A global three-dimensional model analysis of the atmospheric budgets of HCN and CH 3 CN: Constraints from aircraft and ground measurements

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A global three-dimensional model analysis of the atmospheric budgets of HCN and CH₃CN:
Constraints from aircraft and ground measurements

Qinbin Li, ¹ Daniel J. Jacob, ¹ Robert M. Yantosca, ¹ Colette L. Heald, ¹ Hanwant B. Singh, ²
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[1] We construct global atmospheric budgets of HCN and CH₃CN through a three-dimensional (3-D) model simulation of the HCN-CH₃CN-CO system constrained and evaluated with aircraft observations from the Transport and Chemical Evolution Over the Pacific (TRACE-P) mission over the NW Pacific in February–April 2001. Observed background vertical gradients of HCN and CH₃CN imply a dominant ocean sink for both gases, with deposition velocity of 0.13 cm s⁻¹ for both and saturation ratios of 0.79 for HCN and 0.88 for CH₃CN. Observations for both gases in the free troposphere imply a dominant source from biomass burning. Enhancement of HCN observed in Chinese urban plumes is attributed tentatively to residential coal burning. Biomass burning and residential coal burning emission ratios relative to CO of 0.27% and 1.6%, respectively, for HCN, and of 0.20% and 0.25%, respectively, for CH₃CN, are consistent with observations in biomass burning and Chinese urban plumes. They provide the best model simulation of the ensemble of TRACE-P observations including vertical profiles and HCN-CH₃CN-CO correlations. They also allow successful simulation of the long-term observations of HCN columns at sites in the Northern Hemisphere, and of the CH₃CN vertical distribution observed over the northern Indian Ocean. Global biomass burning and Asian residential coal burning sources in the model are 0.63 and 0.2 Tg N yr⁻¹, respectively, for HCN and 0.47 and 0.03 Tg N yr⁻¹, respectively, for CH₃CN. Ocean uptake is the dominant sink for both gases, with oxidation by OH representing an additional minor sink. The resulting tropospheric lifetimes are 5.3 months for HCN and 5.8 months for CH₃CN. The model predicts very low HCN and CH₃CN concentrations at high southern latitudes, reflecting the assumption of a uniform saturation ratio for ocean uptake; observations in that region are needed. In the free troposphere, the dominance of biomass burning sources (70–85% for HCN and 90–95% for CH₃CN) implies that both gases can be used as biomass burning tracers. In the boundary layer, CH₃CN appears to be a better biomass burning tracer. More work is needed to identify the origin of the Chinese urban source of HCN.

INDEX TERMS: 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504); 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0345 Atmospheric Composition and Structure: Pollution—urban and regional (0305); 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 0368 Atmospheric Composition and Structure: Troposphere—constituent transport and chemistry; KEYWORDS: biomass burning, pollution, nitriles, ocean uptake


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1. Introduction

[2] Hydrogen cyanide (HCN) and methyl cyanide (CH$_3$CN, also called acetonitrile) are atmospheric tracers of biomass burning [Lobert et al., 1990; Holzinger et al., 1999] and could play a nonnegligible role in the nitrogen cycle [Li et al., 2000]. Ocean uptake has been hypothesized as their dominant sink, with corresponding lifetimes of a few months [Hamm and Warneck, 1990; Li et al., 2000]. However, their atmospheric budgets are still poorly understood. We use here a global three-dimensional (3-D) model analysis of HCN and CH$_3$CN observations in Asian outflow from the Transport and Chemical Evolution Over the Pacific (TRACE-P) aircraft mission over the NW Pacific [Singh et al., 2003] to improve the constraints on the sources and sinks of these two gases. The TRACE-P data represent the first in situ measurements for HCN in the troposphere, and one of the first for CH$_3$CN. Previous data for HCN are from remote sensing of the total column at several sites around the world [Mahieu et al., 1995, 1997; Rinssland et al., 1999, 2000, 2001, 2002; Zhao et al., 2000, 2002]. Previous in situ measurements of CH$_3$CN have been made over the Indian Ocean [de Laat et al., 2001] and over the Amazon [Williams et al., 2001].

[3] It is well established from laboratory and field experiments that biomass burning is a major source for both HCN (0.1–3.2 m Tg N yr$^{-1}$) and CH$_3$CN (0.2–1.1 Tg N yr$^{-1}$) (Table 1). It is also well established that sources from automobile exhaust and industrial processes are negligible in comparison [Lobert et al., 1991; Bange and Williams, 2000; Holzinger et al., 2001]. A recent field experiment indicates no emission of HCN from domestic biofuels [Bertschi et al., 2003]. Atmospheric sinks of HCN and CH$_3$CN from reaction with OH and O (2D), photolysis, and scavenging by precipitation yield lifetimes of a few years [Cicerone and Zellner, 1983; Brassere et al., 1983]. The solubilities of HCN and CH$_3$CN are sufficiently high for ocean uptake to impose atmospheric lifetimes of a few months if loss in the oceanic mixed layer is sufficiently rapid [Hamm and Warneck, 1990; Li et al., 2000]. There is some evidence that HCN and CH$_3$CN are consumed biologically in the ocean [Singh et al., 2003]. Li et al. [2000] showed in a global 3-D model study that the observed seasonal variation of the HCN column in different regions of the world is consistent with a scenario where biomass burning provides the main source and ocean uptake provides the main sink. They inferred a global HCN biomass burning source of 1.4–2.9 m Tg N yr$^{-1}$, and an oceanic saturation ratio of 0.83 or less. Observed vertical gradients of HCN and CH$_3$CN in remote marine air in TRACE-P confirm the importance of the ocean sink [Singh et al., 2003].

