fig. 8), resulting in anomalously high contributions to atmospheric HCN in late 2002 (Fig. 7), that begin to overlap in time with lofted African airmasses. During 2004/05, the burning season over IND+AUS was longer than normal (Fig. 8) and BB emissions over SA were anomalously large (Fig. 8). This resulted in anomalously high HCN contributions from both regions, overlapping in time with lofted African airmasses. During 2005/06, anomalously high BB emissions from SA (Fig. 8) provide similar contributions to the HCN budget in the lower and mid-troposphere than emissions from Africa (Fig. 7), resulting in anomalously large HCN concentrations. The temporal overlapping of relatively regular African BB emissions and emissions from other continents is key in establishing the apparent bienniel cycle of HCN in the UTLS.

Why is this transition between annual and bienniel variations not observed in other trace gases? This is probably due to the atmospheric lifetime of the tracer being stud-

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ied. For CO, with an atmospheric lifetime much less than HCN, especially in the stratosphere, the signals due to surface emissions are too weak in the LS.

4.2 The HCN source from CH_3CN+OH

As discussed above, our quantitative understanding of the HCN source from the oxidation of CH_3CN by OH is incomplete (Kleinboehl et al., 2006 and references therein). In our control simulation we used a 30% molar HCN yield that reconciled model calculations and balloon measurements at mid and high latitudes (Kleinboehl et al., 2006). This atmospheric source of HCN is generally small in the troposphere (<1% of total HCN concentrations) but plays a larger role in the stratosphere (typically 5%), particularly at high latitudes (>7%). We find that including this HCN source does help to decrease (~25%) the discrepancy between model and ACE-FTS observed HCN concentrations in the stratosphere (figure not shown) but does not improve further the model ability to capture observed HCN variations.

5 Concluding remarks

We have interpreted observed variations of HCN in the troposphere and lower stratosphere using the GEOS-Chem global 3-D model of atmospheric chemistry and transport. We found that the observed annual and semi-annual variations in column HCN at three ground-based stations at low and mid-latitudes are described by the model with a positive bias of 5%. Using GEOS-Chem, we find that these variations are largely determined by biomass burning, with a number of superimposed regional burning signals in tropical latitudes. Using HCN measurements from ACE-FTS and MLS, we find that in the UTLS the dominant period of variability is close to 24 months. This is the case for both the 28 months which overlap our GEOS-Chem simulation and for the entire operating period to date of both instruments. Using GEOS-Chem, we were able to reproduce the observed variability, typically with a negative bias of 7%, over the

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28 months. Putting that observation period into a longer temporal perspective, by inspecting model variability from the previous four years, we observe a strong variability on a timescale of 24 months in the lower stratosphere.

We find that tropical biomass burning is the largest single source of HCN and represents most of variability in the UTLS over the tropics, with the remainder of the variability due to atmospheric transport processes, including an influence from the quasi-biennial oscillation (QBO) in the upper stratosphere. However, there is no clear evidence linking QBO to HCN in the UTLS and in this study we do not attempt to address the observed variation in the upper stratosphere. We find that the extent of temporal overlap between African BB emissions and those from other continents, particular Indonesia, Australia and South America, is key in establishing the apparent bienniel cycle in the UTLS. Transition from the annual and semi-annual variations of trace gases in the upper troposphere to the 2-year variation in the lower stratosphere has not been observed previously, perhaps due to the shorter life time of the other trace gases studied.

The main objective of this paper was to develop HCN as a reliable tracer for biomass burning, which we could use to infer surface sources and sinks. Without first reconciling the apparent discrepancy between available observations it would be difficult to achieve that objective. Using a global 3-D chemistry transport model was key in achieving this reconciliation. The model was able to reproduce the magnitude and variability of observed column concentrations over a limited number of available ground stations. GEOS-Chem was only able to reproduce the broad scale features of the HCN distributions observed by ACE-FTS and MLS but it successfully predicted the timing and magnitude of observed fluctuations of HCN in the upper troposphere and lower stratosphere, reflecting the model ability to reproduce atmospheric transport. Reducing the discrepancy between model and observed HCN concentrations will require better constraints on the surface emissions and also on the atmospheric chemistry. We acknowledge that using upper tropospheric measurements of HCN to infer surface sources and sinks will be difficult without stronger constraints on the rest of the troposphere.

