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Saturation anomalies of alkyl nitrates in the tropical Pacific Ocean

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[1] This paper reports the first measurements of the saturation state of low molecular weight alkyl nitrates (methyl, ethyl, isopropyl, and n-propyl nitrate) in the tropical Pacific Ocean. These compounds were supersaturated with saturation anomalies as high as 2000%. Air/sea flux estimates based on these measurements suggest that surface ocean emissions are sufficient to account for observed levels of tropospheric alkyl nitrates in this region. Model calculations suggest that atmospheric loss rates are faster than can be explained by photolysis and reaction with OH alone. The implication is that removal via transport is important, and there must be a net export of alkyl nitrates from the tropics to other regions of the atmosphere.

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1. Introduction

[2] Alkyl nitrates can account for a substantial portion of the tropospheric reactive nitrogen pool [Atlas, 1988; Day *et al.*, 2003; Jones *et al.*, 1999; Talbot *et al.*, 2000], and play a role in the cycling of ozone in the troposphere. Tropospheric levels of alkyl nitrates over the tropical Pacific Ocean cannot be accounted for by gas phase photochemistry, and indicate that the oceans in this region are a likely source of low-molecular weight alkyl nitrates to the troposphere [i.e., Blake *et al.*, 2003; Atlas *et al.*, 1993; Thompson *et al.*, 1993]. In the Atlantic Ocean, methyl and ethyl nitrate saturation anomalies up to 800% have been reported [Chuck *et al.*, 2002] confirming that the sea to air flux is a major contributor to the atmospheric levels of these compounds. This study presents measurements of methyl, ethyl, isopropyl, and n-propyl nitrate saturation anomalies in the tropical Pacific Ocean. This study was carried out as part of the Pacific Halocarbon Air-Sea Exchange cruise (PHASE-1) aboard the R/V *Wecoma* during May–July, 2004. The cruise track is shown in Figure 1.

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2. Experimental

[3] The air inlet was a ~80 m length of Dekabon tubing running from the bow jackstaff to the ship's laboratory. Air was continuously pumped through this line at ~8 L min⁻¹. An acrylic Weiss-type equilibrator was used, with seawater obtained from the ship's flow-through pumping system. The equilibrator showers seawater through a headspace containing continuously recirculating air [Butler *et al.*, 1988; Johnson, 1999]. An automated gas chromatograph/mass spectrometer (GC/MS) instrument analyzed samples of air and seawater-equilibrated air roughly every three hours.

[4] The GC/MS system described by Yvon-Lewis *et al.* [2004] was used in this study with the following modifications. A Nafion membrane dryer was used instead of magnesium perchlorate, and the system was programmed to sequence through three discrete seawater samples, ambient air, seawater-equilibrated air, and a gas standard. Analysis of each sample took 40 minutes. The system was calibrated for alkyl nitrates using a 6-liter electropolished steel flask filled with air from Key Biscayne, FL. The mixing ratio of alkyl nitrates in the flask was determined using the system described by Dahl *et al.* [2003] using a calibration curve generated by serial dilutions of pure alkyl nitrates.

[5] Sea surface saturation state is expressed as saturation anomaly, i.e. the departure from equilibrium, as follows:

$$\text{Saturation Anomaly(\%)} = \frac{\rho_{\text{sw}} - \rho_{\text{air}}}{\rho_{\text{air}}} * 100\%$$

where ρ_{sw} and ρ_{air} are the partial pressures of the alkyl nitrate in seawater (temperature corrected from the equilibrator headspace) and air, respectively. A saturation anomaly of zero indicates equilibrium, and positive saturation anomalies represent fluxes from sea to air. Simultaneous measurements of CFC-11 saturation anomalies demonstrate that recent heating/cooling effects did not exert a significant effect on the alkyl nitrate saturation state.

3. Results

3.1. Saturation Anomaly Measurements

[6] The observed air and seawater levels of methyl, ethyl, isopropyl, and n-propyl nitrates are shown in Figure 2. Alkyl nitrate levels were low in the western Pacific warm pool waters (west of 170E), but increased markedly as the ship crossed 2.5°N and entered the equatorial upwelling

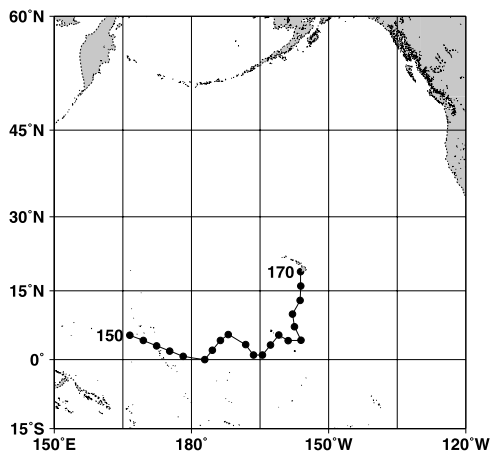


Figure 1. Cruise track of the portion of the R/V *Wecoma* PHASE-1 cruise where saturation anomalies of alkyl nitrates were determined. The black dots represent midnight GMT starting on May 29, 2004 (JD 150) and ending on June 18, 2004 (JD 170).