[4] The TRACE-P mission was conducted in February–April 2001 over the NW Pacific to study the transport and chemical evolution of Asian outflow over the Pacific [Jacob et al., 2003]. It used two NASA aircraft, a DC-8 and a P-3B, operating out of Hong Kong and Japan, and with additional transit flights and sorties over the North Pacific. Biomass burning in SE Asia is an important component of Asian outflow [Liu et al., 1999; Chan et al., 2000; Bey et al., 2001b]. During TRACE-P, Asian biomass burning and anthropogenic sources had contributions of similar magnitude to CO concentrations observed in Asian outflow [Liu et al., 2003].

[5] Both HCN and CH$_3$CN were measured by gas chromatography aboard the DC-8 aircraft [Singh et al., 2003]. The measurement accuracy was ±25% and the detection limit 30 pptv. Other measurements aboard the DC-8 used in this analysis include CO, perchloroethylene (C$_2$Cl$_4$), and methyl chloride (CH$_3$Cl). CO is a general tracer of combustion, C$_2$Cl$_4$ (a synthetic organic chemical used in dry cleaning) is an anthropogenic pollution tracer, and CH$_3$Cl is a biomass burning tracer [Blake et al., 2003]. These measurements can be used to place constraints on the sources of HCN and CH$_3$CN [Singh et al., 2003]. Some of the results shown by Singh et al. [2003] are reproduced here for purpose of comparison to model results. Throughout this paper, model comparisons to observations will use model results sampled along the DC-8 flight paths. All linear regressions are calculated using the reduced major axis (RMA) method, which allows for errors in both variables.

2. Model Simulation

[6] We simulate the distributions of HCN, CH$_3$CN, and CO observed in TRACE-P with the GEOS-CHEM global 3-D model of tropospheric chemistry. A detailed description of the model is presented by Bey et al. [2001a]. We use here GEOS-CHEM version 4.33 (see http://www-as.harvard.edu/chemistry/trop/geos). The model is driven by assimilated meteorological fields from the Goddard Earth Observing System (GEOS) of the NASA Data Assimilation Office (DAO). We use meteorological fields for 2000–2001 (GEOS 3) which are provided with 6-hour temporal resolution (3-hour for surface variables and mixed layer depths), $1^\circ \times 1^\circ$ horizontal resolution, and 48 vertical sigma levels. We degrade the horizontal resolution to $2^\circ \times 2.5^\circ$ for application in GEOS-CHEM. The simulations are conducted for a 16-month period (January 2000–April 2001). The first 13 months are used for initialization and we present results for the February–April 2001 TRACE-P period.

[7] Sources and sinks of HCN and CH$_3$CN in the model are described in section 3. The CO simulation follows that of Duncan et al. [2003] and uses archived OH concentration fields (monthly mean) from a full chemistry simulation [Li et al., 2002] to calculate CO loss. Anthropogenic sources of CO (including contributions from hydrocarbon precursors) are as described by Duncan et al. [2003], except for Asia where the Streets et al. [2003] inventory is used. Other TRACE-P studies have shown that the domestic fuel source of CO from China is too low in the Streets et al. [2003] inventory [Carmichael et al., 2003; Palmer et al., 2003]. For our simulation we double the residential coal source from China, resulting in a total anthropogenic (fossil fuel plus biofuel) source of CO from Asia of 184 Tg CO yr$^{-1}$. Biomass burning sources are as described by Heal et al. [2003]. The global biomass burning CO source is 487 Tg CO yr$^{-1}$ for 2000, while the global CO sources from fossil fuel and biofuel are 395 and 200 Tg CO yr$^{-1}$, respectively. For the TRACE-P period (February–April 2001), the global biomass burning CO source is 129 Tg CO and about half of that source is in SE Asia.
3. Model Sources and Sinks of HCN and CH₃CN

3.1. Sinks

3.1.1. Ocean Uptake

[9] Constraints on ocean uptake for HCN and CH₃CN can be obtained from the vertical gradients of concentrations measured in background air over the North Pacific during TRACE-P [Singh et al., 2003]. We implement this constraint here by using the observed gradients to infer a saturation ratio for these two gases that we can then extrapolate globally in the 3-D model simulation.

[10] Figure 1 shows the vertical distributions of HCN, CH₃CN, and CO observed for the ensemble of the data in TRACE-P (dots and red lines). The CO mixing ratios decrease from the boundary layer to the free troposphere, while the opposite is seen in the mixing ratios of HCN and CH₃CN. Median mixing ratios at 2–4 km are 220 pptv for HCN and 140 for CH₃CN, while the corresponding values at 0–2 km are 195 and 104 pptv, respectively. This is consistent with an ocean sink for HCN and CH₃CN also with the dominant biomass burning source for these two gases.

