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A persistent imbalance in HOx and NOx photochemistry of the upper troposphere driven by deep tropical convection

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Abstract. Convection in the tropics turns over the upper troposphere at rates (0.08 d^{-1}) comparable to photochemical processes controlling the absolute abundance of HO_x (OH + HO_2) and the abundance of NO_x (NO + NO_2) relative to HNO_3. Here we identify convection of boundary-layer CH_3OOH as a primary source of HO_x to the upper troposphere. Turnover of NO_x leads to NO/HNO_3 ratios much higher than predicted for local photochemical steady-state. Through convective transport the upper troposphere is more photochemically active in producing O_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_x (OH + HO_2) and NO_x (NO + NO_2) in the upper troposphere. Deep convection in the tropics flushes the upper tropical troposphere, brings in fresh sources of NO (e.g., from soils, combustion, lightning) and HO_x reservoirs (H_2O_2, CH_3OOH, CH_2O), drives the photochemical balance away from local photochemical steady-state (LPSS), and increases the net production of ozone (O_3) in the upper troposphere. Specifically, we predict that convection of boundary-layer CH_3OOH is a major source of HO_x and O_3 in the upper troposphere.

Convective mass fluxes on a global average are not readily measurable, even from meteorological analyses; and we adopt the convection statistics from the GISS general circulation model, version II-prime, which includes a significantly improved convection scheme [*DelGenio and Yao*, 1992; *Rind and Lerner*, 1996]. Figure 1 summarizes the deep, non-entraining convective flux over the equatorial region (12°S - 12°N) for May through August. The sigma-levels of the GISS GCM are shown along with the flux of air into and out-of each layer in g m^{-2} s^{-1}. Although these rates are equatorial averages, similar values apply up to 30°N in summer. The effective turnover rates for each level are shown on the right: e.g., the lowest layers (999-870 hPa) are vented at a rate of 18% per day and the uppermost level from 11 to 17 km altitude (100-255 hPa) is turned over at a rate of 8% per day.

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_3, H_2O_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_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_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_y family (NO, NO_2, NO_3, HONO, HNO_3, HNO_4, N_2O_5) and the HO_y family (OH, HO_2, H_2O_2, CH_3OOH, CH_3OO, CH_2O, HONO, HO_2NO_2), 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_y injected into the upper troposphere by convection will be primarily in the form of NO_x because HNO_3 will be rained out. Thus, loss of NO_y in the upper tropical troposphere from convective turnover is assumed to be balanced by a fresh source of NO_x (e.g., lightning or surface emissions). The HO_y family is made photochemically from H_2O and CH_4. Observations in the tropics show rapid decline with altitude in the concentrations of H_2O_2, CH_3OOH, and CH_2O, following the decline of H_2O [*Heikes et al.*, 1996; *Jacob et al.*, 1996]. Concentrations of these species, which are the main components of the HO_y family and the main reservoirs of HO_x 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_x to the upper troposphere. Both CH_3OOH and CH_2O 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. *Chatfield and Crutzen* [1984] have argued for the potential importance of H_2O_2 convection, yet H_2O_2 is highly soluble and a large fraction should be rained out. In our analysis we assume a scavenging efficiency of 75% for H_2O_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 HO_x 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_3OOH, 0-45 pptv d^{-1} for H_2O_2, and 15 pptv d^{-1} for CH_2O (Table 1). Although H_2O_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 HO_x, NO_x, and O_3 Tendency

In Table 1 we estimate the impact of these additional HO_x sources at 14 km by calculating HO_x yields (molecule of HO_x produced per reservoir molecule destroyed) from the two peroxides and formaldehyde, multiplying by the convective source, and then comparing with the known HO_x sources (pptv d^{-1}) from oxidation of water vapor by $O(^1D)$ and from photolysis of acetone ($CH_3C(O)CH_3$) [*McKeen et al.*, 1997]. H_2O at 42 ppmv and acetone at 300 pptv [*Singh et al.*, 1995] supply comparable sources. Convective injection of CH_3OOH can double the source from water plus acetone. The source from H_2O_2 would be even larger, but 75% scavenging leaves it just comparable to water and acetone. The source from CH_2O is insignificant.

With this representative box-model of the upper tropical troposphere, we calculate the impact of convective pumping on NO_y and HO_y 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_y 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_3OOH ($S_{HOy} = 90$ pptv d^{-1}) boosts noontime 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_y reservoirs ($S_{HOy} = 150$ pptv $d^{-1} = 90$ pptv d^{-1} $CH_3OOH + 45$ pptv d^{-1} $H_2O_2 + 15$ pptv d^{-1} CH_2O) increases OH another 13% with similar change in NO/HNO_3. Without acetone the impact of convective pumping of CH_3OOH 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_y is similar to the standard case with 50 pptv NO.

Ozone production for a given NO concentration is proportional to HO_2 concentration, and the net O_3 tendency (ppb d^{-1}) increases substantially when HO_y 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_y 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_y reservoirs is about 5 ppbv additional ozone in the tropical upper troposphere as compared with a model that did not include convection of the HO_x precursors.