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However, these observations provide information about mechanisms of stratosphere-troposphere exchange (STE) of air and the origin of that air, particularly if they are used in conjunction with concurrent measurements of CO and O_3 which we will explore in future work.

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Table 1. Latitude and longitude definitions of geographical source regions and associated HCN flux estimates (Tg N/year) over 2001–2006 (BB+domestic biofuel burning).

	Geographical source regions							
	SE AS	IND+AUS	NAF	SAF	SA	NA	EU	BA
Latitude and longitude definition	7° N–45° N; 60° E–152° E	50° S–7° N; 88° E–165° E	1° S–36° N; 18° W–60° E	48° S–1° S; 5° E–60° E	57° S–16° N; 95° W–32° W	16° N–88° N; 173° W–50° W	36° N–88° N; 18° W–60° E	45° N–88° N; 60° E–180° E
HCN emission estimate	0.18	0.11	0.14	0.13	0.11	0.04	0.03	0.14

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Table 2. The 2001–2006 mean percentage contribution of regional BB emissions to the global and stratosphere HCN budgets.

	Biomass burning regions						
	IND+AUS	NAF	SAF	SA	SE AS	BA	Other regions
Contribution (%) to global HCN budget	12.2	15.8	14.6	12.5	5.9	10.9	6.3
Contribution (%) to tropical stratospheric HCN budget	15.2	19.5	14.3	11.4	8.6	4.8	2.9

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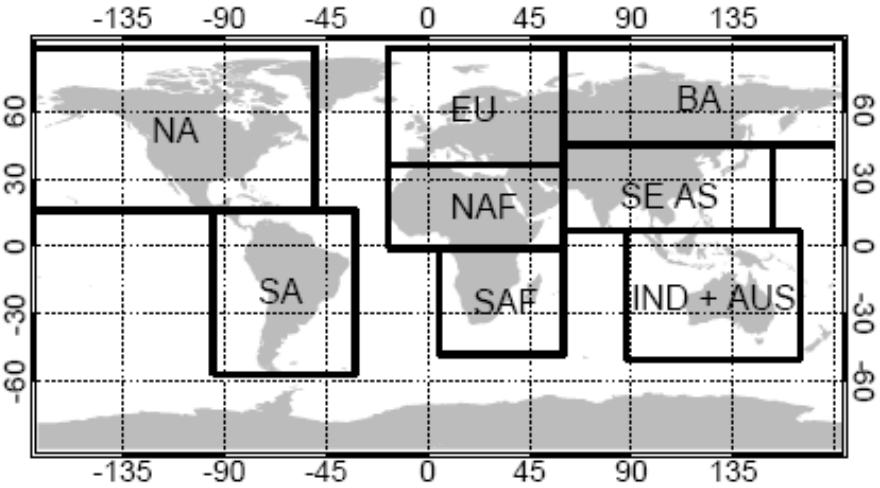

Fig. 1. Geographical source regions for the linearly decomposed HCN simulation. The regions are denoted North America (NA), South America (SA), Europe (EU), boreal Asia (BA), North Africa (NAF), southern Africa (SAF), Southeast Asia (SE AS), and Indonesia and Australia (IND+AUS). See Table 1 for latitude and longitude definitions and associated flux estimates.

