Title
A persistent imbalance in HO\textsubscript{x} and NO\textsubscript{x} photochemistry of the upper troposphere driven by deep tropical convection

Permalink
https://escholarship.org/uc/item/7wf9f45j

Journal
Geophysical Research Letters, 24(24)

ISSN
00948276

Authors
Prather, Michael J
Jacob, Daniel J

Publication Date
1997-12-15

DOI
10.1029/97GL03027

License
CC BY 4.0

Peer reviewed
A persistent imbalance in HO\textsubscript{x} and NO\textsubscript{x} photochemistry of the upper troposphere driven by deep tropical convection

Michael J. Prather
Earth System Science, University of California at Irvine

Daniel J. Jacob
Department of Earth & Planetary Sciences, Division of Engineering and Applied Sciences, Harvard University

Abstract. Convection in the tropics turns over the upper troposphere at rates (0.08 d\textsuperscript{-1}) comparable to photochemical processes controlling the absolute abundance of HO\textsubscript{2} (OH + HO\textsubscript{2}) and the abundance of NO\textsubscript{y} (NO + NO\textsubscript{2}) relative to HNO\textsubscript{3}. Here we identify convection of boundary-layer CH\textsubscript{3}OOH as a primary source of HO\textsubscript{2} to the upper troposphere. Turnover of NO\textsubscript{y} leads to NO/HNO\textsubscript{3} ratios much higher than predicted for local photochemical steady-state. Through convective transport the upper troposphere is more photochemically active in producing O\textsubscript{3}, an important greenhouse gas.

Introduction
Deep convection in the tropics moves air from the marine and continental boundary layers rapidly to the upper troposphere [Emanuel, 1994]. Convective (anisotropic) plumes as diagnosed from a general circulation model were built into early chemistry-transport models [CTMs] [Russell and Lerner, 1981]. Such convective transports have been recognized as being important to tropospheric chemistry [Gidel, 1983; Chatfield and Crutzen, 1984; Ehhalt et al., 1992; Liu et al., 1997] through the transport of ozone and its precursors [Pickering et al., 1992; Jacob et al., 1993]. These works have shown the importance of convective transport in determining the upper tropospheric composition for relatively long-lived tracers such as radon or ozone [e.g., Liu et al., 1984; Jacob et al., 1997]. This paper focuses on the ability of convective transport to control even the rapid photochemical balance of HO\textsubscript{2} (OH + HO\textsubscript{2}) and NO\textsubscript{y} (NO + NO\textsubscript{2}) in the upper troposphere. Deep convection in the tropics flushes the upper tropical troposphere, bringing in fresh sources of NO (e.g., from soils, combustion, lightning) and HO\textsubscript{2} reservoirs (H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}OOH, CH\textsubscript{2}O), drives the photochemical balance away from local photochemical steady-state (LPSS), and increases the net production of ozone (O\textsubscript{3}) in the upper troposphere. Specifically, we predict that convection of boundary-layer CH\textsubscript{3}OOH is a major source of HO\textsubscript{2} and O\textsubscript{3} in the upper troposphere.

Convection of Tracers
What does boundary-layer air bring to the upper troposphere? Cumulus transport from the surface to the 11-17 km region involves condensation of more than 99% of the water vapor and hence removal of a large fraction of soluble species such as HNO\textsubscript{3}, H\textsubscript{2}O\textsubscript{2}, and aerosols from uplifted air. To balance this source, uniform removal of species in the 11-17 km region occurs through convective turnover (i.e., net subsidence). What chemical species will be impacted by such turnover? Water vapor is controlled by convection but is not predictable in this framework. The long-lived gases like CH\textsubscript{4} and CO have tropospheric distributions determined by large-scale transport outside of the tropical troposphere and cannot be predicted within a model of vertical turnover. Likewise, O\textsubscript{3} in this 11-17 km region is controlled in part by transport from other regions (e.g., the stratosphere and other latitudes) not just from exchange with the boundary layer. Thus we fix the concentrations of these slowly varying chemicals by observation. The NO\textsubscript{y} family (NO, NO\textsubscript{2}, NO\textsubscript{3}, HONO, HNO\textsubscript{3}, HNO\textsubscript{4}) and the HO\textsubscript{x} family (OH, HO\textsubscript{2}, H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}OOH, CH\textsubscript{2}O, HONO, H\textsubscript{2}O\textsubscript{2}, NO\textsubscript{2}) are made photochemically from CH\textsubscript{4} and O\textsubscript{3}, however, are built up and destroyed in a matter of days; and thus their partitioning and absolute abundance may be readily impacted by convective turnover.