Table 1. Literature Estimates of Global HCN and CH₃CN Sources (m Tg N yr⁻¹)

<table>
<thead>
<tr>
<th>Biomass Burning</th>
<th>Biofuels</th>
<th>Car Exhaust</th>
<th>Residential Coal</th>
<th>Biogenic</th>
<th>Total</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.2</td>
<td>Ciccone and Zellner [1983]a</td>
</tr>
<tr>
<td>0.37–1.89</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lobert et al. [1990]b</td>
</tr>
<tr>
<td>0.64–3.18</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lobert et al. [1991]c</td>
</tr>
<tr>
<td>0.1–0.3</td>
<td></td>
<td>0.47</td>
<td></td>
<td></td>
<td></td>
<td>Holzinger et al. [1999]d</td>
</tr>
<tr>
<td>1.4–2.9</td>
<td>1.4–2.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Li et al. [2000]f</td>
</tr>
<tr>
<td>0.26</td>
<td>0.21</td>
<td></td>
<td>0.4</td>
<td>0.2</td>
<td>1.1</td>
<td>Andreae and Merlet [2001]g</td>
</tr>
<tr>
<td>0.7–0.9</td>
<td>&lt;0.02</td>
<td></td>
<td>0.2</td>
<td>0.2</td>
<td></td>
<td>Singh et al. [2003]h</td>
</tr>
<tr>
<td>0.63</td>
<td></td>
<td></td>
<td>0.2</td>
<td>0.2</td>
<td>0.83</td>
<td>this worki</td>
</tr>
<tr>
<td>CH₃CN</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.36</td>
<td>Hamm and Warneck [1990]i</td>
</tr>
<tr>
<td>0.27</td>
<td></td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
<td>Lobert et al. [1990]i</td>
</tr>
<tr>
<td>0.14–0.75</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Lobert et al. [1991]j</td>
</tr>
<tr>
<td>0.23–1.13</td>
<td>0.01</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Holzinger et al. [1999, 2001]k</td>
</tr>
<tr>
<td>0.27</td>
<td>0.17</td>
<td></td>
<td></td>
<td></td>
<td>0.44</td>
<td>Andreae and Merlet [2001]l</td>
</tr>
<tr>
<td>0.4–0.5</td>
<td>&lt;0.02</td>
<td></td>
<td>0.2</td>
<td>0.2</td>
<td>0.7</td>
<td>Singh et al. [2003]m</td>
</tr>
<tr>
<td>0.47</td>
<td></td>
<td></td>
<td>0.03</td>
<td></td>
<td>0.5</td>
<td>this workn</td>
</tr>
</tbody>
</table>

*aSource needed to balance the global sink from oxidation by OH. However, we now know that this reaction makes only a small contribution to the total HCN sink [Li et al., 2000].
*bBased on emission factors per unit nitrogen of 2.42 ± 1.79% for HCN and 0.95 ± 0.74% for CH₃CN measured in laboratory biomass burning experiments and a global biomass burning nitrogen volatilization estimate of 24–57 m Tg yr⁻¹ [Crutzen and Andreae, 1990].
*cBased on biomass burning molar emission ratios relative to CO of 1.1% for HCN and 0.25% for CH₃CN measured in laboratory biomass burning experiments, combined with a global biomass burning CO source estimate of 480–860 Tg CO yr⁻¹. No detail of the car exhaust source estimate is given.
*dBiomass burning sources based on molar emission ratios (relative to CO) of 0.12% for HCN and 0.13% for CH₃CN measured in a laboratory biomass burning experiment, combined with a global biomass burning CO source estimate of 210–550 Tg CO yr⁻¹. The automobile exhaust source estimate of CH₃CN is based on a measured CH₃CN molar emission ratio of 0.06 relative to benzene, combined with an emission ratio of 0.6 g benzene per unit fuel (kg C) consumed in traffic at 0–2 km are 195 and 104 pptv, respectively. This is consistent with an ocean sink for HCN and CH₃CN also with the dominant biomass burning source for these two gases.
*eBased on biomass burning molar emission ratios relative to CO of 0.11% for all vegetation types. These ratios are extrapolated globally in the 3-D model simulation (GEOS-CHEM version 3.4) with biomass burning as the only source and ocean uptake as the dominant sink.
*fBased on emission factors per unit nitrogen of 2.42 ± 1.79% for HCN and 0.95 ± 0.74% for CH₃CN measured in laboratory biomass burning experiments and a global biomass burning nitrogen volatilization estimate of 24–57 m Tg yr⁻¹ [Crutzen and Andreae, 1990].
*gBased on biomass burning molar emission ratios relative to CO of 0.11% for HCN and 0.25% for CH₃CN measured in laboratory biomass burning experiments, combined with a global biomass burning CO source estimate of 480–860 Tg CO yr⁻¹. No detail of the car exhaust source estimate is given.
*hSource needed to balance the HCN loss derived from the relative seasonal amplitude of the column observations, when fitted in a global model simulation (GEOS-CHEM version 3.4) with biomass burning as the only source and ocean uptake as the dominant sink.
*iGlobal 3-D model study with biomass burning molar emission ratios relative to CO of 0.26% for HCN and 0.15% for CH₃CN and a global biomass burning CO source estimate of 487 Tg CO yr⁻¹ [Duncan et al., 2003]. The residential coal burning source (in Asia) is invoked to explain enhanced HCN and CH₃CN in Chinese urban plumes. It assumes molar emission ratios relative to CO of 0.20% for HCN and 0.16% for CH₃CN and a global biofuel CO source estimate of 210 Tg CO yr⁻¹. Additional biogenic sources for both gases are invoked to balance estimated loss from ocean uptake.
*jGlobal 3-D model study with biomass burning molar emission ratios relative to CO of 0.26% for HCN and 0.15% for CH₃CN and a global biomass burning CO source estimate of 487 Tg CO yr⁻¹ [Duncan et al., 2003]. The residential coal burning source (in Asia) is invoked to explain enhanced HCN and CH₃CN in Chinese urban plumes. It assumes molar emission ratios relative to CO of 0.20% for HCN and 0.16% for CH₃CN and a global biofuel CO source estimate of 210 Tg CO yr⁻¹. Additional biogenic sources for both gases are invoked to balance estimated loss from ocean uptake.

