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Oceanic alkyl nitrates as a natural source of tropospheric ozone

Jessica L. Neu,[1] Michael J. Lawler,[1] Michael J. Prather,[1] and Eric S. Saltzman[1]

[1] Observations have revealed widespread emissions of alkyl nitrates from the tropical and Southern Oceans. We present the first chemical transport model simulations to examine the global impact of these emissions. Matching observed atmospheric abundances, we derive a total oceanic flux of methyl nitrate ($MeONO_2$) and ethyl nitrate ($EtONO_2$) equivalent to 0.35 Tg of N per year, which contributes as much as 1 DU to the tropospheric ozone column in the Western Pacific and is responsible for about 3% of the global oxidative capacity of the troposphere. **Citation:** Neu, J. L., M. J. Lawler, M. J. Prather, and E. S. Saltzman (2008), Oceanic alkyl nitrates as a natural source of tropospheric ozone, *Geophys. Res. Lett.*, *35*, L13814, doi:10.1029/2008GL034189.

1. Introduction

[2] Atmospheric observations indicate that low molecular weight (C_1-C_4) alkyl nitrates are ubiquitous over the tropical and Southern Oceans [*Atlas et al.*, 1993; *Blake et al.*, 1999, 2003] and can be a significant component (20–80%) of the total reactive nitrogen in remote marine air [*Jones et al.*, 1999; *Talbot et al.*, 2000]. Recent ship-borne measurements show supersaturation of alkyl nitrates in tropical surface waters, confirming an oceanic source [*Chuck et al.*, 2002; *Moore and Blough*, 2002; *Dahl et al.*, 2005]. This work presents the first 3-D chemical transport model (CTM) simulations to examine the role of oceanic alkyl nitrates in global chemistry, using observational constraints.

[3] Alkyl nitrates are generated in seawater through aqueous phase photochemistry [*Dahl et al.*, 2003]. Production can occur via the reaction of ROO + NO in seawater, with photolysis of colored dissolved organic matter generating the peroxy radicals and nitrite photolysis generating NO. Biogenic production may also occur, but as yet there is no direct evidence for enzymatically mediated production. Alkyl nitrates are removed from the atmosphere by photolysis and reaction with OH, yielding NO_2; tropical lifetimes range from several days to a month, depending on molecular weight. The contribution of alkyl nitrates to the remote NO_x (=NO + NO_2) budget is not well-constrained by observations [*Schultz et al.*, 1999; *Olson et al.*, 2001]. Emissions of these NO_x precursors may play an important role in the ozone budget in remote regions, where NO_x abundances are small.

[4] In this study, we incorporate $MeONO_2$ and $EtONO_2$ in the chemical mechanism of the UCI CTM [*Carver et al.*, 1997] and compare their simulated abundances to observations to derive new estimates of their oceanic fluxes. We assess the relative importance of oceanic alkyl nitrates as a natural source of NO_x in remote regions by evaluating their impact on tropospheric ozone (O_3) and the oxidative capacity of the atmosphere.

2. Method

2.1. Model Description

[5] The UCI CTM [*Wild and Prather*, 2000; *Hsu et al.*, 2005] includes 30 chemical species in the troposphere (Table S1), with a simplified hydrocarbon oxidation scheme as described in *Wild et al.* [2003].[1] The CTM is driven using pieced-forecast meteorological fields for the year 2000 from the ECMWF Integrated Forecast System model, and the simulations presented here are run at $2.8 \times 2.8°$ horizontal resolution with 37 vertical levels from the surface to 10 hPa. The model has undergone several recent updates, including the addition of an innovative scheme for calculating photolysis rates for fractionally cloudy grid boxes [*Neu et al.*, 2007] and a revised scavenging code that accounts for the overlap of precipitating clouds.