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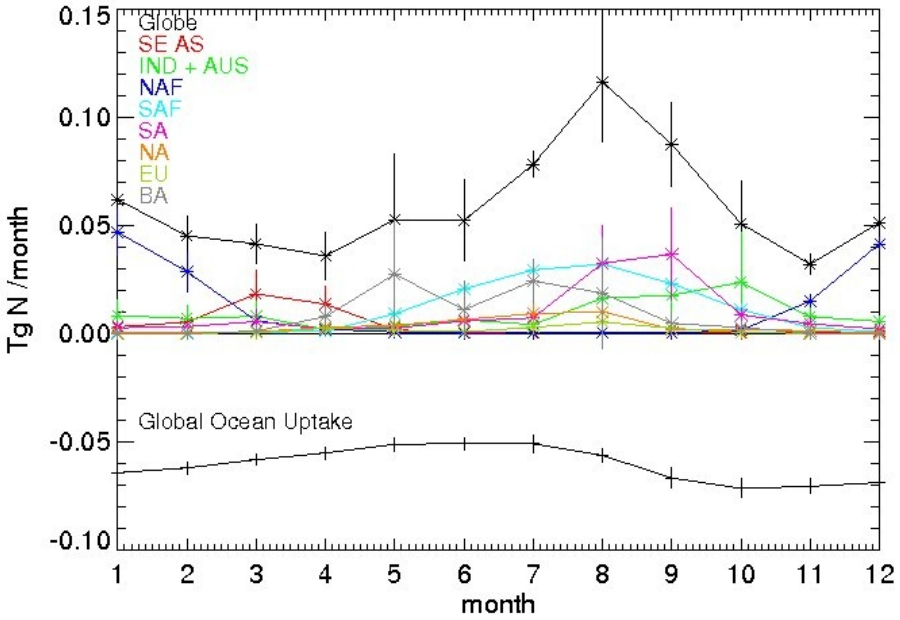

Fig. 2. Seasonal variation of global and regional mean of biomass burning sources and the ocean sink of HCN (Tg N/month) over 2001–2006. Vertical lines denote the 1-standard deviation about the mean value. Biomass burning emissions are based on GFEDv2 (van der Werf et al., 2006) and scaled by using an observed HCN:CO emission ratio of 0.27% (Li et al., 2003). The ocean sink parameterization follows Li et al. (2003).

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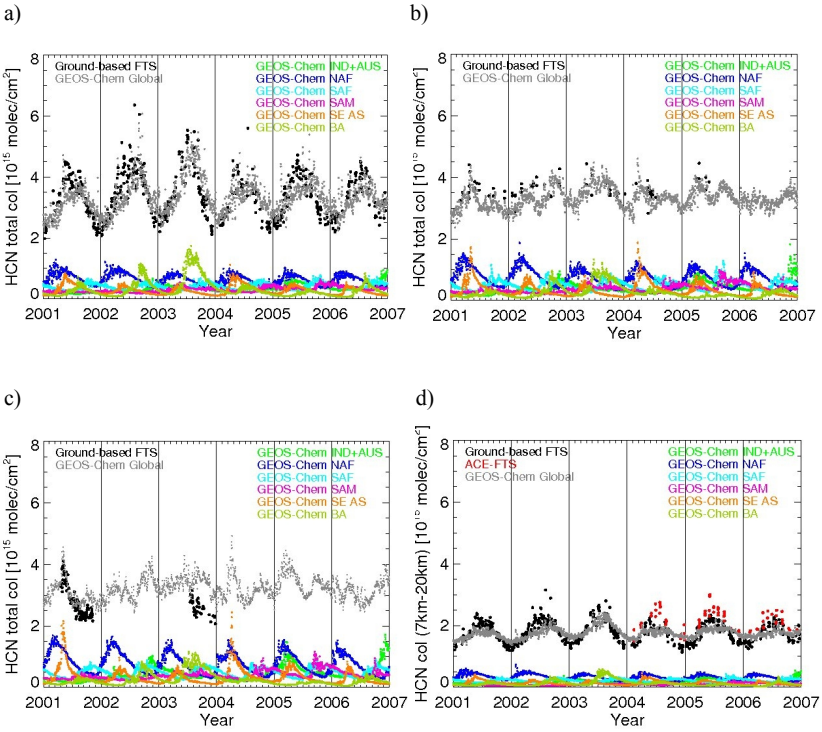

Fig. 3. Time series of FTS-observed (black dots) and GEOS-Chem model (grey dots) HCN total columns (10^{15} molec/cm^2) over **(a)** Jungfraujoch, Switzerland (46.6° N, 8.0° E, altitude 3.58 km); **(b)** Kitt Peak, Arizona (31.9° N, 116° W, altitude 2.09 km); and **(c)** Mauna Loa, Hawaii (19.5° N, 155.6° W, altitude 3.4 km). Panel **(d)** shows observed and model HCN columns between 7 and 20 km over Jungfraujoch station, with the red dots denote HCN columns measured by the ACE-FTS satellite instrument falling within 41–51° N. Other colors denote HCN contributions from regional BB emissions. Vertical lines denote calendar years.