**Note:** Since the model simulations of HCN, CH₃CN, and CO as implemented here are linear with respect to their sources, we resolve the contributions from different source regions and source types in the model by using tagged tracers [Bey et al., 2001b], which can then be added to reconstitute the full concentration field. Tagged tracers resolve sources from biomass burning and residential coal burning, for Asia and for the rest of the world.
gases, in contrast to the large fossil fuel source for CO. Biomass burning outflow during TRACE-P was largely confined to the free troposphere, while there was considerable fossil fuel outflow in the boundary layer [Carmichael et al., 2003; Liu et al., 2003].

[11] Figure 2 shows the vertical distributions of HCN and CH$_3$CN (dots and red lines) observed in TRACE-P over the North Pacific under background conditions, defined here as CO < 120 ppbv and C$_2$Cl$_4$ < 10 pptv [Singh et al., 2003]. Both gases show significantly reduced mixing ratios in the marine boundary layer compared with their free tropospheric values. Asian outflow influence for these conditions is minimal, and the shape of the profiles is evidence for ocean uptake. Median

Figure 1. Vertical distributions of HCN, CH$_3$CN, and CO for the ensemble of TRACE-P data over the NW Pacific (see Jacob et al. [2003] for a map of the area covered). Individual observations are shown as dots. Solid circles, triangles, and horizontal bars represent means, medians, and standard deviations, respectively. Model results are shown for the standard simulation and for tagged combustion tracers. Additional sources of CO in the model include biofuel burning and oxidation of methane and biogenic nonmethane hydrocarbons. See color version of this figure at back of this issue.
mixing ratios for these background conditions at 2–4 km are 201 pptv for HCN and 132 pptv for CH$_3$CN, while the corresponding values at 0–2 km are 161 pptv and 106 pptv, respectively.

[12] Following Singh et al. [2003], the deposition velocities of HCN and CH$_3$CN to the ocean can be derived using a box model of the marine boundary layer (MBL) with no divergence of horizontal flux [Lenschow et al., 1983]. The resulting deposition velocity is 0.13 cm s$^{-1}$C$_0$ for both gases. The comparable deposition velocities despite greater solubility of CH$_3$CN imply faster consumption of HCN/CN$^+$ in the ocean (see discussion below).

[13] Using a two-layer film model for air-to-sea exchange [Liss and Slater, 1974], Singh et al. [2003] estimated saturation ratios of 0.77 for HCN and 0.83 for CH$_3$CN from their TRACE-P data. We derive slightly different saturation ratios of 0.79 for HCN and 0.88 for CH$_3$CN. The difference with Singh et al. [2003] reflects different assumptions on the parameterizations of conductances for mass transfer. In our 3-D model calculation we extrapolate these saturation ratios globally, resulting in atmospheric lifetimes against ocean uptake of 6 months for HCN and 8 months for CH$_3$CN.

[14] Uptake of HCN and CH$_3$CN by the ocean must require consumption (presumably biological) in the oceanic mixed layer OML, and we can readily estimate the implied lifetimes. At steady state, the ocean uptake flux must be balanced by consumption in the OML

$$v_d C_{MBL} = \frac{Z}{\tau} C_{OML},$$

$$S = \frac{H C_{OML}}{C_{MBL}},$$

$$\tau = \frac{Z S}{H v_d},$$

where $v_d$ is the deposition velocity, $Z$ is the oceanic mixed layer depth (about 50 m for the middle-latitude North Pacific in March [Kara et al., 2000]), $\tau$ is the lifetime against consumption in the OML, $C_{MBL}$ and $C_{OML}$ are the respective concentrations in the MBL and OML, $S$ is the saturation ratio, and $H$ is the dimensionless Henry’s law constant defined as the ratio of the concentration in air to that in seawater. Values for $H$ at 298 K are 3.4$ \times $10$^{-3}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ for HCN and 7.6$ \times $10$^{-4}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ for CH$_3$CN (R. Sander, Henry’s law constants (solubilities), 2003, available at http://www.mpch-mainz.mpg.de/$\sim$sander/res/henry.html). The resulting lifetimes against consumption in the OML are three months for HCN(aq)/CN$^+$ and 14 months for CH$_3$CN(aq)/CN$^+$.  

3.1.2. Other Sinks

[15] Additional known losses for atmospheric HCN and CH$_3$CN are reactions with OH and O(1$D$), photolysis, and precipitation scavenging. Of these, only reaction with OH is significant [Cicerone and Zellner, 1983; Brasseur et al., 1983] and is implemented in the model using rate constants from Wine et al. [2002] for HCN and DeMore et al. [1997] for CH$_3$CN, with monthly mean OH fields from a full chemistry simulation [Li et al., 2002]. The recent laboratory study of Wine et al. [2002] indicates a factor of three lower rate constant for the HCN-OH reaction (low-pressure limit 7.4$ \times $10$^{-33}$ cm$^6$ molecule$^{-2}$ s$^{-1}$; high-pressure limit 9.0$ \times $
10^{-15}(T/300)^{3.2} \text{ cm}^{-3} \text{ molecule}^{-1} \text{ s}^{-1}, \text{ where } T \text{ is temperature) than previously measured [Fritz et al., 1984]. The corresponding lifetimes against oxidation by OH are 4.3 years for HCN and 2.2 years for CH3CN, much longer than the lifetimes against ocean uptake.}

3.2. Sources

3.2.1. Biomass Burning

[16] Both HCN and CH3CN are mainly emitted in the low-temperature smoldering phase of biomass burning, similarly to CO [Lobert et al., 1990]. Different fuel types and fire temperatures result in different emission ratios [Lobert et al., 1991]. Past studies have indicated a large range of molar emission ratios for HCN (0.03–1.1%) and a narrower range for CH3CN (0.12–0.25%) [Lobert et al., 1991; Hurst et al., 1994a, 1994b; Yokelson et al., 1997, 1999, 2003; Holzinger et al., 1999; Goode et al., 2000]. Emission ratios throughout this paper are in molar units relative to CO. When compounded with a range of global biomass burning CO emission estimates (200–800 Tg CO yr^{-1}), one obtains global biomass burning sources of 0.1–3.2 m Tg N yr^{-1} for HCN and 0.1–1.1 m Tg N yr^{-1} for CH3CN (Table 1).