We expect that NO\subscript{y} injected into the upper troposphere by convection will be primarily in the form of NO\textsubscript{2} because HNO\textsubscript{3} will be rained out. Thus, loss of NO\textsubscript{2} in the upper tropical troposphere from convective turnover is assumed to be balanced by a fresh source of NO\textsubscript{2} (e.g., lightning or surface emissions). The HO\textsubscript{2} family is made photochemically from H\textsubscript{2}O\textsubscript{2} and CH\textsubscript{4}. Observations in the tropics show rapid decline with altitude in the concentrations of H\textsubscript{2}O\textsubscript{2}, CH\textsubscript{3}OOH, and CH\textsubscript{2}O, following the decline of H\textsubscript{2}O [Heikes et al., 1996; Jacob et al., 1995]. Concentrations of these species, which are the main components of the HO\textsubscript{x} family and the main reservoirs of HO\textsubscript{2} within this family, are typically one order-of-magnitude less in the upper troposphere than in the lower troposphere (Table 1). Convective pumping can thus provide a large source of HO\textsubscript{2} to the upper troposphere. Both CH\textsubscript{4}-
OH and CH$_2$O have sufficiently low Henry's Law solubilities [Betterton and Hoffmann, 1988; Lind and Kok, 1994] that they should reach the upper troposphere without significant scavenging by convective precipitation. Chaifield and Crutzen [1984] have argued for the potential importance of H$_2$O$_2$ convection, yet H$_2$O$_2$ is highly soluble and a large fraction should be rained out. In our analysis we assume a scavenging efficiency of 75% for H$_2$O$_2$ in deep, wet convection.

An instructive model of the upper tropical troposphere (11-17 km) is built here as a single box (~14 km) that is ventilated by convective plumes and large-scale subsidence. For the HOx reservoirs convection induces a net source proportional to the difference between the mean boundary-layer and upper-troposphere mixing ratios. Based on observations from the TRACE-A and PEM-West aircraft observations over the tropical Atlantic and tropical western Pacific, respectively [Gregory and Scott, 1995; Davis et al., 1996; Heikes et al., 1996; Jacob et al., 1996], we estimate sources to the upper troposphere of 50-90 pptv d$^{-1}$ for CH$_3$OOH, 0-45 pptv d$^{-1}$ for H$_2$O$_2$, and 15 pptv d$^{-1}$ for CH$_2$O (Table 1). Although H$_2$O$_2$ is highly soluble, recent observations show some enhancements in convective outflows in the upper troposphere [Lee et al., 1997], consistent with our adopted partial scavenging.

**Perturbations to HOx, NOx, and O$_3$ Tendency**

In Table 1 we estimate the impact of these additional HOx sources at 14 km by calculating HOx yields (molecule of HOx produced per reservoir molecule destroyed) from the two peroxides and formaldehyde, multiplying by the convective source, and then comparing with the known HOx sources (pptv d$^{-1}$) from oxidation of water vapor by O(1D) and from photolysis of acetone (CH$_3$C(O)CH$_3$) [McKeen et al., 1997]. H$_2$O$_2$ at 42 ppmv and acetone at 300 pptv [Singh et al., 1995] supply comparable sources. Convective injection of CH$_3$OOH can double the source from water plus acetone. The source from H$_2$O$_2$ would be even larger, but 75% scavenging leaves it just comparable to water and acetone. The source from CH$_2$O is insignificant.

With this representative box-model of the upper tropical troposphere, we calculate the impact of convective pumping

