Latitudinal, vertical, and seasonal variations of C$_1$-C$_4$ alkyl nitrates in the troposphere over the Pacific Ocean during PEM-Tropics A and B: Oceanic and continental sources

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We present concentration distributions of C$_1$-C$_4$ and ethyl nitrate (EtONO$_2$) and the other alkyl nitrates in the troposphere over the Pacific Ocean during PEM-Tropics A and B (March–April 1999). The total geographic range for PEM-Tropics A was 45°N–72°S latitude and 153°E–75°W longitude, and for PEM-Tropics B was 40°N–36°S latitude and 149°E–75°W longitude. The maximum altitude for these missions was 12 km. These experiments provide the most extensive set of tropospheric measurements collected to date over the tropical Pacific Ocean. We observed high methyl nitrate (MeONO$_2$), CH$_3$ONO$_2$) mixing ratios (approximately 50 pptv) at low altitudes in a latitude band between 8°N to 13°S stretching across the equatorial Pacific, illustrating the oceanic source of MeONO$_2$. This source may be associated with the high-nutrient, low-chlorophyll character of equatorial Pacific waters. We discuss MeONO$_2$ and ethyl nitrate (EtONO$_2$), C$_2$H$_5$ONO$_2$), whose abundance is dominated by equatorial oceanic sources, 2-Propyl nitrate (2-PrONO$_2$), 2-C$_3$H$_7$ONO$_2$), which has significant oceanic and northern hemispheric (NH) sources associated with urban/industrial hydrocarbon emissions, and 2-butyl nitrate (2-BuONO$_2$), C$_4$H$_9$ONO$_2$), which has mostly NH sources. PEM-Tropics A and B resulted in remarkably similar equatorial mixing ratios. The excellent correlations between MeONO$_2$ and the other alkyl nitrates in this region produced comparable correlation slopes between the two expeditions. By contrast, NH air masses influenced by urban/industrial emissions typically exhibited much lower MeONO$_2$:EtONO$_2$, MeONO$_2$:2-PrONO$_2$, and MeONO$_2$:2-BuONO$_2$ ratios. These relationships can be useful as a diagnostic of air mass origin. North of 10°N, the springtime PEM-Tropics B mixing ratios of C$_2$-C$_4$ alkyl nitrates were many-fold higher at low-mid altitudes than for late summer PEM-Tropics A, consistent with strong continental outflow of NMHC precursors during spring.

INDEX TERMS: 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: Airborne measurements, equatorial ocean emissions, organic nitrates, methyl nitrate, ethyl nitrate, butyl nitrate

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1. Introduction

The heavier alkyl nitrates (>C$_1$) are known to form photochemically in the atmosphere following the hydroxyl radical initiated oxidation of alkanes in the presence of NO$_x$ [Darnall et al., 1976; Atkinson et al., 1982; Roberts, 1990]. Also, measurements in the remote atmosphere have suggested an additional oceanic source of alkyl nitrates to the tropical equatorial Pacific atmosphere [Atlas et al., 1993; Walega et al., 1992; Blake et al., 1999a]. The lightest alkyl nitrates (<C$_4$) are removed principally by photolysis, with OH reaction playing a progressively more important role as the hydrocarbon chain length increases [Clemitshaw...
Alkyl nitrates have atmospheric lifetimes ranging from about one month to several days, depending on alkyl chain length, thus long range transport is likely to play an important role in their remote tropospheric distributions [Atherton, 1989]. Until recently, few alkyl nitrate measurements had been made in the troposphere over the Pacific. Ridley et al. [1997] reported aircraft measurements of NMHCs and alkyl nitrates made near Hawaii. Most other measurements in the Pacific region have been made during shipboard studies, such as the Soviet-American Gases and Aerosols (SAGA-3) experiment, or at the Mauna Loa Observatory [Atlas et al., 1992; Atlas and Ridley, 1996; Walega et al., 1992]. For SAGA-3, Atlas et al. [1993] reported a broad maximum in the atmospheric mixing ratios of the C2 and C3 alkyl nitrates centered near the equator and concluded that there was a possible oceanic source for these alkyl nitrates related to surface water biota. However, the mechanism of production in seawater is not known [Atlas et al., 1997].

In August–September 1996, PEM-Tropics A provided the first detailed survey of tropospheric chemistry, including the vertical and spatial distributions of NMHCs, halocarbons, and alkyl nitrates over the South Pacific Basin [Hoell et al., 1999; Blake et al., 1999b, 2001]. In addition, MeONO2 concentrations were measured in latitudinal profiles over the Pacific Ocean and during intensive aircraft sampling south of Tasmania, as part of the First Aerosol Characterization Experiment (ACE-1) in November–December 1995 [Blake et al., 1999a]. Maximum ACE-1 MeONO2 concentrations were found over the equatorial regions of the Pacific.