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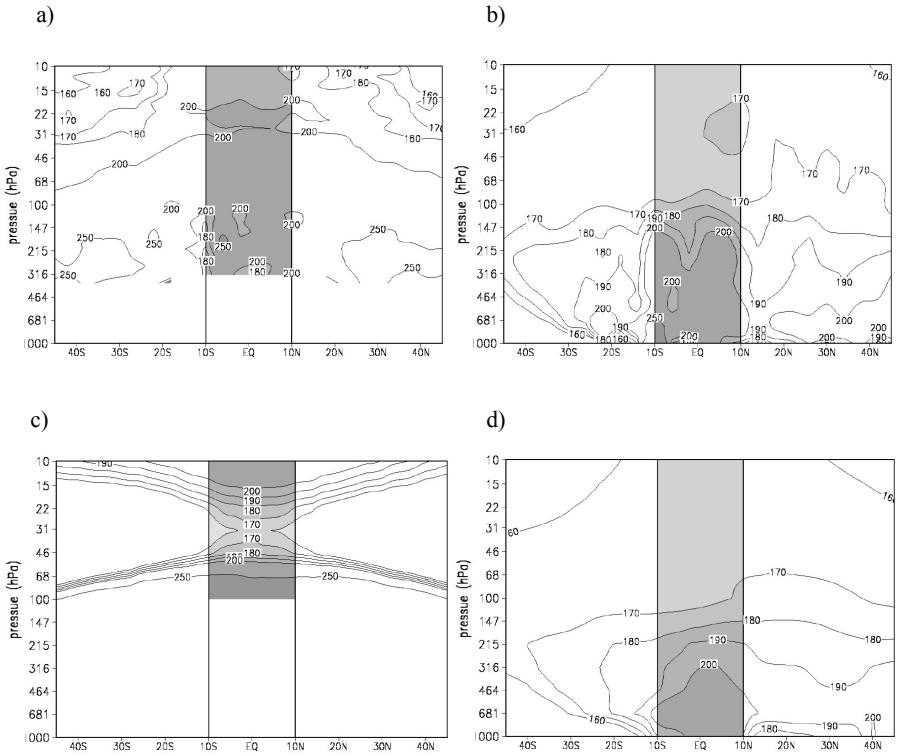

Fig. 4. Zonal mean of ACE-FTS (top left) and MLS (bottom left) measurements of HCN concentrations (pptv) and corresponding GEOS-Chem HCN concentrations, sampled as observed by the satellite instruments (right panels), from 1 September 2004 to 31 December 2006. The shaded regions define the tropical regions (10° S–10° N) over which the HCN anomalies are calculated.