2.2. Treatment of Alkyl nitrates

[6] This study focuses on $MeONO_2$ and $EtONO_2$, which represent approximately 90% of observed oceanic alkyl nitrates [*Blake et al.*, 2003]. Atmospheric photochemical sources of alkyl nitrates from polluted regions are not included. The atmospheric decomposition of $MeONO_2$ and $EtONO_2$ occurs via photolysis and reaction with OH. Photolysis is known to produce NO_2 and an alkoxy radical (MeO or EtO) [*Talukdar et al.*, 1997b], which is assumed to react instantaneously with O_2 to produce an aldehyde (HCHO or MeCHO) and HO_2. The product yields of the OH reactions are not well known, but the reactions are thought to proceed via H- abstraction [*Talukdar et al.*, 1997a] and we assume that the product decomposes into NO_2 and an aldehyde. The photolysis cross sections and OH reaction rate constants are based on the 2004 IUPAC recommendations [http://www.iupac-kinetic.ch.cam.ac.uk].

[7] We define a control run with no alkyl nitrate emissions and compare it to two simulations in which we impose a constant, spatially uniform flux of $MeONO_2$ and $EtONO_2$ from: 1) the tropical oceans ($10°S–10°N$) and 2) the Southern Ocean (south of $45°S$). For the tropical oceans, we derive an a priori flux estimate using a single, average value for both the ocean-atmosphere concentration gradient and surface wind speed in the equatorial Pacific from *Dahl et al.* [2005]. The *Wanninkhof* [1992] gas flux parameterization, corrected for Schmidt number after *Chuck et al.* [2002], yields fluxes of 26.7 mg/m²/yr for $MeONO_2$ and

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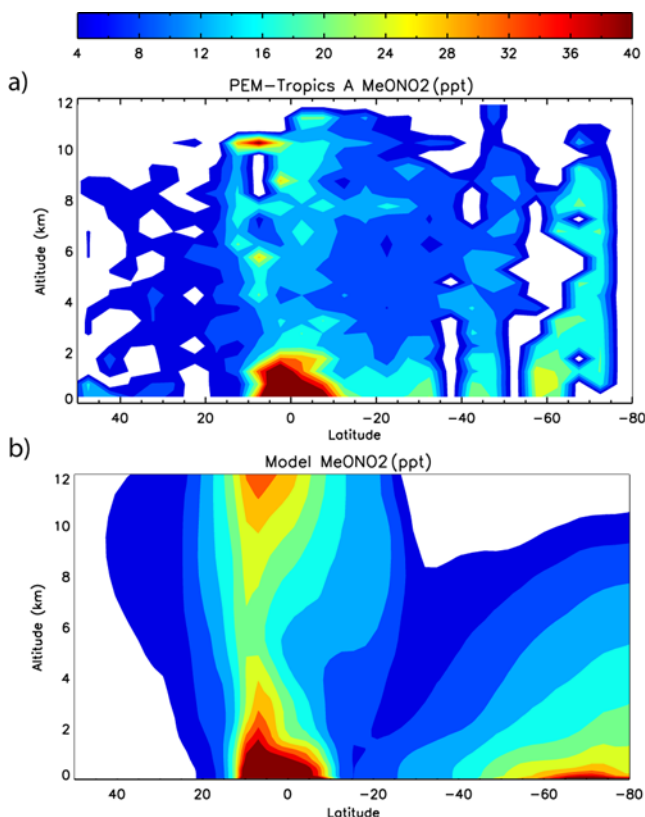[1]Department of Earth System Science, University of California, Irvine, California, USA.

Figure 1. (a) MeONO$_2$ from aircraft observations during PEM-Tropics A (mid Aug – mid Oct 1996), binned at 5° lat by 0.5 km resolution (D. Blake, personal communication, 2007). (b) MeONO$_2$ from a linear combination of tropical and Southern Ocean perturbation runs for Sept, averaged over the Pacific Ocean (160W–130E), scaled to match the observations.

7.18 mg/m^2/yr for EtONO$_2$. Lacking comparable concentration gradient data, we use the same a priori flux for the Southern Ocean. We then scale the results separately for the two oceans using an extensive set of atmospheric abundance observations as described below to derive a posteriori flux estimates. In the Southern Ocean in particular, we expect the fluxes to vary spatially and seasonally based on the availability of organic matter and sunlight, but we do not have the information to be able to incorporate such variability.