Alkyl nitrates have relatively low reactivity compared to other components of atmospheric reactive nitrogen (NOx) and as such are potentially important long-range carriers of NOx to the remote troposphere. However, recent studies suggest that they typically make a relatively small contribution to the remote NOx budget [e.g., Schultz et al., 1999]. Alkyl nitrates have been of particular interest to the atmospheric measurement community as a reservoir of NOx, possibly helping to explain problems with closure of the NOx budget [Roberts, 1995, and references therein]. Talbot et al. [2000] examined the NOx budget for PEM-Tropics A and reported that in the equatorial marine boundary layer, the 50 pptv averaged alkyl nitrate sum comprised a major component (20–80%) of total NOx. In air of tropical origin measured at Mauna Loa, Hawaii, MeONO2 was up to 10% of NOx [Walega et al., 1992]. Recent results from coastal Antarctica indicate that RONO2 can be a high proportion of NOx [Jones et al., 1999]. However, studies of urban/rural air masses have shown alkyl nitrates typically to contribute less than 10% of NOx [e.g., Buhr et al., 1990; Ridley et al., 1990; Flocke et al., 1991; Roberts et al., 1996; Shepson et al., 1993; O’Brien et al., 1995; Talbot et al., 1999].

This paper presents the two most spatially extensive measurements of light alkyl nitrates ever reported. The samples were collected throughout the Pacific region during two seasons: PEM-Tropics A (August–October 1996) and PEM-Tropics B (March–April 1999). The total geographic range for PEM-Tropics A was 45°N–72°S latitude and 153°E–75°W longitude, and for PEM-Tropics B was 40°N–36°S latitude and 149°E–75°W longitude. The maximum altitude for these missions was 12 km. The dataset is so extensive that it enables, for the first time, contour plots to be produced with latitude/longitude distributions and latitude/altitude distributions. By comparison with known biogenic and anthropogenic emissions, as well as with geographical distributions, the relative biogenic/anthropogenic source strengths of the alkyl nitrates are deduced. Since light alkyl nitrates have both oceanic emission sources and continental photochemical sources and long lifetimes, these data will be a valuable asset to the global modeling community in validating emissions, photochemistry and transport in 3-D models.

2. Experiment

Sampling and analytical details can be found in Colman et al. [2001] so will be described here only briefly. Our “in-house” 2-liter electropolished stainless steel sampling canisters, which are conditioned and tested regularly to ensure reliability, were filled with whole air collected from beyond the laminar boundary layer of the NASA DC-8 and P-3B aircraft and pressurized to about 3.8 hPa employing a two-stage metal bellows pump (Parker MB-602XP). Approximately 140 samples were collected during a typical 8-hour DC-8 flight, and 120 canisters for each 8-hour flight aboard the P-3B. These samples were obtained roughly every 3–7 min during horizontal flight legs and 1–3 min during vertical legs. The P-3B typically flew at low levels (0.1–7.5 km) whereas the DC-8 operated at higher altitudes (5–12 km) with occasional excursions into the boundary layer. During both horizontal and vertical flight legs, our sampling duration was a minimum of 8 s at low altitude (150 m) to approximately 90 s at high altitude (12 km). Sampling time during horizontal legs was usually adjusted to be about 1 minute, corresponding to an approximate sampling distance of 8–12 km. Typical vertical sampling distances were 300 m for the DC-8, and 150 m for the P-3B.

After each flight, the filled canisters were transported via courier to our laboratory at the University of California-Irvine (UCI) for analysis, which usually was completed within ten days of sample collection. The analytical procedures are detailed in Colman et al. [2001]. Briefly, each sample was analyzed for more than 50 trace gases comprising hydrocarbons, halocarbons, dimethyl sulfide (DMS) (PEM-Tropics B only), and alkyl nitrates [see also Sive, 1998; Simpson et al., 2001; Blake et al., 2001]. Two identical analytical systems sharing the same standards were operated simultaneously around the clock to improve canister turn-around time. Approximately 15% of the samples were also analyzed in the National Center for Atmospheric Research (NCAR) laboratory using GC/MS techniques. After analysis in the UCI laboratory, samples either were cryogenically transferred to NCAR canisters or the UCI canisters were analyzed directly at NCAR. The agreement between UCI and NCAR values was very good, typically with R2 values better than 0.99.

1520 ± 1 cm3 (STP) of air was preconcentrated in liquid nitrogen, warmed, then quantitatively split into five streams, with each stream directed to a different column-detector combination [Colman et al., 2001]. Silicosteel tubing (0.53 mm O.D.) was used to connect the columns to
the splitter boxes. The split ratio was found to be highly reproducible as long as the specific humidity of the injected air was above 2 g H₂O/kg air. For this reason, as well as to increase the stability of certain compounds in our canisters, about 2.3 kPa of water was added to each (preconditioned, evacuated) canister.

[51] The C₁-C₄ alkyl nitrates were separated analytically employing three of the five column-detector combinations. The first combination (abbreviated as ‘DB5ms/MSD’) was a DB-5ms column (J&W; 60 m, 0.25 mm I.D., 0.5 μm film thickness) output to a quadrupole mass spectrometer detector (MSD) (HP-5973). The second combination (RSTek1701/ECD) was a RESTEK 1701 column (60 m, I.D. 0.25 mm, film 0.5 μm), which was output to an electron capture detector (ECD). A third combination (DB5-RSTek1701/ECD) was a DB-5 (J&W 30 m, I.D. 0.25 mm, film 1 μm) column connected in series to a RSTek 1701 column (5 m, I.D. 0.25 mm, film 0.5 μm), and output to an ECD. The DB5ms/MSD, RSTek1701/ECD, and DB5-RSTek1701/ECD combinations received 10.1%, 7.2%, and 6.8% of the sample flow, respectively. For PEM-Tropics A, the best alkyl nitrate precision was obtained from the RSTek1701/ECD combination. For PEM-Tropics B, the best precision was obtained by averaging the data from the RSTek1701/ECD and DB-5MS/ECD combinations [Colman et al., 2001]. During PEM-Tropics A, an ECD makeup gas that was 99.95% N₂(g) and 0.05% O₂(g) was employed. This technique, known as oxygen doping, significantly enhanced ECD sensitivity toward hydrogen containing halocarbons and organic nitrates. However, oxygen doping was not needed for PEM-Tropics B because the new HP 6890-based ECDs employed were roughly an order of magnitude more sensitive than the HP 5890 ECDs used for PEM-Tropics A [Colman et al., 2001].