[17] The recent review of Andreae and Merlet [2001] recommends biomass burning HCN emission ratios of 0.05% (savanna and grassland) and 0.15% (tropical and extratropical forests) and a biomass burning CH3CN emission ratio of 0.11% for all vegetation types. The HCN recommendation for savanna and grassland is based on field experiments in Australia [Hurst et al., 1994a, 1994b]. Recent measurements in African savanna fires show much higher HCN emission ratios (0.85 ± 0.29%) [Yokelson et al., 2003]. By averaging measurements of biomass burning emissions from different fuel types and from different regions of the world, Goode et al. [2000] found an average biomass burning HCN emission ratio of 0.34%, much higher than the Andreae and Merlet [2001] value.

[18] Correlations with CO in the TRACE-P observations provide important constraints on the emissions of HCN and CH3CN. Singh et al. [2003] used these correlations in biomass burning plumes to derive emission ratios of 0.27 ± 0.12% for HCN and 0.15 ± 0.05% for CH3CN. The HCN emission ratio is consistent with the average value reported by Goode et al. [2000], and is also in accord with the value of 0.28% estimated by Heald et al. [2003] based on multivariate analysis of the TRACE-P CO and HCN data. The CH3CN emission ratio is consistent with the Andreae and Merlet [2001] value. We find in GEOS-CHEM that the best fit to the TRACE-P observations of HCN, CH3CN, and CO, and to the global HCN column data is obtained with biomass burning emission ratios of 0.27% for HCN and 0.20% for CH3CN, consistent with Singh et al. [2003]; we use these values in the simulations presented here. The corresponding sources of HCN and CH3CN in the model are 0.63 and 0.47 m Tg N yr^{-1}, respectively (Table 2), within the range of past estimates (Table 1).

3.2.2. Residential Coal Burning Source in Asia

[19] It is well established that HCN and CH3CN are produced in the early stages of high-temperature combustion but are subsequently oxidized within the combustion chamber [Flagan and Seinfeld, 1988]. Direct measurements in automobile exhaust [Lobert et al., 1991; Holzinger et al., 2001] as well as aircraft measurements by Singh et al. [2003] and de Gouw et al. [2003] over southern California support that the source from fossil fuel combustion is negligible.

[20] However, TRACE-P observations show a strong enhancement of HCN, and a much weaker enhancement of CH3CN, in Chinese urban plumes sampled in the MBL less than two days downwind of the source [Singh et al., 2003]. Figure 3 shows the HCN and CH3CN correlations with CO observed in three major Chinese urban plumes (DC-8 flights 9, 12, 13) sampled in the MBL during TRACE-P. Asian outflow in the MBL was in general advected behind cold fronts and was devoid of biomass burning influence [Carmichael et al., 2003; Liu et al., 2003]. The peak mixing ratios of HCN and CO observed in the Shanghai plume are 1.5 ppbv and 1 ppmv, respectively, while the peak mixing ratio for CH3CN is 300 pptv, much less enhanced. These peak mixing ratios were associated with high mixing ratios of CH3Cl [see Singh et al., 2003, Figure 7a] and carbonyl sulfide (COS). The HCN-CO and CH3CN-CO correlations show slopes of 0.17% and 0.04%, respectively (Figure 3).

[21] Although there is widespread biofuel use in China [Streets et al., 2003], data from Africa suggest negligible

\begin{table}
\centering
\caption{Atmospheric Budgets of HCN and CH3CN} \label{tab:atm-budgets}
\begin{tabular}{lcc}
\hline
 & HCN & CH3CN \\
\hline
Atmospheric burden, Tg N & 0.426 & 0.28 \\
Atmospheric lifetime, months & 6.2 & 6.7 \\
Tropospheric burden, Tg N & 0.38 & 0.25 \\
Tropospheric lifetime, months & 5.3 & 5.8 \\
Sources, Tg N yr^{-1} & \\
Biomass burning & 0.63 & 0.47 \\
Residential coal burning & 0.2 & 0.03 \\
Sinks, Tg N yr^{-1} & \\
Ocean uptake & 0.73 & 0.36 \\
Reaction with OH & 0.1 & 0.14 \\
\hline
\end{tabular}
\end{table}

\textsuperscript{a}For the 1000–100 hPa column.

Figure 3. Observed (top) HCN and (bottom) CH3CN correlations with CO in three Chinese urban plumes sampled during TRACE-P (DC-8 flights 9, 12, and 13) below 2 km altitude. Regression lines (RMA method) are also shown.
nitrile emission from biofuels [Bertschi et al., 2003; Yokelson et al., 2003]. Also, the CH$_3$CN/HCN enhancement ratio is much lower in the Chinese urban plumes than in biomass burning plumes (Figure 4). Singh et al. [2003] suggested that the enhancements of CH$_3$Cl and COS correlated with enhanced HCN in the Chinese urban plumes could indicate a source from hard coal burning, and we follow that suggestion here. Clearly, further work is needed to identify the Chinese source of nitriles.