area. Seawater alkyl nitrate levels remained high throughout the tropics, then dropped again as the ship traveled north along 165°W into North Pacific gyre waters. There is clearly a large-scale relationship between seawater alkyl nitrate levels and chlorophyll, in the sense that both are high in the equatorial upwelling waters, and both are low outside of the equatorial waters. The smaller scale variability of alkyl nitrates within the equatorial high chlorophyll region, was not systematically related to temperature, time of day, or chlorophyll.

[7] The alkyl nitrate saturation anomalies were near zero entering and leaving the tropics. In the equatorial region, the alkyl nitrates were supersaturated by several fold, with saturation anomalies up to several hundred in the case of

methyl and ethyl nitrate, and over 1000 in the case of the propyl nitrates. The saturation anomalies tracked the levels of alkyl nitrates in the water, with the highest saturation anomalies found in the same areas as the highest water levels. The maxima in saturation anomalies for all the alkyl nitrates were found in the region bounded by 0–5°N, 170E–173°W. The high saturation anomalies observed in the tropics indicate that the air/sea flux of alkyl nitrates is controlled primarily by the water side concentration.

[8] The relative abundances of the alkyl nitrates measured in seawater were roughly constant throughout this study region, with ratios of methyl:ethyl:isopropyl:n-propyl nitrates of approximately 3.1:1.0:0.4:0.2. This methyl:ethyl nitrate ratio is slightly higher than the 2.4:1.0 ratio observed in Atlantic equatorial seawater by *Chuck et al.* [2002]. In the tropical Pacific atmosphere, the observed alkyl nitrate ratios were 4.3:1.0:0.2:0.4. This is similar to the ratio observed by *Blake et al.* [2003] of 2.8:1.0:0.3:0.1 during PEM Tropics B between 0–2 km altitude over the equatorial Pacific with the exception of n-propyl nitrate. The reason for the difference in the n-propyl nitrate between the *Blake et al.* [2003] study and this work is not clear.

[9] An increase in atmospheric methyl:ethyl nitrate relative to that in the underlying seawater is expected, given that methyl nitrate has a longer atmospheric lifetime than ethyl nitrate. However, the ratio of the lifetimes of methyl:ethyl:isopropyl nitrate in the tropics due to reaction with OH and photolysis is estimated to be 2.1:1.0:0.6 for methyl, ethyl and isopropyl nitrate respectively [*Talukdar et al.*, 1997b], suggesting that at steady state, the atmospheric ratio of methyl:ethyl:isopropyl nitrate based on the ocean source should be even higher, around 6.5:1.0:0.2.

3.2. Model Calculations

[10] A simple steady-state 2-box model was used to examine the relationship between the oceanic and atmospheric alkyl nitrates (Figure 3). The solubility of ethyl