[10] The typical alkyl nitrate detection limit was 0.02 pptv (0.01 pptv for methyl nitrate) and precision ±5% at mixing ratios above 5 pptv and ±10% below 5 pptv [Colman et al., 2001]. The detection limits for methyl iodide (CH₃I), bromoform (CHBr₃) and DMS are 0.01, 0.01, and 1 pptv, respectively. The precision for CH₃I and CHBr₃ were 3% and 2%, respectively for PEM-Tropics A, and 1.1 and 1.6%, respectively for PEM-Tropics B. For DMS, the precision is approximately 3% at mixing ratios >25 pptv, and 1 pptv or 15%, whichever is higher, at mixing ratios <10 pptv [Colman et al., 2001; Simpson et al., 2001].

[11] Routine alkyl nitrate calibration relied on the regular analysis of whole air working standards, which had been previously calibrated against a synthetic standard prepared at NCAR. The primary standard contained alkyl nitrates from C₁ to C₇ that were prepared from laboratory synthesized compounds or commercially available nitrates. A ppbv level standard was prepared in moist air by injection of a mixture of nitrates into a 35-liter stainless steel canister and pressurization to about 20 hPa. The nitrate levels in the mixture were calibrated by gas chromatography with flame ionization and atomic emission detection. Flow dilution of the primary standard to pptv levels was used to calibrate the secondary, whole air standard.

[12] We note that the sampling and analytical procedures used here do not measure multifunctional nitrate compounds; also tertiary nitrates are not detected with these procedures.

[13] In addition to our measurements [Simpson et al., 2001], DMS measurements were also made in flight by isotopic dilution gas chromatography/mass spectrometry [Bandy et al., 1993]. The detection limit for these DMS measurements was 1 pptv for PEM-Tropics A. All PEM-Tropics A and B measurements and merged data files are archived at NASA Langley Research Center and can be accessed via the GTE web site at http://www-gte.larc.nasa.gov or ftp://ftp-gte.larc.nasa.gov/pub/.

3. Results and Discussion

[14] The PEM-Tropics B field campaign was conducted from March to April 1999, with major deployment sites in Hawaii, Kiritimati (Christmas Island), Tahiti, and Fiji [Raper et al., 2001]. The PEM-Tropics A field campaign is described by Hoell et al. [1999]. For both experiments, whole air samples were collected aboard the NASA Ames/Dryden DC-8 and the NASA Wallops P-3B research aircraft. Sample locations used in this analysis are displayed in Figure 1.

3.1. Latitudinal Distributions

[15] At low altitudes (0–2 km), MeONO₂ displays its highest mean mixing ratios (greater than approximately 15 pptv) along an equatorial band that stretches across the Pacific (Figure 2). This band spans a width of latitudes from about 8°N to about 13°S and is confined to an atmospheric mixing height of about 2 km (Figure 3). These data are consistent with the suggested oceanic source for this gas [Walega et al., 1992; Atlas et al., 1993], and with airborne measurements during the ACE-1 Pacific latitudinal profile [Blake et al., 1999a]. Blake et al. [1999a] report similarly high concentrations (up to 50 pptv) of MeONO₂ in the marine boundary layer (MBL) over the equatorial Pacific near Christmas Island (1–3°N). A strong oceanic source may also contribute to the higher mixing ratios of methyl nitrate in the free troposphere of the South Pacific compared to the North Pacific background. The southern hemisphere is dominated by ocean surface and marine emissions may contribute to the larger atmospheric background of methyl nitrate. For example, above 2 km, mean methyl nitrate mixing ratios are typically between 5–8 pptv at southern latitudes (10°S) but are only 3–4 pptv at latitudes 10°N (Table 1).

[16] The lowest mean MeONO₂ levels (<6 pptv) are observed to the north of the equatorial enhancements, with slightly higher levels (up to 12 pptv) to the south (Figure 2). The highest ethyl nitrate (EtONO₂) levels are found in the same equatorial band as for MeONO₂. However, EtONO₂ exhibits slightly higher mean mixing ratios to the north than to the south of this band.

[17] The highest 2-propyl nitrate (2-PrONO₂) mixing ratios (to 9 pptv) are located at the most northerly PEM-Tropics B latitudes and up to an altitude of about 5 km (Figures 2 and 3). Elevated 2-PrONO₂ mixing ratios (to 6 pptv) are also observed near the equator (Figures 2 and 3). 2-butylnitrate (2-BuONO₂) also displays its highest levels (to about 10 pptv) in the northern hemisphere (NH), but almost no equatorial or southern hemisphere (SH) enhancement (Figures 2 and 3). Blake et al. [2001] report urban/industrial continental outflow associated with elevated
levels of NMHCs (including the 2-PrONO2 and 2-BuONO2 precursors propane and n-butane) and other anthropogenic indicators at the same northern latitudes and altitudes as the highest 2-PrONO2 and 2-BuONO2 mixing ratios. Levels of all C1-C4 alkyl nitrates measured at latitudes near 20°N are consistent with seasonal distributions of alkyl nitrates at the Mauna Loa Observatory during the MLOPEX experiments [Atlas and Ridley, 1996].