2.3. Flux Estimates from Observations

[8] Figure 1a shows atmospheric measurements of MeONO$_2$ over the Pacific Ocean from the PEM-Tropics A aircraft campaign (Aug–Oct 1996) [*Blake et al.*, 2003] that have been corrected based on new standards (2.13 times reported MeONO$_2$ (D. Blake, personal communication, 2007)). Figure 1b shows simulated MeONO$_2$ abundances for September. The tropical and Southern Ocean fluxes were scaled separately to provide the best match to the observations. The simulation clearly reproduces the observed large-scale structures. Results are similar for EtONO$_2$ (scaling discussed below) and for measurements from PEM-Tropics B (not shown).

[9] Using the EtONO$_2$:MeONO$_2$ ratio of the a priori fluxes, our scaling based on the MeONO$_2$ measurements

yields tropical ocean emissions of 21.4 mg MeONO$_2$/m^2/yr and 5.74 mg EtONO$_2$/m^2/yr, in good agreement with the a priori estimate. We find much smaller Southern Ocean fluxes of 2.93 mg MeONO$_2$/m^2/yr and 0.79 mg EtONO$_2$/m^2/yr. The total oceanic flux is equivalent to 0.35 Tg of N per year, with MeONO$_2$ accounting for 82%. The atmospheric measurements of *Blake et al.* [2003] combined with our modeled lifetimes imply a higher ratio of EtONO$_2$ to MeONO$_2$ and would add an additional 0.05 Tg of N per year from EtONO$_2$. We estimate the likely uncertainty range (66%) of the total flux to be 0.2–0.6 Tg of N per year. For comparison, other remote sources of NO$_x$ such as lightning and aviation produce 3.0–7.0 and 0.5–0.8 Tg of N per year, respectively [*Denman et al.*, 2007].

[10] The Southern Ocean fluxes are more uncertain than those in the tropics, because the observations south of 45° are from a single flight leg in September. With a constant flux, the CTM accumulates alkyl nitrates throughout the winter, so that only a small flux is needed to match September atmospheric abundances. Sunlight-dependent production would imply a larger springtime flux. Comparison to ACE-1 campaign measurements [*Blake et al.*, 1999] from a single flight to 60°S in November supports the seasonality of Southern Ocean emissions, indicating higher fluxes are needed in late Spring to match atmospheric observations. Additional measurements are needed to define the amplitude and seasonality of the Southern Ocean source.

3. Results

3.1. Transport and Decomposition of Alkyl Nitrates

[11] Over the tropical oceans, MeONO$_2$ and EtONO$_2$ are lofted by convection directly into the upper troposphere, producing a secondary maximum in abundance (Figure 1) that follows the seasonal shift in the inter-tropical convergence zone. In the Western Pacific, where abundances are largest (Figure 2), there is relatively weak vertical transport over the Southern tropics from January to May (not shown) and stronger transport over the Northern tropics from June to December. Over the Southern Ocean, vertical transport is limited, and the alkyl nitrates remain within the lower troposphere.

[12] The average lifetime of MeONO$_2$ in the tropical marine boundary layer is ~40 days, approximately twice that of EtONO$_2$. Photolysis is the dominant loss mechanism for MeONO$_2$ throughout the troposphere. In the lower troposphere, photolysis accounts for ~60% of EtONO$_2$ loss, with the OH reaction making up the rest. In the upper troposphere, photolytic EtONO$_2$ loss increases to 80% of the total.