[22] We estimate the residential coal burning emission ratios of HCN and CH$_3$CN relative to CO from the Chinese urban plumes observed in TRACE-P (Figure 3). Residential coal burning accounts for about 15% of anthropogenic CO emissions for China in the model. Combined with the slopes of the HCN-CO and CH$_3$CN-CO correlations observed in the Chinese urban plumes (Figure 3), we obtain residential coal burning molar emission ratios of 1.2% for HCN and 0.26% for CH$_3$CN relative to CO. Simulation of the TRACE-P data with GEOS-CHEM (section 4) indicates a best fit for residential coal burning emission ratios of 1.6% for HCN and 0.25% for CH$_3$CN.

[23] When scaling the above emission ratios by the fraction of urban CO from residential coal burning in China, the resulting HCN/CO source ratio (0.24% for Shanghai, for example) is comparable to biomass burning (0.27%) while the resulting CH$_3$CN/CO source ratio (0.04% for Shanghai, for example) is much lower than biomass burning (0.20%). The total residential coal burning sources in Asia in the model are 0.2 for HCN and 0.03 m Tg N yr$^{-1}$ for CH$_3$CN (Table 2). This source could have a seasonal variation associated with heating [Streets et al., 2003], but uncertainties are sufficiently large that we do not bother to include it here.

3.2.3. Biogenic Source

[24] There is indication that HCN is produced by higher plants [see Cicerone and Zellner, 1983, and references therein]. Recent laboratory results by Fall et al. [2001] show that wounded clover releases HCN in addition to large amounts of acetone. In the TRACE-P data, HCN is correlated with both acetone ($r = 0.81$, slope = 0.3 pptv ppbv$^{-1}$, $n = 746$) and methanol ($r = 0.86$, slope = 137 pptv ppbv$^{-1}$, $n = 744$), which have strong biogenic sources. In particular, methanol is generally considered a tracer for continental biogenic emissions [Heikes et al., 2002]. Figure 5 (top) shows the correlation of HCN with methanol observed during TRACE-P. A similarly strong correlation was found for CH$_3$CN. The biogenic source of methanol is estimated to be 50–280 Tg yr$^{-1}$ [Heikes et al., 2002]. If the HCN-methanol correlation were to reflect a common biogenic source, then the implied biogenic HCN source would be
3–17 m Tg N yr\(^{-1}\), far too large to be reconciled with the observed HCN concentrations [Li et al., 2000]. Additionally, the highest methanol and HCN concentrations in TRACE-P were observed in the Chinese urban plumes. Methanol in TRACE-P was also strongly correlated with CO (r = 0.73, slope = 82 ppbv ppbv\(^{-1}\), n = 1034) and was highest (together with HCN) in the Chinese urban plumes (Figure 5, bottom), implying an anthropogenic source. Thus we find no convincing evidence of a biogenic source of nitriles and do not include such a source in our simulations.

4. Simulation of Observations

[25] In this section we examine the GEOS-CHEM model simulation of the TRACE-P observations for HCN and CH\(_3\)CN and discuss what constraints this simulation provides. The model evaluation also considers CO, since our source specifications for HCN and CH\(_3\)CN are based on relationships with CO. We also examine the consistency of our simulation with the global data sets of HCN columns previously used as constraints by Li et al. [2000] and with the INDOEX data of de Laat et al. [2001].

[26] As a general assessment of our simulation, in Figure 6 we show the frequency distributions of the observed and simulated HCN, CH\(_3\)CN, and CO concentrations along the ensemble of TRACE-P flight tracks. The simulated mean and median values agree with the observed values to within 10 pptv for HCN, 5 pptv for CH\(_3\)CN, and 5 ppbv for CO. There are no systematic biases or obvious anomalies in the simulated frequency distributions. Figure 7 shows scatterplots of simulated versus observed concentrations of HCN and CH\(_3\)CN for the ensemble of TRACE-P data. The bulk of the points are strongly correlated, but the correlations are much smaller at high mixing ratios (primarily in the boundary layer), likely because of model errors in the location of plumes [Kiley et al., 2003]. For further evaluation of the simulation we examine vertical distributions and correlations between species.

4.1. Vertical Distributions

[27] The observed and simulated vertical profiles of HCN, CH\(_3\)CN, and CO for the ensemble of TRACE-P measurements are shown in Figure 1. The model reproduces the increase of CO mixing ratios and the decrease of HCN and CH\(_3\)CN mixing ratios from the free troposphere to the MBL. For the background conditions over the NW Pacific (Figure 2), the model reproduces the gradients of HCN and CH\(_3\)CN between the free troposphere and the MBL driven by ocean uptake. Without ocean uptake in the model there would be no such gradients. Also shown in Figure 1 are the relative contributions from biomass burning and residential coal burning simulated in the model using tagged tracers. Biomass burning accounts for 70–85% of total HCN and 90–95% of total CH\(_3\)CN in the free troposphere (above 2 km), while in the boundary layer the fractions are 45% and 75%, respectively. Thus it appears that CH\(_3\)CN is a better tracer for biomass burning. Simulated and observed mean vertical profiles of HCN and CH\(_3\)CN show enhancements at 2–4 km and 8–11 km (Figure 1). These correspond to preferential altitudes for frontal and convective outflow of biomass burning pollution, respectively [Bey et al., 2001b; Liu et al., 2003].