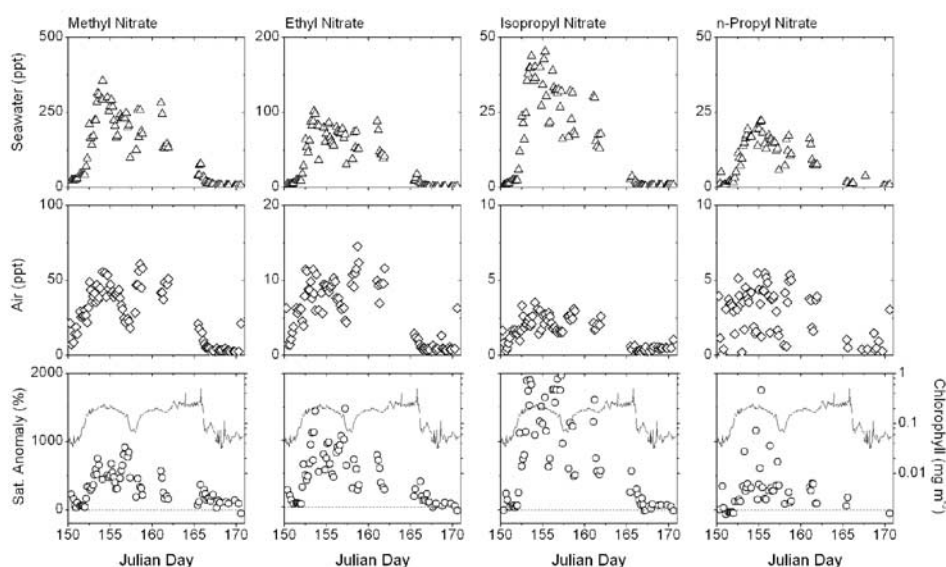


Figure 2. (top) Alkyl nitrates in surface seawater. (middle) Alkyl nitrates in air. (bottom) Saturation anomalies (open circles) plotted with chlorophyll concentration (solid lines) extracted from the June monthly MODIS chlorophyll image. Note that the axis scaling for the air and water mixing ratios varies between methyl, ethyl, and propyl nitrates.

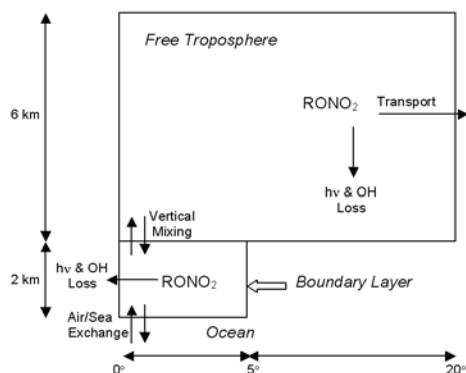


Figure 3. Schematic of the 2-box model used to assess the impact of observed levels of oceanic alkyl nitrates on the troposphere.

nitrate in pure water at 25°C is 1.6 M/atm (for comparison, $H_{\text{DMS}} \approx 0.5$ M/atm [De Bruyn *et al.*, 1995]) [Kames and Schurath, 1992]. The flux of alkyl nitrates to the troposphere is controlled by the water-side resistance. This model simulates the high alkyl nitrate equatorial region, with one box representing the tropical boundary layer (0–5°N) and the other representing the free troposphere from 0–20°N. The budgets of alkyl nitrates in the two boxes are defined as follows:

$$\left(\frac{d\text{RONO}_2}{dt}\right)_{\text{BL}} = P_{\text{air-sea}} - L_{\text{vert}} - L_{\text{phot}} - L_{\text{OH}}$$

$$\left(\frac{d\text{RONO}_2}{dt}\right)_{\text{FT}} = P_{\text{vert}} - P_{\text{vert}} - L_{\text{phot}} - L_{\text{OH}} - L_{\text{horiz}}$$

where the various terms represent the net fluxes due to air/sea exchange, vertical exchange between the boundary layer

Table 1. Various Parameter Values Used in the Boundary Layer (BL) and Free Tropospheric (FT) for Steady State Box Model Simulations

Rate Constant	BL	FT
$k_{\text{mix}}, \text{cm s}^{-1}$	Case 1 1	1
$k_{\text{mix}}, \text{cm s}^{-1}$	Case 2 2	2
$k_{\text{mix}}, \text{cm s}^{-1}$	Case 3 4	4
$k_{\text{trans}}, \text{s}^{-1}$	-	1×10^{-7}
Z, km	2	6
$[\text{OH}], \text{mol cm}^{-3\text{a}}$	1×10^6	2×10^6
$k_{\text{OH}}, \text{cm}^3 \text{mol}^{-1} \text{s}^{-1\text{b}}$	2.4×10^{-13}	2.4×10^{-13}
$k_{\text{hv}}, \text{s}^{-1\text{c}}$	3.2×10^{-7}	4.1×10^{-7}
$k_{\text{OH}}, \text{m}^3 \text{mol}^{-1} \text{s}^{-1\text{b}}$	1.8×10^{-13}	1.8×10^{-13}
$k_{\text{hv}}, \text{s}^{-1\text{c}}$	6.4×10^{-7}	7.2×10^{-7}
$k_{\text{OH}}, \text{cm}^3 \text{mol}^{-1} \text{s}^{-1\text{b}}$	3.6×10^{-13}	3.6×10^{-13}
$k_{\text{hv}}, \text{s}^{-1\text{c}}$	9.5×10^{-7}	1.0×10^{-6}

^aFrom Spivakovsky *et al.* [2000].

^bFrom Talukdar *et al.* [1997a].