[13] MeONO$_2$ and EtONO$_2$ exhibit a surprising degree of longitudinal inhomogeneity in the tropics, given our spatially uniform fluxes. Maximum mixing ratios occur near the surface over the Western Pacific from May to October, despite large loss frequencies (MeONO$_2$ shown in Figure 2). This reflects the convergence of the trade winds in this region. Large abundances are also found off the western coasts of South America and Africa, where cloudy conditions persist during most of the year, reducing photochemical loss frequencies. Observations of high alkyl nitrate concentrations over biologically active upwelling regions have generally been interpreted as indicating a stronger
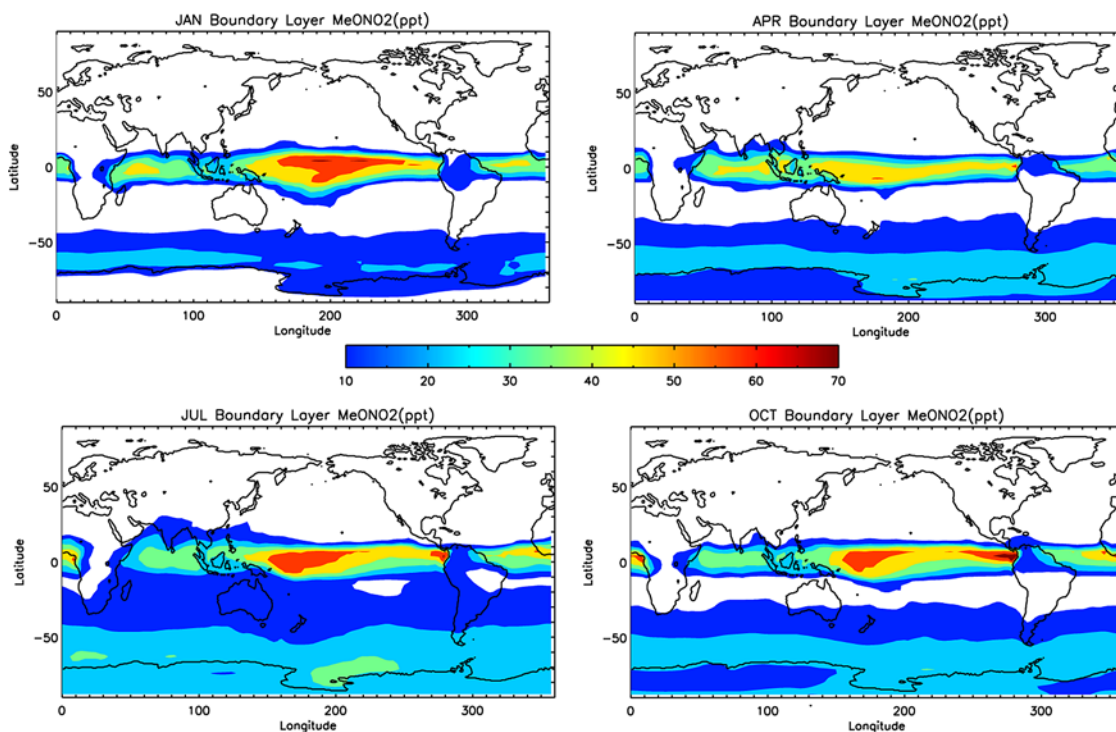
Figure 2. Monthly mean MeONO$_2$ averaged over the boundary layer (below 850 mb) for Jan, Apr, Jul, and Oct.

source [*Chuck et al.*, 2002; *Dahl et al.*, 2007], but it is clear that long photolysis lifetimes also play a role in driving up abundances in these regions. From November to April, alkyl nitrates are more evenly spread across the surface of the tropical oceans, but the highest levels are always found over the Pacific. In the southern extratropics, alkyl nitrates reach a maximum from July to September due to their accumulation during winter (a consequence of maintaining constant fluxes throughout the year).

3.2. Impact on NO$_x$ and O$_3$ Chemistry

[14] Oceanic alkyl nitrates cause measurable increases in both NO$_x$ and O$_3$ in marine air. Their largest impact is seen over the equatorial Western Pacific (Figure 3). There is a persistent minimum in both NO$_x$ and O$_3$ (Figure 3a) in this region, where the circulation isolates the marine boundary layer, resulting in sustained photochemical loss of O$_3$ and a deep minimum throughout the tropospheric O$_3$ column. At the same time, the circulation acts to accumulate alkyl nitrates in the Western Pacific (see Figure 2), and they drive up boundary layer NO$_x$ abundances by as much as 250%. This leads to O$_3$ increases of up to 20% (Figures 3b and 3f), with the largest increases occurring from May to October. From December to March (not shown), the relative increases in NO$_x$ and O$_3$ are smaller, but are still concentrated in the Western Pacific even though the alkyl nitrates are spread more evenly across the Pacific during these months. The geographic pattern of the alkyl nitrate influence persists into the middle and upper troposphere (Figures 3c-3d and 3g-3h), with reduced relative impact because of the larger lightning NOx source. However, the largest zonal mean increases in mixing ratio, 3–8 ppt for NOx and 1 ppb for O$_3$, occur in the tropical upper and middle troposphere, respectively (Figure 4).