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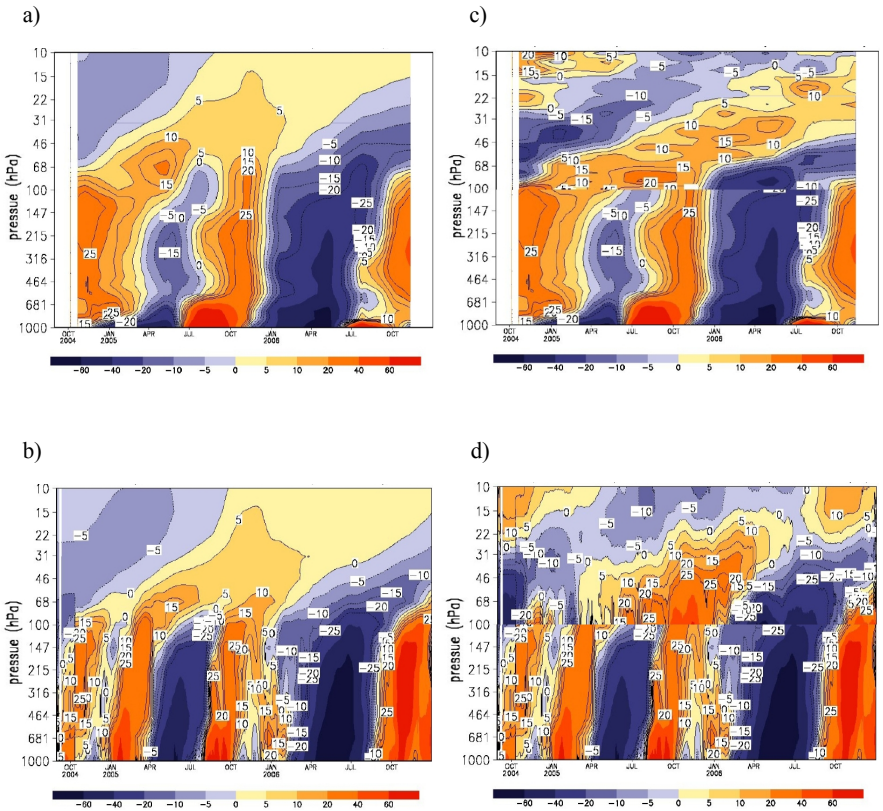

Fig. 5. Model tropical (10° S–10° N) HCN anomalies (pptv) between September 2004 and December 2006 as would be observed by **(a)** ACE-FTS and **(b)** MLS; and the superposition of UTLS HCN anomalies observed (100 hPa–10 hPa) by **(c)** ACE-FTS and **(d)** MLS on model (1000 hPa–100 hPa) anomalies.

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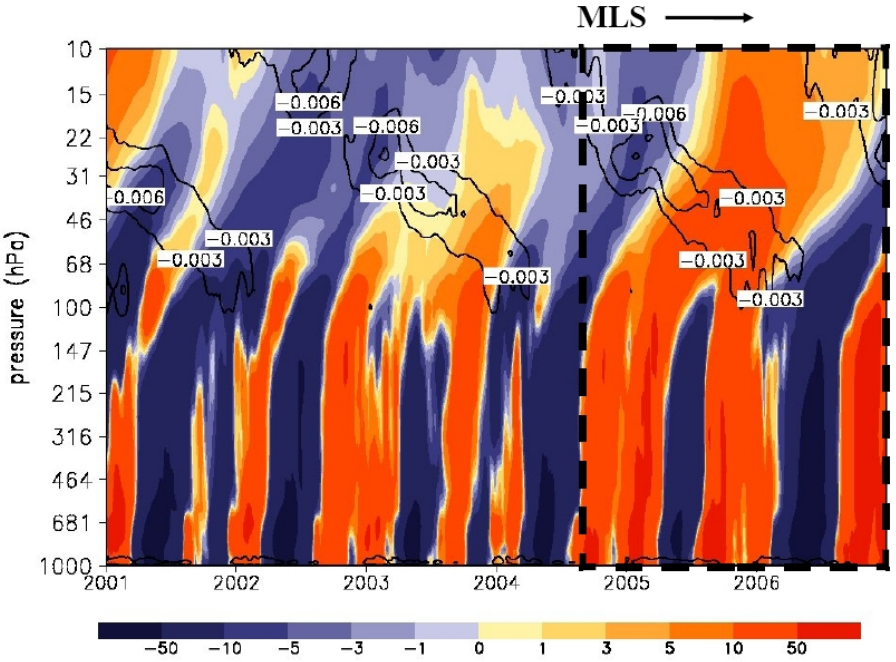

Fig. 6. Model tropical (10° S–10° N) HCN anomalies (pptv) between 2001 and 2006. The tropical zonal mean wind shear (s^{-1}), a proxy for the QBO determined from GEOS4 meteorology, is denoted by the negative contours. The Aura MLS observing time period (1 September 2004–1 December 2006) is denoted with the dashed lines.

