



Alkyl nitrate (C₁-C₃) depth profiles in the tropical Pacific Ocean

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[1] This paper reports the first depth profile measurements of methyl, ethyl, isopropyl and n-propyl nitrates in the tropical Pacific Ocean. Depth profile measurements were made at 22 stations during the Project Halocarbon Air Sea Exchange cruise, in warm pool, equatorial, subequatorial, and gyre waters. The highest concentrations, up to several hundred pM of methyl nitrate, were observed in the central Pacific within 8 degrees of the equator. In general, alkyl nitrate levels were highest in the surface mixed layer, and decreased with depth below the mixed layer. The spatial distribution of the alkyl nitrates suggests that there is a strong source associated with biologically productive ocean regions, that is characterized by high ratios of methyl:ethyl nitrate. However, the data do not allow discrimination between direct biological emissions and photochemistry as production mechanisms. Alkyl nitrates were consistently detectable at several hundred meters depth. On the basis of the estimated chemical loss rate of these compounds, we conclude that deep water alkyl nitrates must be produced in situ. Possible sources include free radical processes initiated by radioactive decay or cosmic rays, enzymatically mediated reactions involving bacteria, or unidentified chemical mechanisms involving dissolved organic matter.

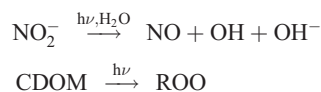
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1. Introduction

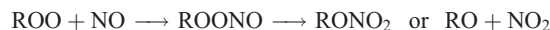
[2] Alkyl nitrates represent a small but significant portion of the tropospheric reactive nitrogen pool [Atlas, 1988; Day *et al.*, 2003; Jones *et al.*, 1999; Talbot *et al.*, 2000], and have an impact on the formation and distribution of tropospheric ozone. Atmospheric alkyl nitrates are normally associated with polluted air, and are formed from the reaction of alkyl peroxy radicals with NO [Darnell *et al.*, 1976].

[3] During the SAGA-3 expedition in the equatorial Pacific, an equatorial maximum in atmospheric ethyl and isopropyl nitrate was observed [Atlas *et al.*, 1992]. This maximum was correlated with bromoform and associated with the pattern of equatorial upwelling [Atlas *et al.*, 1993; Thompson *et al.*, 1993]. Neither long-range transport nor in situ atmospheric production could account for the observed maximum, and it was hypothesized that the oceans are a source of alkyl nitrates [Atlas *et al.*, 1993; Thompson *et al.*, 1993]. More recent studies by Blake *et al.* [1999, 2003] and Dahl *et al.* [2005] have corroborated that the equatorial Pacific Ocean is a source of alkyl nitrates.

[4] Chuck *et al.* [2002] measured depth profiles of methyl and ethyl nitrate along north to south transects in the Atlantic Ocean. They observed concentrations between ~0.1 to 25 pM [Chuck *et al.*, 2002]. Moore and Blough [2002] observed similar levels in the Atlantic Ocean. The ethyl nitrate depth profiles measured by Chuck *et al.* [2002] were similar to those of nitrate and they suggested that nitrate ions could have a role in oceanic ethyl nitrate production. The methyl nitrate depth profiles decreased in concentration below the chlorophyll maximum, suggesting a possible algal source [Chuck *et al.*, 2002]. Dahl *et al.* [2003] observed photochemical production of alkyl nitrates in laboratory experiments. They suggested a photochemical source involving photolysis of nitrite to produce NO [Zafiriou and True, 1979; Zafiriou and MacFarland, 1981] and photolysis of CDOM to produce ROO radicals [Kieber and Blough, 1990; Blough, 1997; Zika, 1987].



These radicals can then react further to produce alkyl nitrates.



The free radical formation of alkyl nitrates in solution was previously observed by Shelton and Kapcaewski [1967] and Padmaja and Huie [1993].