[15] Over the Southern Ocean, the alkyl nitrate impact is more modest but also more longitudinally widespread in the boundary layer and middle troposphere. As expected, the largest increases in NO$_x$ and O$_3$ occur during the photochemically active austral summer (not shown), with increases in boundary layer O$_3$ of 8–10% over much of the region.

[16] The O$_3$ produced by NO$_x$ from alkyl nitrates fills in the minimum in the tropospheric O$_3$ column over the Western Pacific, adding more than 1 DU, with a maximum in October (Figure 3e). The global average increase in tropospheric O$_3$ column varies with season from 0.35 to 0.42 DU.

3.3. Change in Global Oxidative Capacity

[17] Through these NO$_x$ and O$_3$ changes, alkyl nitrates increase the tropospheric abundance of OH radicals, which determines the atmospheric lifetime of many gases. In these simulations, the OH increase attributable to alkyl nitrates decreases the lifetime and global mean abundance of CO by 3.4% (from 1.80 to 1.74 months). The CH$_4$ lifetime is less sensitive to the OH increases in the upper troposphere caused by alkyl nitrates and is reduced by only 1.7% (from 9.44 to 9.28 years). In steady state, the resulting change in CH$_4$ abundance feeds back on OH and amplifies this effect [*Prather and Ehhalt*, 2001], and the abundance is predicted to decrease by 2.4%.

3.4. Comparison to Aviation NO$_x$

[18] Our estimated oceanic alkyl nitrate emissions of 0.35 Tg N/yr are approximately half of the direct NO$_x$ emissions from aviation in our model, 0.79 Tg N/yr [*Baughcum et al.*, 1996] (scaled using *Denman et al.* [2007]). It is well known that NO$_x$ from aircraft and lightning, which is emitted above the boundary layer, has
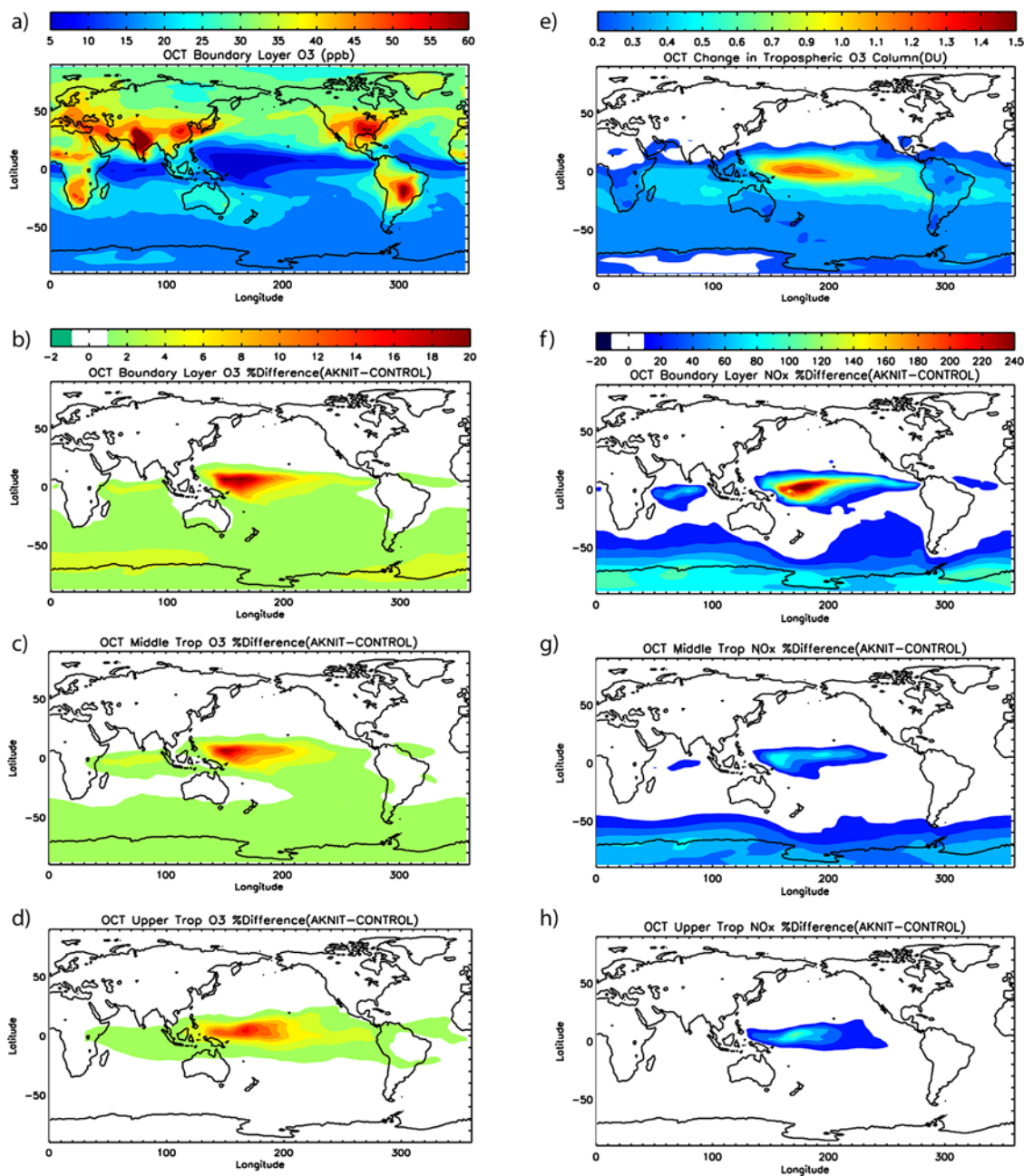
Figure 3. (a) Oct monthly mean O$_3$ mixing ratio averaged over the boundary layer (below 850 mb) for the control simulation. (b)-(d) Oct monthly mean percent difference in O$_3$ (perturbation – control) in the boundary layer, mid-troposphere (850-500 mb) and upper troposphere (500 – 150 mb). (e) Oct change in tropospheric O$_3$ column caused by alkyl nitrates in Dobson Units (DU). (f)-(h) Same as Figures 3b-3d, but for NO$_x$.