In addition, the mean mixing ratios of 2-PrONO2 and 2-BuONO2 are enhanced close to the coast of Central America (Figure 2). Fresh local biomass burning and urban emissions were noted in this region [Blake et al., 2001]. Therefore, all data from DC-8 Flight 22 and part of DC-8 Flight 21 have been removed from the data subset hereafter referred to as “remote Pacific”.

3.2. Emission Signatures

Figure 4 reveals good correlations over the remote Pacific in the NH (north of 10°N) between EtONO2, 2-PrONO2, and 2-BuONO2 and the industrial tracer C2Cl4, strongly indicating co-located sources for the longer-chain alkyl nitrates and C2Cl4. This alkyl nitrate source is most likely to be in the form of urban/industrial emissions of NMHCs. After methyl nitrate (which has no significant correlation with C2Cl4), ethyl nitrate exhibits the lowest enhancement ratio (0.45 pptv/pptv of C2Cl4) (Figure 4) but has a very good correlation (R² = 0.95), suggesting that a small amount originates from NH urban/industrial emissions of NMHCs and subsequent transformations. In the SH, EtONO2 shows no significant correlation to C2Cl4, supporting the hypothesis that the main equatorial/SH source is oceanic in origin. 2-Butyl nitrate has the highest enhancement (1.1 pptv/pptv of C2Cl4) but a relatively poor correlation (R² = 0.72). This gas is produced from its parent NMHC, n-butane [Roberts et al., 1990, 1998], but 2-BuONO2 has a shorter lifetime than EtONO2 (and a much shorter atmospheric lifetime than C2Cl4), resulting in depleted levels after long-range transport for some samples shown in Figure 4.

By contrast with the longer-chain alkyl nitrates, MeONO2 remained at very low mixing ratios (less than 5 pptv) north of 10°N during PEM-Tropics B, with a mean value of 3.4 pptv (Table 1) and no correlation with C2Cl4 (Figure 4). Other trace gases known to have principally oceanic sources, CH3I (Figure 4) and DMS (not shown), were also not correlated with C2Cl4 north of 10°N. Bromoform had a relatively poor, but significant correlation with C2Cl4 and a low enhancement ratio, suggesting that we encountered air masses with some small component from urban/industrial emissions of CHBr3 north of 10°N (it is used in manufacturing as a cleaning solvent). However, natural sources of bromoform from oceanic emissions in northern latitudes can’t be excluded [e.g., Yokouchi et al., 1997].

Ethyl nitrate is very well correlated with MeONO2 (R² = 0.98) south of 10°N (Figure 5), indicating a tightly linked common (oceanic) source that is 3 times stronger for MeONO2. 2-Propyl nitrate is also well correlated (R² = 0.93), but has a lower enhancement per molecule of mixing ratio (4.5 pptv/pptv of C2Cl4). By contrast with the longer-chain alkyl nitrates, MeONO2 remained at very low mixing ratios (less than 5 pptv) north of 10°N during PEM-Tropics B, with a mean value of 3.4 pptv (Table 1) and no correlation with C2Cl4 (Figure 4). Other trace gases known to have principally oceanic sources, CH3I (Figure 4) and DMS (not shown), were also not correlated with C2Cl4 north of 10°N. Bromoform had a relatively poor, but significant correlation with C2Cl4 and a low enhancement ratio, suggesting that we encountered air masses with some small component from urban/industrial emissions of CHBr3 north of 10°N (it is used in manufacturing as a cleaning solvent). However, natural sources of bromoform from oceanic emissions in northern latitudes can’t be excluded [e.g., Yokouchi et al., 1997].

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2-butyl nitrate is fairly well correlated with MeONO$_2$ ($R^2 = 0.60$), so also seems to have a small ocean source, but only one molecule of 2-BuONO$_2$ is emitted for approximately every 50 of MeONO$_2$ (Figure 5).

Table 2 shows that the equatorial mixed layer alkyl nitrate correlations with MeONO$_2$ are remarkably similar for both PEM-Tropics A and PEM-Tropics B. EtONO$_2$ versus MeONO$_2$ have the most similar slope and the best $R^2$ values. Bromoform has a similar, but somewhat higher correlation ratio versus MeONO$_2$ for PEM-Tropics B compared to A (Table 2). These observations are consistent with previous measurements in the Central Pacific by Atlas et al.