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_y partitioning from LPSS is driven by convective turnover (i.e., removal of NO_y species and replacement by NO), but the HO_x levels and production of ozone are controlled by the convective sources of CH_3OOH and possibly H_2O_2. There is clear evidence from measurements during the STRAT campaign [*Wennberg et al.*, 1997; *Jaeglé 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_2O_2 and CH_3OOH (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_x [*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 HO_y precursors may be more rapidly destroyed in these concentrated plumes; however, *Jaeglé et al.*, [1997] have shown that the elevated HO_x levels in these convective plumes will take a week or more to decay in the upper troposphere because of recycling within the HO_y 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 HO_y change our predictions of tropospheric O_3 increases from aircraft and biomass burning? Convective transport of NO and HO_x precursors is necessary in tropospheric chemistry models. The added source of HO_x to the upper tropical troposphere makes it more likely that ozone production there is limited by the supply of NO_x [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.

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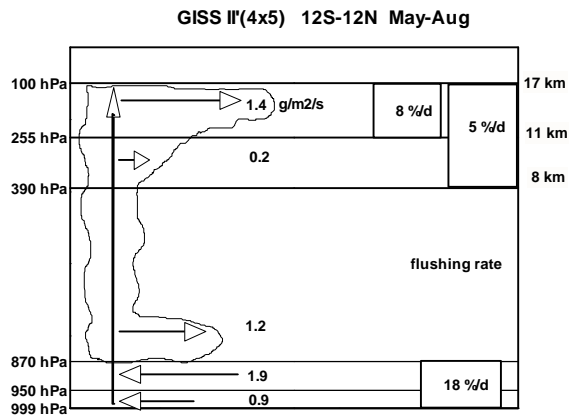
GISS II'(4x5) 12S-12N May-Aug

Figure 1. Convective transport of boundary layer air to the equatorial upper troposphere (12°S-12°N) in the GISS II-prime general circulation model during May-June-July-August. Zonally averaged, upward convective fluxes (g m^{-2} s^{-1}) are shown. These are balanced by large-scale subsidence (not shown). Middle tropospheric GCM layers are not shown. The mean turnover rates (% d^{-1}) for air as a result of deep convection and subsidence are indicated for each blocked region.

Table 1. HO$_x$ Precursors in the Upper Tropical Troposphere

Tropospheric Concentrations[a]			S$_{HOy}$[b] pptv/d	Yield[c] v/v	S$_{HOX}$[d] pptv/d
	Lower	Upper			
CH$_3$OOH, pptv					
TRACE-A	1200	60	90	~1.4	125
PEM-WEST	820	200	50		70
H$_2$O$_2$, pptv					
TRACE-A	2800	150	45	~1.4	65
PEM-WEST	1100	240	3		4
CH$_2$O, pptv					
TRACE-A	200	<40	15	~0.7	10
H$_2$O, ppmv		42			50
CH$_3$C(O)CH$_3$, pptv		300			85

[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 HO$_x$ per peroxide/formaldehyde molecule in the upper troposphere. Yields are 24-hour averages for high HO$_x$ conditions at 14 km (CNV/standard with S$_{HOy}$ = 150 in Table 2), including removal by convective turnover (0.08 d^{-1}).
[d] Source of HO$_x$ in the upper troposphere (24-hr average) is the product of S$_{HOy}$ and HO$_x$-yield columns (peroxides/formaldehyde) or is modeled (water and acetone).

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

Chemical Model	S$_{NO}$ pptv/d	S$_{HOy}$ pptv/d	NO pptv	NO$_2$ pptv	HNO$_3$ pptv	HNO$_4$ pptv	NO/ HNO$_3$	OH pptv	HO$_2$ pptv	dO$_3$/dt ppbv/d
LPSS:	0	0	50	5.4	70	19	0.72	0.31	8.3	+0.94
CNV: standard	5.90	0	50	5.4	27	16	1.88	0.30	7.9	+0.90
	6.95	90	50	5.9	35	20	1.42	0.36	10.0	+1.15
	7.45	150	50	6.2	40	21	1.25	0.40	10.9	+1.24
CNV: no acetone	4.70	0	50	4.6	17	12	2.91	0.21	5.5	+0.61
	6.25	90	50	5.4	30	18	1.70	0.32	8.5	+0.96
	6.82	150	50	5.7	35	19	1.44	0.36	9.6	+1.08
CNV: 2 x NO	11.4	0	100	9.8	64	18	1.58	0.43	6.5	+1.40
	13.2	90	100	10.7	81	22	1.24	0.52	8.0	+1.78
	14.1	150	100	11.0	91	23	1.11	0.57	8.7	+1.95

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$_3$C(O)CH$_3$ = 300 pptv, no aerosols, no PAN, no non-methane hydrocarbons other than acetone and methane oxidation products, overhead ozone column = 236 DU, surface albedo = 0.10). Photochemical 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(^{1}D), H, OH, HO$_2$, H$_2$O$_2$, CH$_3$, CH$_3$O, CH$_3$OO, CH$_3$OOH, CH$_2$O, NO, NO$_2$, NO$_3$, N$_2$O$_5$, HNO$_3$, HO$_2$NO$_2$, and HONO, plus the average net photochemical tendency of ozone, dO$_3$/dt. Acetone photochemistry is taken from McKeen 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$_y$ 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$_2$O). Additional cases without acetone and with twice the NO are included.