**Table 1. HOx Precursors in the Upper Tropical Troposphere**

<table>
<thead>
<tr>
<th>Tropospheric Concentrations$^a$</th>
<th>Lower</th>
<th>Upper</th>
<th>$S_{HOx} ^b$</th>
<th>Yield$^c$</th>
<th>$S_{HOx} ^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$OOH, pptv</td>
<td>TRACE-A</td>
<td>1200</td>
<td>60</td>
<td>90</td>
<td>-1.4</td>
</tr>
<tr>
<td></td>
<td>PEM-WEST</td>
<td>820</td>
<td>200</td>
<td>50</td>
<td>70</td>
</tr>
<tr>
<td>H$_2$O$_2$, pptv</td>
<td>TRACE-A</td>
<td>2800</td>
<td>150</td>
<td>45</td>
<td>-1.4</td>
</tr>
<tr>
<td></td>
<td>PEM-WEST</td>
<td>1100</td>
<td>240</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>CH$_2$O, pptv</td>
<td>TRACE-A</td>
<td>200</td>
<td>&lt;40</td>
<td>15</td>
<td>-0.7</td>
</tr>
<tr>
<td>H$_2$O, ppmv</td>
<td></td>
<td>42</td>
<td></td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>CH$_3$C(O)CH$_3$, pptv</td>
<td></td>
<td>300</td>
<td></td>
<td>85</td>
<td></td>
</tr>
</tbody>
</table>

$^a$ Concentrations of peroxides/formaldehyde based on tropical aircraft campaigns TRACE-A [Heikes et al., 1996; Jacob et al., 1996] and PEM-West A/B [B G. Heikes reported by Gregory and Scott, 1995]. Data are averages of lower (0-4 km or marine boundary layer) and upper troposphere (8-12 km).

$^b$ Source of peroxides/formaldehyde in upper troposphere based on convective turnover of 0.08 d$^{-1}$ (Fig. 1). H$_2$O$_2$ is soluble and scavenged (75%) from wet convective updrafts; negligible scavenging is expected for CH$_3$OOH and CH$_2$O (much lower solubilities).

$^c$ Mean yield of HOx per peroxide/formaldehyde molecule in the upper troposphere. Yields are 24-hour averages for high HOx conditions at 14 km (CNV/standard with $S_{HOx} = 150$ in Table 2), including removal by convective turnover (0.08 d$^{-1}$).

$^d$ Source of HOx in the upper troposphere (24-hr average) is the product of $S_{HOx}$ and HOx-yield columns (peroxides/formaldehyde) or is modeled (water and acetone).
on NO$_x$ and HO$_x$ partitioning using a series of sensitivity studies. As defined in Table 2, the model adopts typical conditions for 14 km altitude in the tropics. NO mixing ratios of 50 pptv are typical in the tropical upper troposphere (e.g., Figure 11 of Carroll et al., [1992]). We constrain the 24-hour diel cycle to be in steady state with 50 pptv NO at noon by adjusting NO$_x$ for local photochemical steady state (LPSS) or by specifying a NO source (S$_{NO}$) for convective turnover (CNV). For LPSS HNO$_3$ builds up to 70 pptv and OH to 0.31 pptv resulting in a NO/HNO$_3$ ratio of 0.72. With convective turnover (CNV), S$_{NO}$ equal to 5.90 pptv d$^{-1}$ is needed; the OH levels are essentially unchanged; but the HNO$_3$ levels drop almost a factor of 3 increasing the NO/HNO$_3$ ratio to 1.88. (At 12 km, this ratio shifts by a similar factor from 0.43 (LPSS) to 1.04 (CNV)). These larger ratios are in much better agreement with observations in the tropics [Davis et al., 1996; Jacob et al., 1996]. The lifetime for NO$_x$ conversion to HNO$_3$ ranges from 7 to 15 days for the cases in Table 2, and thus a convective turnover time of 12.5 days significantly perturbs the LPSS. Ehhalt et al.'s [1992] convective model study of mid-latitude NO$_x$ indicated that NO/NO$_y$ ratios in the upper troposphere were far from steady state (i.e., their Figure 13).

The addition of a convective source of CH$_3$OOH (S$_{CH3OOH}$ = 90 pptv d$^{-1}$) boosts noon time OH by 20% and reduces the NO/HNO$_3$ ratio to 1.42 (still a factor of 2 greater than LPSS). The further addition of other HO$_x$ reservoirs (S$_{HOx}$ = 150 pptv d$^{-1}$ = 90 pptv d$^{-1}$ CH$_3$OOH + 45 pptv d$^{-1}$ H$_2$O$_2$ + 15 pptv d$^{-1}$ CH$_3$O) increases OH another 13% with similar change in NO/HNO$_3$. Without acetone the impact of convective pumping of CH$_3$O-OH is more pronounced and OH increases by 50%. At twice these NO levels, 100 pptv, the HO$_x$ balance shifts to more OH and less HO$_2$ with slightly smaller NO/HNO$_3$ ratios; however, the relative impact of convective HO$_x$ is similar to the standard case with 50 pptv NO.