Figure 3. Vertical profiles of the light alkyl nitrates for 3 latitude ranges over the remote Pacific during NASA PEM-Tropics A and PEM-Tropics B.
Table 1. Mixing Ratios (pptv) for Three Altitude and Three Latitude Ranges Over the Remote Pacific

|                | MeONO₂ | EtONO₂ | 2-PrONO₂ | n-PrONO₂ | 2-BuONO₂ | CH₃I | CHBr₃ | DMS | Propane |
|----------------|--------|--------|----------|----------|----------|------|-------|-----|---------|
|                | PTA    | PTB    | PTA      | PTB      | PTA      | PTB  | PTB   | PTB | PTB     |
| latitude > 10°N |        |        |          |          |          |      |       |     |         |
| 8–12.2 km. N = 83, 111 |        |        |          |          |          |      |       |     |         |
| Median          | 2.8    | 3.2    | 1.2      | 1.6      | 0.84     | 0.96 | 0.05  | 0.17| 0.16    |
| Mean            | 4.3    | 4.1    | 1.4      | 1.7      | 0.99     | 1.08 | 0.08  | 0.20| 0.27    |
| SD              | 4.1    | 2.3    | 1.2      | 0.8      | 0.62     | 0.68 | 0.11  | 0.15| 0.40    |
| 2–8 km. N = 234, 418 |        |        |          |          |          |      |       |     |         |
| Median          | 3.2    | 2.9    | 1.0      | 1.8      | 0.61     | 1.26 | 0.07  | 0.26| 0.17    |
| Mean            | 4.0    | 3.1    | 2.1      | 2.1      | 0.76     | 1.85 | 0.09  | 0.36| 0.28    |
| SD              | 2.5    | 1.5    | 0.6      | 0.8      | 0.58     | 1.38 | 0.09  | 0.28| 0.35    |
| 0–2 km. N = 90, 164 |        |        |          |          |          |      |       |     |         |
| Median          | 3.0    | 3.4    | 1.1      | 3.2      | 0.85     | 4.34 | 0.11  | 0.86| 0.25    |
| Mean            | 3.7    | 3.3    | 1.3      | 3.3      | 1.09     | 4.82 | 0.97  | 0.37| 0.49    |
| SD              | 2.0    | 0.5    | 0.7      | 1.1      | 0.69     | 2.60 | 0.17  | 0.53| 0.34    |
| latitude > 10°S |        |        |          |          |          |      |       |     |         |
| 8–12 km. N = 81, 113 |        |        |          |          |          |      |       |     |         |
| Median          | 8.8    | 10.2   | 1.8      | 2.9      | 0.47     | 0.72 | 0.03  | 0.12| 0.08    |
| Mean            | 10.1   | 9.9    | 2.3      | 2.8      | 0.61     | 0.77 | 0.06  | 0.13| 0.09    |
| SD              | 4.3    | 3.3    | 1.8      | 0.9      | 0.39     | 0.28 | 0.07  | 0.05| 0.08    |
| 2–8 km. N = 253, 531 |        |        |          |          |          |      |       |     |         |
| Median          | 8.4    | 9.6    | 1.8      | 2.8      | 0.72     | 0.93 | 0.07  | 0.17| 0.12    |
| Mean            | 9.5    | 11.2   | 2.1      | 3.3      | 0.80     | 1.03 | 0.10  | 0.18| 0.16    |
| SD              | 4.0    | 5.0    | 1.2      | 1.5      | 0.42     | 0.51 | 0.11  | 0.09| 0.13    |
| 0–2 km. N = 258, 554 |        |        |          |          |          |      |       |     |         |
| Median          | 35.1   | 26.0   | 11.5     | 8.8      | 3.42     | 3.19 | 0.51  | 0.57| 0.56    |
| Mean            | 33.5   | 28.3   | 12.0     | 9.4      | 3.16     | 3.21 | 0.51  | 0.56| 0.60    |
| SD              | 11.3   | 11.3   | 5.5      | 3.8      | 1.19     | 1.20 | 0.28  | 0.23| 0.37    |
| latitude > 10°S |        |        |          |          |          |      |       |     |         |
| 8–12 km. N = 454, 497 |        |        |          |          |          |      |       |     |         |
| Median          | 4.3    | 7.6    | 0.9      | 1.7      | 0.35     | 0.34 | 0.02  | 0.05| 0.04    |
| Mean            | 4.9    | 8.1    | 1.0      | 1.9      | 0.42     | 0.45 | 0.02  | 0.06| 0.08    |
| SD              | 2.6    | 4.0    | 0.6      | 1.2      | 0.37     | 0.39 | 0.03  | 0.06| 0.16    |
| 2–8 km. N = 1366, 840 |        |        |          |          |          |      |       |     |         |
| Median          | 4.6    | 5.8    | 1.1      | 1.4      | 0.54     | 0.35 | 0.05  | 0.06| 0.08    |
| Mean            | 5.2    | 6.6    | 1.3      | 1.6      | 0.63     | 0.42 | 0.06  | 0.07| 0.13    |
| SD              | 2.5    | 2.9    | 0.8      | 0.8      | 0.36     | 0.25 | 0.06  | 0.04| 0.16    |
| 0–2 km. N = 378, 445 |        |        |          |          |          |      |       |     |         |
| Median          | 8.3    | 7.3    | 2.4      | 2.1      | 0.77     | 0.60 | 0.12  | 0.11| 0.22    |
| Mean            | 8.8    | 9.2    | 2.7      | 2.7      | 0.85     | 0.78 | 0.14  | 0.14| 0.28    |
| SD              | 2.6    | 5.1    | 1.2      | 1.8      | 0.36     | 0.61 | 0.08  | 0.10| 0.22    |

*Comparison of PEM-Tropics A (PTA) with PEM-Tropics B (PTB). N, no of UCI whole air samples collected during PTA and PTB, respectively. Asterisk indicates Drexel in-situ DMS data merged to whole air sample time base.