[28] We also compare model results in Figure 8 to aircraft measurements of CH\(_3\)CN made over the northern Indian Ocean during the INDOEX campaign [de Laat et al., 2001]. In contrast to TRACE-P, the INDOEX observations show maximum concentrations in the MBL due to boundary layer outflow from the Indian subcontinent associated with the winter-spring monsoon. The model reproduces this enhancement, which is thus consistent with our representation of the ocean sink.

4.2. Correlations Between HCN, CH\(_3\)CN, and CO

[29] Figure 9 compares the observed and simulated correlations between HCN, CH\(_3\)CN, and CO for the ensemble of the TRACE-P data in the free troposphere and in the boundary layer. The model reproduces the slopes of the correlations to within their expected errors. Differences in slopes between the free troposphere and the boundary layer reflect the dominant influence of biomass burning in the free troposphere, and the added influences from the urban source.
and the deposition sink in the MBL. The CH$_3$CN-CO correlation is poor in the boundary layer ($r = 0.29$ in the observations and $r = 0.24$ in the model), while the HCN-CO correlation is strong ($r = 0.85$ in the observations and $r = 0.77$ in the model), reflecting the similarity between urban and biomass burning emission ratios for HCN/CO but the much lower urban ratios for CH$_3$CN/CO. The CH$_3$CN-HCN correlation in the free troposphere above 2 km (Figure 9a) shows less variability in the model than in the observations, which likely reflects the assumption of uniform biomass burning emission ratios of HCN and CH$_3$CN in the model, while in reality these emission ratios vary for different fuel types and fire temperatures [Lobert et al., 1991]. The CH$_3$CN-CO relationship in the boundary layer (Figure 9b) shows two branches, both in the model and in the observations, reflecting (1) the subsidence of biomass burning influence from the free troposphere (high CH$_3$CN, low CO) and (2) the urban outflow influence (low CH$_3$CN, high CO).

4.3. HCN Columns

[S95] Spectroscopic measurements of HCN atmospheric columns were made at three Japanese sites during TRACE-P as part of a long-term observational program [Zhao et al., 2000, 2002]. The three sites are Moshiri (44°N, 142°E, 0.28 km altitude), Rikubetsu (43.5°N, 144°E, 0.37 km altitude), and Tsukuba (36°N, 140°E, 0.03 km altitude). The data for the TRACE-P period are shown in Figure 10 (solid circles). The columns at Tsukuba show much higher variation than at Moshiri and Rikubetsu, reflecting the latitudinal difference and the proximity of Tsukuba to the main channel of Asian outflow at 25°N–
The increases in the columns from February to April are consistent with the previous observation of a spring-summer HCN column maximum at these sites [Zhao et al., 2000, 2002], and can be explained by the seasonal variation of biomass burning emissions [Li et al., 2000].

Figure 10 compares model results for the TRACE-P period with observed HCN columns at the three Japanese sites. The averaging kernel and a priori vertical profile from the retrievals [Zhao et al., 2000, 2002] were applied to the model results. The HCN columns average $4 \times 10^{15}$ molecules cm$^{-2}$ with high values of $5-7 \times 10^{15}$ molecules cm$^{-2}$, both in the observations and the model, consistent with previous column measurements at northern middle latitudes [Mahieu et al., 1995, 1997; Zhao et al., 2000, 2002]. A scatterplot of simulated versus observed HCN columns is shown in Figure 11. There is strong correlation ($r = 0.82$), reflecting in part the seasonal increase from February to April (Figure 12), and no significant bias.

Multiyear measurements of HCN columns are available from several sites in the Northern Hemisphere and provide another important test for the model. We used these data of Li et al. [2000] to evaluate our previous simulation of HCN. The present model has a weaker HCN source and a longer HCN lifetime to match the TRACE-P constraints, and it is imperative to determine whether these changes degrade the simulation of the HCN column data. Figure 12 compares model results for 2000 to the seasonal variations in these multiyear records, including data from the Japanese sites [Zhao et al., 2000, 2002], Kitt Peak in Arizona [Mahieu et al., 1995, 1997], and Ny Alesund in Spitsbergen [Li et al., 2000]. Data for the two Japanese sites are monthly means and vertical bars indicate standard deviations. The solid lines represent simulated daily average HCN total columns for 2000.
Observations for 1998 were excluded because of anomalous fire influence throughout the Northern Hemisphere \cite{Rinsland1999, Rinsland2000, Zhao2002}. We find that we achieve a similar or better simulation than in the study of Li et al. \cite{Li2000}. The reader is referred to that paper for discussion of the seasonal features.

5. Global Budgets and Distributions of HCN and CH$_3$CN

The global atmospheric budgets of HCN and CH$_3$CN in the model are shown in Table 2. Biomass burning contributes 0.63 m Tg N yr$^{-1}$ to global HCN and 0.47 m Tg N yr$^{-1}$ to global CH$_3$CN, while the corresponding sources from residential coal burning in Asia are 0.2 and 0.03 m Tg N yr$^{-1}$, respectively. Ocean uptake dominates the loss of both HCN (0.73 m Tg N yr$^{-1}$) and CH$_3$CN (0.36 m Tg N yr$^{-1}$), while the sink from reaction with OH is relatively small (0.1 m Tg N yr$^{-1}$ for HCN and 0.13 m Tg N yr$^{-1}$ for CH$_3$CN). The resulting tropospheric lifetimes (for the 1000–100 hPa column) are 5.3 months for HCN and 5.8 months for CH$_3$CN.