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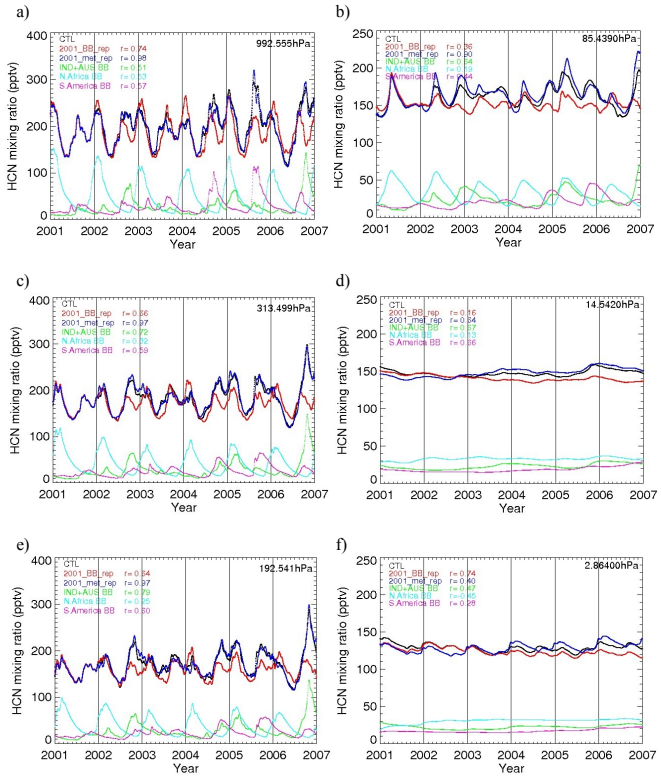

Fig. 7. GEOS-Chem 2×2.5 resolution model HCN mixing ratios (pptv) averaged between 10° S–10° N during 2001–2006 in the troposphere (left) and the stratosphere (right): control (black line); constant 2001 BB emissions (red line); and constant 2001 meteorology (dark blue line). Other colors denote HCN contributions from regional BB emissions. The correlation coefficient *r* denotes the correlation between HCN mixing ratios and the total HCN mixing ratio of the control; correlations >0.1 are statistically significant to the 99% confidence level.

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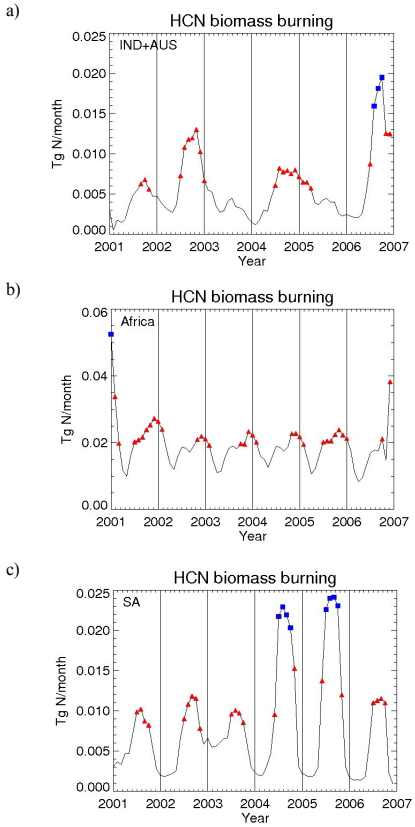

Fig. 8. Timeseries (solid line) of HCN biomass burning emission (Tg N/month) between 2001 and 2006 over **(a)** IND+AUS; **(b)** Africa; and **(c)** SA. Emissions above the 2001–2006 mean value are denoted by red triangles, and emissions 2.5 times above this mean value are denoted by blue squares. Emissions are based on GFEDv2 (van der Werf et al., 2006) and scaled using an observed HCN:CO emission ratio of 0.27% (Li et al., 2003). Vertical lines denote calendar years.

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