[1993], who found that the equatorial maxima of EtONO₂ and 2-PrONO₂ were related to maxima in brominated hydrocarbons, as well as chlorophyll and nitrate (which are oceanographic indicators of enhanced marine productivity and upwelling).

[24] Although remote MBL alkyl nitrate mixing ratios are well correlated with each other and with CHBr₃, suggesting a common oceanic emission mechanism, CH₃I and DMS are not closely correlated with MeONO₂ (Table 2 and Figure 5). This wide spatial variability in mixing ratios of ocean source gases is illustrated by the vertical profiles of MeONO₂, CHBr₃, DMS, and CH₃I from a single DC-8 flight (Flight 12 from Fiji and back) on March 25 1999 (Figure 6). As in Figure 5, MeONO₂ and CHBr₃ show similar relative distributions. Even then, the far south profile in Figure 6 (at 18°S) is greatly enhanced in CHBr₃ for the lowest altitude sample compared to MeONO₂. (See also oceanic emission fluxes calculated by S. Onley (manuscript in preparation, 2002). Close correlation of tracers from ocean sources depends on common oceanic production mechanisms, saturation state, and specific source distributions. For example, while MeONO₂ has a maximum over the equator, CH₃I tends to show boundary layer maxima at latitudes both north and south of the equator. Similarly, DMS production depends on emissions of precursors from certain plankton species that may not be related to the same processes that contribute to emissions of alkyl nitrates.

[25] For compounds with a common surface source, vertical profiles of different gases should reflect something about their respective chemical lifetimes. It follows that a measure of the relative lifetimes might be a comparison of BL to FT concentrations. MeONO₂ and CHBr₃ have lifetimes on the order of 15–30 days (nominally), but CH₃I is much shorter (2–4 days), and DMS has a lifetime of only a few hours. Indeed, the black profile at 5°S on Figure 6 illustrates this lifetime dependence, with the presence of marine cumulus providing shallow convection up to 1.5 km, then mixing ratios falling in the order MeONO₂ & CHBr₃, CH₃I, DMS. However, the blue profile at 5°S (Figure 6) shows that BL/FT ratios for CH₃I, MeONO₂, and CHBr₃ are all fairly similar, except for DMS. Table 1
also reveals similar ratios for averaged equatorial data in the <2 km bin compared to 2–8 km for CH₃I, MeONO₂, and CHBr₃, but higher values for DMS. The difference between these two 5°C profiles is that the blue profile was influenced by recent convection up to at least 6 km, as evidenced by the DMS enhancements visible to this altitude. Figure 7 reveals that a high incidence of rainfall, corresponding to a southern branch of the ITCZ, was observed near 5°C–10°C during PEM-Tropics B, illustrating the important role played by convection in this region of the atmosphere. Comparison of the profiles and lifetimes may be able to highlight convective outflow and indicate the speed of ascent and merits future investigation, including studying the role of horizontal transport, which may also play a significant role.

3.3. Ocean-Atmosphere Flux of N

[26] Another potentially interesting aspect of the emission of alkyl nitrates from the surface ocean is that it results in a local loss of some nutrient N from the ocean to the atmosphere. Oxidation will presumably return the N to the sea surface, but at some location distant from the source.

[27] If we assume steady state loss of C₁-C₄ alkyl nitrates then:

\[
\text{Average mixing ratio} \times \text{BL height} \times \text{loss rate} = \frac{\text{Amount lost}}{\text{area} \times \text{day}}
\]

From this we estimate a contribution to the lower 2 km of the equatorial Pacific of ≈2.43 μg N/m²/day (≈0.89 mg N/m²/yr) based on PEM-Tropics B mixing ratios (Table 1) and calculated lifetimes with respect to photolysis and reaction with OH and Cl radicals. Typical wet deposition of NO₃ is in the range of 8–43 mg N/m²/yr [Group of Experts on the Scientific Aspects of Marine Pollution (GESAMP), 1989] and comparable sedimentation loss of N from the euphotic zone is on the order of total N inputs. Thus, this atmospheric loss is small relative to sources of NO₃ to the ocean (for example from rainwater). Our calculated atmospheric NO contribution from photochemical aging of alkyl nitrates is almost double the 0.52 mg N/m²/yr estimated for the central equatorial Pacific for the NO flux attributed to solar photolysis of nitrite ion [Zafirou and McFarland, 1981]. Schultz et al. [1999] reported that the long range transport of...
PAN (from southern hemisphere biomass burning) and its subsequent thermal decomposition at low altitudes was the dominant source of NOx to the remote atmosphere over the equatorial South Pacific during PEM-Tropics A. Below 2 km, Schultz et al. estimated methyl nitrate photolysis to contribute only about 6% to NOx production, with loss of HNO3 (by photolysis and OH reaction) contributing about 10%. However, it has recently been suggested that the mixing ratios of PAN that were encountered during both PEM-Tropics A and B were so frequently below instrument detection limits as to skew any calculations performed employing only the above LOD subset of data in favor of overestimating the role played by PAN in the remote marine boundary layer NOx budget [Olson et al., 2001].