Ozone production for a given NO concentration is proportional to HO$_x$ concentration, and the net O$_x$ tendency (ppb d$^{-1}$) increases substantially when HO$_x$ reservoirs are convectively pumped to the upper troposphere as shown in Table 2. Because the chemical time scale for O$_3$ change in the upper troposphere is over a month–long compared to the turnover time—we can use the instantaneous tendency multiplied by the turnover time (12.5 d) to estimate the incremental buildup. At 50 pptv NO and without acetone, the local photochemistry would accumulate an additional 8 ppbv O$_3$ above background levels (as compared without NO). With acetone the buildup is 11 ppbv, and with convective pumping of HO$_x$ reservoirs the increase could be as much as 16 ppbv. At 100 pptv NO the ozone increases are not twice as large since HO$_2$ falls with increasing NO, but the ozone buildup could be as much as 24 ppbv! For all of the CNV cases in Table 2 the added effect of convecting HO$_x$ reservoirs is about 5 ppbv additional ozone in the tropical upper troposphere as compared with a model that did not include convective of the HO$_x$ precursors.

### Table 2. HO$_x$ levels and NO$_x$/NO$_y$ balance in Upper Troposphere (noontime mixing ratios).

<table>
<thead>
<tr>
<th>Chemical Model</th>
<th>S$_{NO}$/pptv/d</th>
<th>S$_{HOx}$/pptv/d</th>
<th>NO/pptv</th>
<th>NO$_2$/pptv</th>
<th>HNO$_3$/pptv</th>
<th>HNO$_4$/pptv</th>
<th>NO/ HNO$_3$</th>
<th>OH/pptv</th>
<th>HO$_x$/pptv</th>
<th>dO$_3$/dt</th>
<th>pptv/d</th>
<th>pptv/pptv/d</th>
<th>pptv/d</th>
</tr>
</thead>
<tbody>
<tr>
<td>LPSS:</td>
<td>0</td>
<td>0</td>
<td>50</td>
<td>5.4</td>
<td>70</td>
<td>19</td>
<td>0.72</td>
<td>0.31</td>
<td>8.3</td>
<td>+0.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNV: standard</td>
<td>5.90</td>
<td>0</td>
<td>50</td>
<td>5.4</td>
<td>27</td>
<td>16</td>
<td>1.88</td>
<td>0.30</td>
<td>7.9</td>
<td>+0.90</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.95</td>
<td>90</td>
<td>50</td>
<td>5.9</td>
<td>35</td>
<td>20</td>
<td>1.42</td>
<td>0.36</td>
<td>10.0</td>
<td>+1.15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>7.45</td>
<td>150</td>
<td>50</td>
<td>6.2</td>
<td>40</td>
<td>21</td>
<td>1.25</td>
<td>0.40</td>
<td>10.9</td>
<td>+1.24</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNV: no acetone</td>
<td>4.70</td>
<td>0</td>
<td>50</td>
<td>4.6</td>
<td>17</td>
<td>12</td>
<td>2.91</td>
<td>0.21</td>
<td>5.5</td>
<td>+0.61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.25</td>
<td>90</td>
<td>50</td>
<td>5.4</td>
<td>30</td>
<td>18</td>
<td>1.70</td>
<td>0.32</td>
<td>8.5</td>
<td>+0.96</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>6.82</td>
<td>150</td>
<td>50</td>
<td>5.7</td>
<td>35</td>
<td>19</td>
<td>1.44</td>
<td>0.36</td>
<td>9.6</td>
<td>+1.08</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CNV: 2 x NO</td>
<td>11.4</td>
<td>0</td>
<td>100</td>
<td>9.8</td>
<td>64</td>
<td>18</td>
<td>1.58</td>
<td>0.43</td>
<td>6.5</td>
<td>+1.40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>13.2</td>
<td>90</td>
<td>100</td>
<td>10.7</td>
<td>87</td>
<td>22</td>
<td>1.24</td>
<td>0.52</td>
<td>8.0</td>
<td>+1.78</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>14.1</td>
<td>150</td>
<td>100</td>
<td>11.0</td>
<td>91</td>
<td>23</td>
<td>1.11</td>
<td>0.57</td>
<td>8.7</td>
<td>+1.95</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tropical atmosphere, equinoctial conditions at 14 km (156 hPa, 211 K, H$_2$O = 42 ppmv (80% RH), O$_3$ = 60 ppbv, CH$_4$ = 1700 ppbv, CO = 100 ppbv, CH$_3$OC(CH$_3$) = 300 ppbv, no aerosols, no PAN, no non-methane hydrocarbons other than acetone and methane oxidation products, overhead ozone column = 236 DU, surface albedo = 0.10). Photoschemical box-model is a tropospheric version of Prather and Jaffe [1990; updated to JPL-94, DeMore et al., 1994] calculating diel cycles for O($^3$P), O($^3$D), H, OH, HO$_x$, H$_2$O$_2$, CH$_3$H, CH$_3$OO, CH$_3$OH, CH$_2$O, NO, NO$_2$, NO$_3$, N$_2$O$_5$, HNO$_2$, HO$_2$, NDN$_3$, and HNO$_3$, plus the average net photochemical tendency of ozone, dO$_3$/dt. Acetone photochemistry is taken from McKee et al. [1997]. LPSS denotes local photochemical steady state (i.e., no convective "removal" of any species); CNV denotes convective turnover (removal) of species at 0.08 d$^{-1}$. The source of NO (S$_{NO}$ e.g., lightning, surface emissions) is chosen to maintain 50 or 100 pptv NO at noon. The HO$_x$ convective sources are 0 (none), 90 (pptv d$^{-1}$ CH$_3$OOH), or 150 (90 pptv d$^{-1}$ CH$_3$OOH + 45 pptv d$^{-1}$ H$_2$O$_2$ + 15 pptv d$^{-1}$ CH$_3$O). Additional cases without acetone and with twice the NO are included.