a far greater impact on global tropospheric chemistry on a per-molecule-emitted basis than NO$_x$ from northern industrial sources or biomass burning [*Wild et al.*, 2001; *Derwent et al.*, 2001]. To assess the relative activity of NO$_x$ from alkyl nitrates, we compare the simulations shown here to a perturbation with the aviation NO$_x$ source cut in half. This perturbation, when properly scaled, produces results similar to those found previously for aviation by *Wild et al.* [2001], despite significant changes to the CTM. With NO$_x$ emissions roughly equivalent to those from alkyl nitrates, the aviation impact is smaller by about 1/3 for the tropospheric O$_3$ column and about 1/2 for the CH$_4$ lifetime. This

difference is largely due to the difference in source locations. Higher latitude aviation emissions have a smaller impact than tropical alkyl nitrates.

4. Discussion

[19] In the tropical Pacific, our modeled MeONO$_2$ and EtONO$_2$ are roughly consistent with atmospheric observations and ship-based flux estimates. These data, however, are limited both in terms of geographic and seasonal coverage. The *Chuck et al.* [2002] measurements from the tropical Atlantic show large differences in both seawater
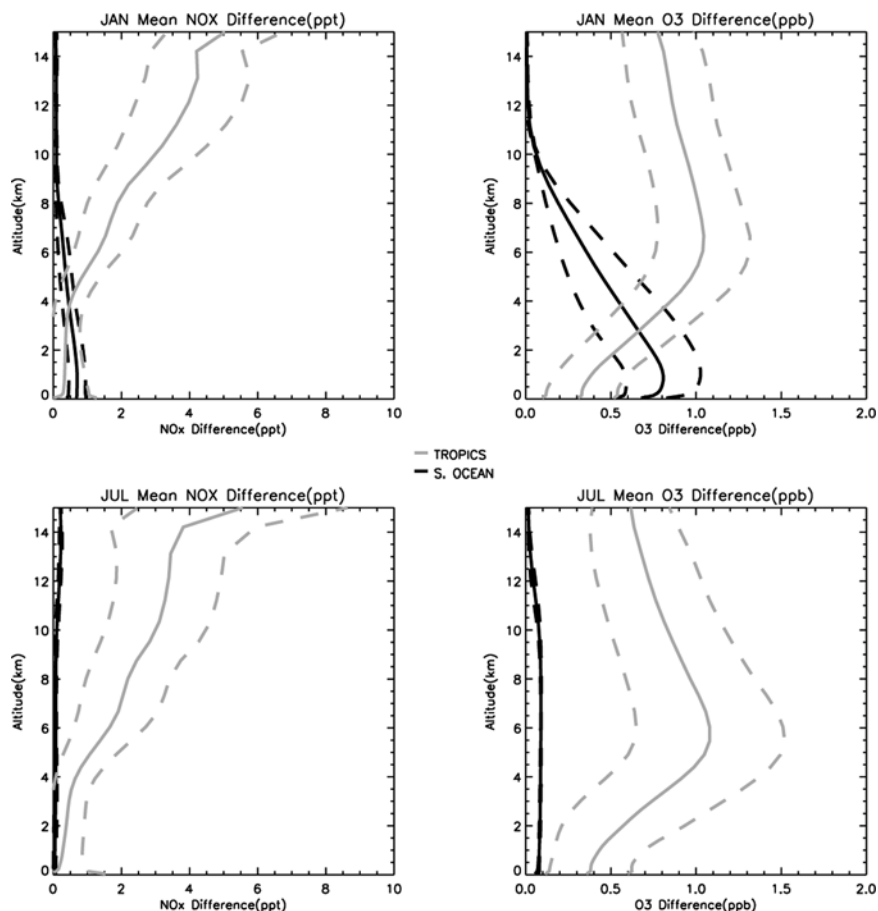
Figure 4. Profiles of the mean difference (solid lines) ± the standard deviation (dashed lines) in O_3 and NO_x mixing ratios averaged over the tropics (grey) and southern extratropics (black) for Jan and Jul (perturbation – control).

and atmospheric alkyl nitrate concentrations between cruises along the eastern and western Atlantic basin. Furthermore, even the largest flux reported by *Chuck et al.* is about a factor of 3 smaller than the tropical flux derived here. Given the lack of airborne measurements over the Atlantic, the question of whether Atlantic emissions are smaller than those from the Pacific remains open. Atmospheric measurements with greater spatial and temporal coverage and further understanding of the production mechanisms are needed.

[20] We expect Southern Ocean alkyl nitrate emissions to undergo large seasonal variations; hence assessment of this source is severely limited by the availability of observations. If the alkyl nitrate flux scales with sunlight, then we underestimate the peak summertime flux by scaling to early springtime measurements. The impact of the Southern Ocean emissions will be larger than we find here, perhaps appreciably so since the peak flux would occur when there is maximum photochemical activity. Austral summer measurements will provide better constraints on the Southern Ocean source.

[21] Oceanic alkyl nitrates are necessary to accurately model NO_x in the tropical remote marine environment, since they are responsible for 15–20% of the O_3 in the Western Pacific. The coincident location of the maximum alkyl nitrate impact and the deep minimum in O_3 over the Western Pacific is a fascinating consequence of the conver-

gence of the trade winds, but will make it difficult to detect an alkyl nitrate signature in O_3.

[22] At current levels, alkyl nitrates have a modest climate impact. From a simple scaling [*Wild et al.*, 2001], the global increase in tropospheric column O_3 will have a radiative forcing of about 16 mW/m^2. In steady state, this will be almost entirely offset by the reduced CH_4 lifetime, which produces a roughly equal negative radiative forcing. Surprisingly, a comparison to *Wild et al.* [2001] shows that on a per-molecule basis, alkyl nitrates have the largest impact on O_3 and CH_4 of any NO_x source analyzed to date. This seems to be a consequence of their long lifetime combined with efficient transport to the tropical upper troposphere. With a 2.4% effect on CH_4 lifetime, a 5-fold increase in alkyl nitrate emissions during glacial periods would account for roughly 1/3 of the 300 ppb drop in CH_4 seen between interglacials and glacials.

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