3.4. Comparison of PEM-Tropics A and B

During PEM-Tropics B the ITCZ in the Pacific Basin was not well defined. As can be seen from Figure 7, two zonal bands of convection were usually observed, one on either side of the equator at 5°–10°N and 5°–10°S [Fuelberg et al., 2001; Hu et al., 2001; Avery et al., 2001]. This is typical for March–April [Hu et al., 2001]. Convective activity during this period appeared to alternate between these branches of the ITCZ in the NH and the SH [Hu et al.,

Table 2. Correlation Slopes and R² Values for C1-C4 Alkyl Nitrates and CHBr3 Versus MeONO2 During PEM-Tropics A (PTA) and PEM-Tropics B (PTB) for Samples Collected South of 10°N and Below 2 km Over the Remote Pacific

|           | EtONO2 | 2-PrONO2 | n-PrONO2 | 2-BuONO2 | CHBr3 |
|-----------|--------|----------|----------|----------|-------|
| PTA       | 0.39   | 0.34     | 0.09     | 0.016    | 0.015 |
| PTB       | 0.11   | 0.020    | 0.015    | 0.018    | 0.031 |
| PTA       | 0.94   | 0.98     | 0.93     | 0.74     | 0.39  |
| PTB       | 0.93   | 0.60     | 0.70     | 0.80     | 0.054 |

Figure 5. Correlation plots of light alkyl nitrates, CHBr3, CH3I, and DMS with MeONO2 at altitudes <2 km over the remote Pacific during NASA PEM-Tropics B.
March average rainfall rates were higher for the southern branch than those for April (Figure 7). By contrast, tropical rainfall associated with the ITCZ was confined to a more idealized single solid band at 5°–10°N during PEM-Tropics A (Figure 7). As a result of the better-defined ITCZ during PEM-Tropics A, deep convection associated with that convergence was much stronger and persistent than Tropics B [Fuelberg et al., 2001].

Despite the different convective conditions, remarkably similar levels of MeONO2 were observed during both PEM-Tropics A and B for all latitude and altitude ranges (Figures 3 and 8 and Table 1). At equatorial latitudes, median PEM-Tropics A and B levels were also comparable for all the measured alkyl nitrates and CH3I, CHBr3, DMS, and propane (Table 1 and Figure 3). The equatorial enhancements of MeONO2 were greatest at low altitude (<2 km) but persisted to the highest sampling altitudes as the result of fast equatorial convection associated with the ITCZ (Figures 7 and 8), suggesting that MeONO2 is a useful marker for high altitude air masses of marine equatorial origin. Even though the maximum ITCZ convection is not co-located with the maximum equatorial marine boundary layer mixing ratios, Figure 8 shows that equatorial marine boundary layer air enhanced with MeONO2 is frequently entrained into ITCZ convection (consistent with Hu et al. [2001]). The active southern branch of the ITCZ (Figure 7) appears to have contributed to the slightly higher mixing ratios of MeONO2 observed in the upper troposphere south of the equator during PEM-Tropics B compared to PEM-Tropics A (Figure 8). In fact, MeONO2 is quite consistently enhanced above background levels up to the DC-8 flight ceiling altitude of 12 km in the free troposphere near the equator, especially for PEM-Tropics B.

Using CH3I as a marine tracer (which also exhibits enhanced free tropospheric mixing ratios), Wang et al. [2001] suggest that the observed vertical distribution implies stronger outflow in the middle troposphere than predicted using current general circulation models. In a further study designed to improve such regional and global model parameterizations, Pickering et al. [2001] describe a cloud-resolved model simulation of a strong tropical marine SPCZ (South Pacific Convergence Zone) convection event that was sampled near 17°S during PEM-Tropics B. They employ measured CH3I, CO and O3 as tracers for upward...
transport of marine boundary layer air. According to this simulation, the cloud reached a height of about 16 km, with an overshooting top to nearly 18 km. Elevated CH$_3$I mixing ratios were predicted up to about 16 km, with maximum values near 12 km that agreed quite well with observations. MeONO$_2$ was not enhanced at altitude during this event because the convection inflow occurred in an area where its boundary layer concentration was relatively low. However, employing MeONO$_2$ for this type of analysis of deep ITCZ convection may help to improve cloud parameterizations as well as understanding of stratosphere-troposphere exchange. Measurements of MeONO$_2$ would be a useful addition to CH$_3$I as a diagnostic of ITCZ convection. Sampling at altitudes above 12 km is needed to confirm whether mixing ratios of such gases increase above 12 km in ITCZ outflow, which reaches altitudes of approximately 14–18 km.

[30] North of about 10°N MeONO$_2$ levels are very low for both PEM-Tropics A and B (Figure 8), suggesting that MeONO$_2$ had no significant NH continental sources during either PEM-Tropics measurement period. Another large section in Figure 8 that exhibited very low MeONO$_2$ mixing ratios is in the southern tropical mid-upper troposphere (above about 4 km) during PEM-Tropics A. PEM-Tropics A was flown at a time when this region of the atmosphere was strongly influenced by aged biomass burning plumes [Blake et al., 1999b], so the fact that MeONO$_2$ levels are so low suggests that the transport of MeONO$_2$ from biomass burning is minimal. Median mixing ratios of both 2-PrONO$_2$ and 2-BuONO$_2$ were very low (<1 pptv) in the SH during both PEM-Tropics A and B (Table 1), but Figure 3 shows that peak PEM-Tropics A values were somewhat higher than for PEM-Tropics B. These small PEM-Tropics A enhancements could result from the influence of biomass burning. By contrast, the PEM-Tropics B field campaign took place in the southern-tropical wet season, when the influence from biomass burning was minimal.