### Discussion

In summary, convective pumping of the upper tropical troposphere at rates predicted by general circulation models will lead to a persistent chemical imbalance. The shift of NO$_x$ partitioning from LPSS is driven by convective turnover (i.e., removal of NO$_x$ species and replacement by NO), but the HO$_x$ levels and production of ozone are controlled by the convective sources of CH$_3$OOH and possibly H$_2$O$_2$. There is clear evidence from measurements during the STRAT campaign [Wennberg et al., 1997; Jaegle et al., 1997] that OH levels are often—but not always—much higher than can be explained by LPSS and are consistent with elevated levels of H$_2$O$_2$ and CH$_3$OOH (not measured on STRAT).

What could be wrong with this model assessment? First, we looked only at the mean altitude (14 km) in the upper tropics. This level is just above the TRACE and PEM-West flight altitudes and at the lower range of ER-2 data on HO$_3$ [Wennberg et al., 1997]. The impact of convective pumping is diluted as we go to lower altitudes: flushing rates are not so...
rapid, and local photochemistry is more active and less susceptible to convective turnover. The global importance of convective pumping of peroxides and formaldehyde must be integrated with a 3-D chemical transport model. Second, convective outflow from the top of cumulus towers will shear into laminae and may remain chemically isolated for days before mixing with the background atmosphere. It is possible that HOx precursors may be more rapidly destroyed in these concentrated plumes; however, Jaegle et al. [1997] have shown that the elevated HOx levels in these convective plumes will take a week or more to decay in the upper troposphere because of recycling within the HOx family. Thus, the approximation here of the upper troposphere as a well mixed box may be a reasonable simulation of the mean state but, of course, is not adequate for comparison with observations.

How would this convective transport of HOx change our predictions of tropospheric O3 increases from aircraft and biomass burning? Convective transport of NO and HOx precursors is necessary in tropospheric chemistry models. The added source of HOx to the upper tropical troposphere makes it more likely that ozone production there is limited by the supply of NOX, e.g., Brasseur et al., 1996. Through such transports, the upper troposphere is more photochemically active and plays a greater role in controlling ozone, an important, anthropogenically perturbed, greenhouse gas.

Acknowledgments. This research was supported by NASA's Atmospheric Chemistry Modeling & Analysis, Atmospheric Effects of Aviation, and Global Tropospheric Experiment Programs, and by NSF's Atmospheric Chemistry Program. MP thanks those at the Conference on Modelling of Global Climate Change & Variability, Hamburg, for the opportunity to discuss these ideas.

References


M. J. Prather, Earth System Science Department, University of California, Irvine, CA 92697-3100. (e-mail: mprather@uci.edu)

D. J. Jacob, Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138. (e-mail: djj@europa.harvard.edu)

(Received May 31, 1997; revised September 15, 1997; accepted October 17, 1997)