^cPhotolysis rates at 30°N from Talukdar *et al.* [1997b].

and free troposphere, atmospheric losses due to reaction with OH and photolysis, and horizontal transport. The air/sea flux is parameterized as

$$P_{\text{air-sea}} = \frac{k_{\text{airsea}}}{Z} * (C_{\text{W}} - C_{\text{BL}} * H)$$

where C_{W} and C_{BL} are alkyl nitrate concentrations in surface seawater (mol m^{-3}) and air (atm), k_{airsea} is the gas exchange coefficient (m d^{-1}). H is the temperature dependent Henry's Law coefficient (M/atm) [Kames and Schurath, 1992] using a salt out coefficient of 0.75, and Z is the height of the atmospheric boundary layer (m). The concentrations of alkyl nitrates in seawater used in the model are presented in Figure 2. The concentrations were converted from ppt to moles m^{-3} and atm for calculation purposes.

[11] The gas exchange coefficient (k_{airsea}) for each alkyl nitrate was estimated using the quadratic wind-speed dependent parameterization of Wanninkhof [1992] for CO_2 , scaled by Schmidt number, (using $S_{\text{c}}^{-1/2}$). Schmidt numbers were estimated relative to that of CO_2 using the relationship $S_1/S_2 = (V_1/V_2)^{0.6}$ where V is molar volume determined using the Le Bas method [Wilke and Chang, 1955; Reid *et al.*, 1987]. The loss of alkyl nitrates in the boundary layer was due to photolysis (k_{hv}), reaction with OH (k_{OH}), and mixing with the free troposphere (k_{mix}). Lifetimes of methyl, ethyl, and isopropyl nitrate with respect to photolysis and OH under these conditions are ~ 29 , 14, and 8.5 days, respectively [Talukdar *et al.*, 1997b]. Calculations for n-propyl nitrate were not carried out because OH and photolysis rate constants were not available.

[12] Steady state solutions were obtained for the model equations using the cruise measurements from latitudes 0–5°N as input, and the parameters given in Table 1. Three cases were run for each point, assuming a range of vertical exchange rates. These vertical exchange rates correspond to boundary layer lifetimes for the alkyl nitrates of 2.3, 1.2, and 0.6.

[13] Steady-state boundary layer mixing ratios of methyl nitrate are plotted with observed atmospheric mixing ratios in Figure 4. Reasonable agreement between measured and calculated boundary layer alkyl nitrate levels was obtained

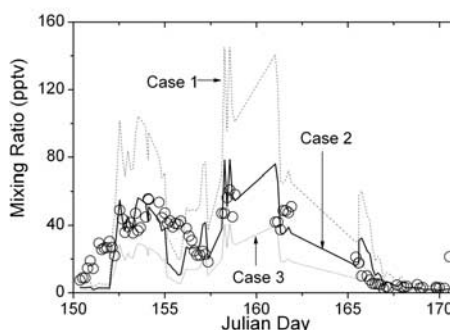


Figure 4. Model calculations of the atmospheric boundary layer mixing ratios plotted with the observed mixing ratios (open circles) of methyl nitrate in air determined during the study. The model mixing ratios were calculated for vertical mixing rates of 1 (case 1), 2 (case 2), and 4 (case 3) cm s^{-1} .

using a vertical mixing rate of 2 cm s^{-1} (Case 2). Cases 1 (1 cm/s) and 3 (4 cm/s) significantly over and underestimated the observed levels, respectively. Similar results were obtained for ethyl and isopropyl nitrate. All the model cases underestimated the boundary layer observations for the low saturation anomaly conditions in the western Pacific warm pool (JD 150–152).

[14] The model results suggest that in the tropical Pacific, the oceanic source of alkyl nitrates is sufficient to account for the observed levels of these gases in the marine boundary layer. The agreement between observations and model requires a loss mechanism for the alkyl nitrates that is considerably faster than photolysis and oxidation by OH. Without rapid removal, into the free troposphere, the concentration of alkyl nitrates in the boundary would be considerably higher, the atmosphere would approach saturation with respect to the surface ocean, and the sea to air flux would decrease. A lifetime of about 1–2 days is needed to maintain the observed saturation state. In the tropical boundary layer, this additional loss is probably due primarily to vertical mixing into the free troposphere. The same line of reasoning implies that there is significant export of alkyl nitrates from the tropical boundary layer to other regions of the atmosphere.

4. Conclusions

[15] The surface waters of the equatorial Pacific Ocean are highly supersaturated in low molecular weight alkyl nitrates making this region a strong source to the atmosphere. This source is sufficient to account for observations of alkyl nitrates over the Pacific Ocean in this study and previous studies [i.e., Blake *et al.*, 2003; Atlas *et al.*, 1993]. These compounds are relatively long lived in the atmosphere, and transport away from the source region is an important control on the atmospheric levels and on the air/sea concentration gradient. A 3D chemical transport model is needed to more fully investigate the pathways for transport of alkyl nitrates away from this region, and their impact of oceanic alkyl nitrates on the NO_x and ozone chemistry of the atmosphere.

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