[31] PEM-Tropics A reached much further south during flights that were based out of New Zealand (Figure 1). These most southerly data reveal slightly elevated levels of MeONO$_2$ at low and mid-altitudes (Figure 8). These observations are consistent with the enhanced MeONO$_2$ concentrations (up to 30 pptv) observed previously over polar waters south of Tasmania during December 1995 [Blake et al., 1999a]. They are also consistent with high MeONO$_2$ and EtONO$_2$ seen on the coast of Antarctica by Jones et al. [1999].

[32] Both equatorial Pacific and southern polar waters are regions characterized by upwelling of high nutrient waters. However, only some of the nutrients transported to the surface by upwelling are taken up by photosynthesis, allowing chlorophyll levels to remain relatively low, so are known as high-nutrient, low-chlorophyll (HNLC) eco-
systems. These nutrients persist in the surface layer because the production of phytoplankton is known to be limited by the supply of the trace nutrient iron [Cullen, 1991; Landry et al., 1997; Coale et al., 1996]. Fe concentrations tend to be highest in waters close to continental landmasses, which are comparatively rich in Fe, and from Fe-enriched atmospheric dust. Atmospheric dust deposition in the two major HNLC areas, the equatorial Pacific and Antarctic oceans, are the lowest in the world [Prospero, 1981; Uematsu, 1987].

It appears that in these HNLC waters, a lack of Fe availability selects a flora dominated by small cells which efficiently recycle nitrogen as NH₃ and strongly constrain the annual utilization of NO₃, leaving the system persistently rich in major nutrients [Miller et al., 1991]. We suggest that a portion of this excess NO₃ (or perhaps nitrite) may be transformed (either photochemically, or biogenically by biota which are specially adapted to these specific conditions) into alkyl nitrates or their precursors. The link between HNLC waters, which can be independently defined by satellite measurements of chlorophyll and by routine measurements of oceanic nitrate, and alkyl nitrates may facilitate calculations to better estimate the large-scale influence of alkyl nitrates on the atmospheric chemistry of these remote ocean regions.

[31] In the springtime NH troposphere sampled during PEM-Tropics B, mixing ratios of C₂-C₄ alkyl nitrates were very much higher (3-12-fold) at low-mid altitudes compared to summertime PEM-Tropics A (Table 1). This alkyl nitrate increase is consistent with the seasonal increase for their NMHC precursors reported by Blake et al. [2001] and with the seasonal data from Mauna Loa [Atlas and Ridley, 1996]. E.g., the 2-PrONO₂ precursor, propane, exhibits a 10-fold increase (see also Table 1). NMHCs build up at high latitudes during the winter months when sunlight, and therefore OH, are minimized. In springtime, strong easterly continental outflow transports these and other continental pollutants long distances across the North Pacific [Blake et al., 1997, 2001]. Previous observations of alkyl nitrates at high latitudes support a winter build-up of alkyl nitrates along with NMHCs [Beine et al., 1996; Swanson et al., 2002].

[34] Low mixing ratios of n-PrONO₂ compared with 2-PrONO₂ in Table 1 reflect its lower chemical formation yield [Atkinson et al., 1982]. The fact that the low altitude 2-PrONO₂:n-PrONO₂ ratios remain close to 6:1 for all 3 latitude bands in Table 1 indicate a similar (photochemical) formation mode for both the equatorial oceanic source and the Northern Hemisphere industrial source.
4. Conclusions

[35] The spatial distributions of light alkyl nitrates are remarkably similar for both the September–October 1996 PEM-Tropics A and March–April 1999 PEM-Tropics B. The consistently high equatorial mixing ratios observed provide the strongest evidence yet to establish the ocean as the major source for MeONO2. Further, these results support the suggestion that CH2I, CHBr3, and DMS emissions are not necessarily coupled to the emission of biogenically produced C1-C3 alkyl nitrates. We suggest a link between our equatorial findings and the enhanced MeONO2 concentrations observed previously over the other major area of high nutrient-low chlorophyll waters, the Southern Ocean around Antarctica. Integrating these observations with HNLC regions, as defined by satellite measurements of chlorophyll and oceanic nitrate analysis, may assist calculations that better assess the large-scale influence of ocean-source alkyl nitrates on the remote atmosphere.

[36] Ethyl nitrate has a dominant oceanic source in equatorial regions, but at mid NH latitudes a small additional source is associated with urban/industrial emissions. The low altitude distribution of 2-PrONO2 appears to be almost equally influenced by equatorial oceanic and by anthropogenic NH emissions. Similar equatorial MBL mixing ratios were observed for both PEM-Tropics A and B, so no seasonal factors (which are minimal at the equator) were apparent. These stable oceanic emission factors may make a useful diagnostic for air masses that have recently been at low altitude over the equatorial Pacific Ocean, compared to the much lower EtONO2:MeONO2 ratios typically observed in air masses which have been influenced by urban/industrial emissions. The high 2-PrONO2:MeONO2 and 2-ButOONO2:MeONO2 ratios for the corresponding anthropogenic-influenced NH air masses also provide a useful air mass characterization signature.

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