Our HCN lifetime is longer, and the implied global source smaller, than in our previous study \cite{Li2000} using the constraints from the observed relative seasonal variation of HCN columns \cite[Table 1]{Li2000}. In that study we used the relative seasonal amplitude of the observed columns at constraint on the HCN lifetime and derived a global source by mass balance. We considered that the seasonal amplitude of the columns constrained the lifetime to be less than 4 months, whereas the TRACE-P constraints imply a longer lifetime (5.3 months). As shown in Figure 12, it appears that this longer lifetime is still compatible with the constraints from the HCN column observations.

Figure 13 shows simulated global mean distributions of HCN and CH$_3$CN in April 2001. Surface concentrations are maximum over biomass burning regions in SE Asia, central America, and central Africa (>1000 pptv). Surface concentrations are very low (<50 pptv) at high southern latitudes, reflecting the remoteness from sources and the sink from ocean uptake under our assumption of uniform
saturation ratios. Observations in this part of the world are evidently needed. Concentrations in the middle troposphere at 500 hPa are highest over SE Asia and downwind, with a circumpolar band of relatively high concentrations (>200 pptv for HCN) at 5°N–40°N due to biomass burning influence.

6. Conclusions

[36] We used a global 3-D model analysis of in situ HCN-CH$_3$CN-CO aircraft observations made over the NW Pacific during the TRACE-P aircraft mission (February–April 2001) to improve understanding of the atmospheric budgets of both gases. Vertical gradients of HCN and CH$_3$CN observed in remote marine air confirm the previous hypotheses of a dominant ocean sink for HCN [Li et al., 2000] and CH$_3$CN [Hamm and Warneck, 1990]. Following Singh et al. [2003], we used these gradients to derive deposition velocities of 0.13 cm s$^{-1}$ for both gases, corresponding to saturation ratios of 0.79 for HCN and 0.88 for CH$_3$CN. These deposition velocities imply lifetimes of three months for HCN(aq)/CN$^-$ and 14 months for CH$_3$CN(aq)/CN$^-$ against consumption in the oceanic mixed layer.

[37] Biomass burning plumes from SE Asia observed during TRACE-P confirmed the importance of biomass burning as a global source for HCN and CH$_3$CN, while observations in southern California confirmed that automobile exhaust is not a significant source for either gas [Singh et al., 2003]. However, HCN and CH$_3$CN observed in fresh Chinese urban plumes indicate emissions of anthropogenic origin with a much higher HCN/CH$_3$CN ratio than from biomass burning. We tentatively attribute these enhancements to residential coal burning in Asia.

[38] Our global model uses biomass burning and residential coal burning emission ratios (molar) relative to CO of 0.27% and 1.6% respectively for HCN, and 0.2% and 0.25%, respectively, for CH$_3$CN, as providing the best fit to the TRACE-P observations within the constraints offered by the HCN-CH$_3$CN-CO relationships observed in biomass burning and urban plumes. The resulting simulation captures the observed frequency distributions of HCN and CH$_3$CN concentrations in TRACE-P, their vertical distributions, and their correlations with CO. It offers a good simulation of ground-based measurements of HCN columns, at sites in Japan and elsewhere in the Northern Hemisphere, both during TRACE-P and over the multyear record. It also reproduces the mean CH$_3$CN vertical distribution observed over the northern Indian Ocean during the INDOEX aircraft campaign.

[39] Our global budgets of HCN and CH$_3$CN indicate biomass burning sources of 0.63 and 0.47 m Tg N yr$^{-1}$, respectively, and residential coal burning sources in Asia of 0.2 and 0.03 m Tg N yr$^{-1}$, respectively. Ocean uptake is the dominant sink for both; oxidation by OH is an additional minor sink. The resulting tropospheric lifetimes are 5.3 months for HCN and 5.8 months for CH$_3$CN. The HCN lifetime is longer, and the global source smaller, than in our previous model analysis [Li et al., 2000], but it still provides an unbiased simulation of the relative seasonal cycle of HCN columns which was the main constraint in that previous analysis. The model predicts maximum surface air concentrations of HCN and CH$_3$CN over biomass burning regions and very low (<50 pptv) concentrations at high southern latitudes due to ocean uptake under the assumption of a uniform saturation ratio. Observations are evidently needed to test this assumption. Concentrations in the middle troposphere are highest over tropical biomass burning regions and downwind, with a circumpolar band of high concentrations at 5°N–40°N. Although both HCN and CH$_3$CN appear to be good tracers of biomass burning in the free troposphere, CH$_3$CN is a better tracer in the boundary layer due to the relatively large Chinese urban source of HCN. More work is needed to characterize the nature of this Chinese urban source.

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LI ET AL.: ATMOSPHERIC BUDGETS OF HCN AND CH₃CN

Figure 1. Vertical distributions of HCN, CH₃CN, and CO for the ensemble of TRACE-P data over the NW Pacific (see Jacob et al. [2003] for a map of the area covered). Individual observations are shown as dots. Solid circles, triangles, and horizontal bars represent means, medians, and standard deviations, respectively. Model results are shown for the standard simulation and for tagged combustion tracers. Additional sources of CO in the model include biofuel burning and oxidation of methane and biogenic nonmethane hydrocarbons.

GTE 48 - 4
Figure 2. Vertical distributions of HCN and CH$_3$CN observed in TRACE-P over the North Pacific under background conditions (CO < 120 ppbv and C$_2$Cl$_4$ < 10 pptv). Individual observations are shown as dots. Solid circles, triangles, and horizontal bars represent means, medians, and standard deviations, respectively.
Figure 13. Simulated global distributions of HCN and CH$_3$CN concentrations in surface air and at 500 hPa for April 2001.