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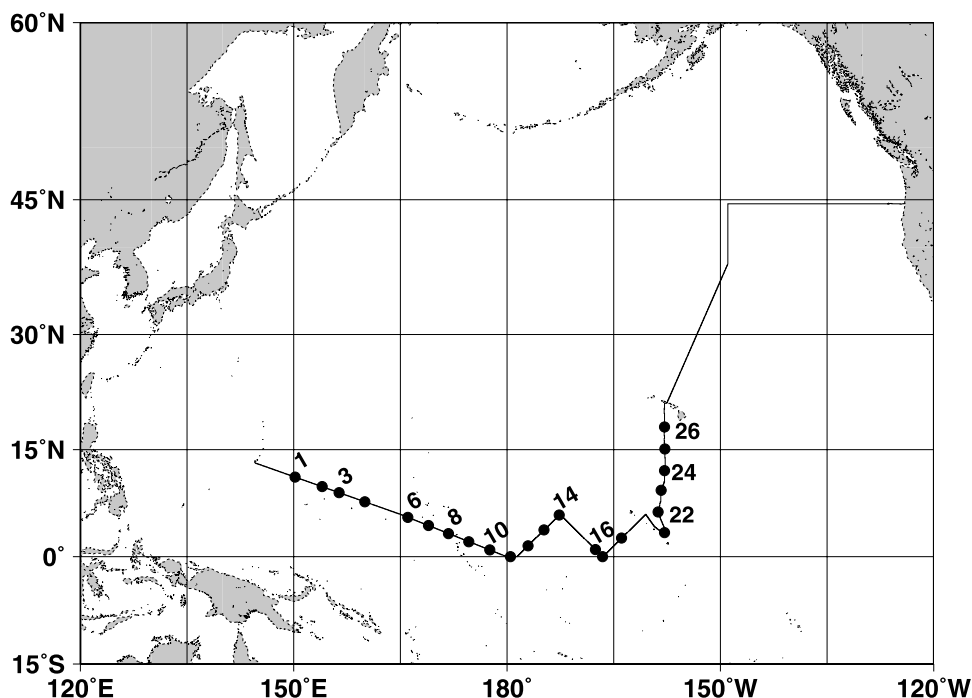


Figure 1. PHASE-1 cruise track. The dots indicate locations of the depth profile stations labeled with the station number.

[5] *Dahl et al.* [2005] recently published measurements of the saturation state of alkyl nitrated in the surface waters of the equatorial Pacific Ocean, from the Project Halocarbon Air Sea Exchange (PHASE-1) cruise. This study presents depth profiles of methyl, ethyl, isopropyl, and n-propyl nitrate from the same cruise. These measurements are the first published alkyl nitrate depth profiles measured in the tropical Pacific Ocean.

2. Experiment

[6] C_1 - C_3 alkyl nitrates were measured in depth profiles during the PHASE-1 study aboard the R/V *Wecoma* from May to June 2004. A map of the cruise track with the depth profile sample locations is shown in Figure 1. Alkyl nitrate measurements were made using seawater samples from 22 hydrocasts during this study. All of the casts were taken in the morning at approximately 6 a.m. local time. Seawater samples at different depths were collected using a rosette with twelve 10-liter Niskin bottles (PVC with Buna-N o-rings). The rosette also contained a Seabird CTD for conductivity, temperature, and depth measurements. Water samples were collected to depths of 750 m for all stations. The seawater samples for alkyl nitrate analysis were collected from the Niskin bottles using 100 ml borosilicate glass syringes fitted with stopcocks. The sample syringes were stored upright with plungers pushing down and refrigerated prior to analysis.

[7] Alkyl nitrates were measured on ~ 70 cc samples, using a purge and trap system with GC/MS detection [*Yvon-Lewis et al.*, 2004]. The purge efficiency of the system for alkyl nitrates was determined by repeatedly sparging several representative seawater samples. The field calibration of this system was based on a calibrated whole

air standard. This was a pressurized 6-liter electropolished steel tank filled with air from Key Biscayne, FL (~ 100 psi, humid air). The mixing ratio of alkyl nitrates in the flask was determined in the laboratory using standards based on the dilution of pure alkyl nitrates, as described by *Dahl et al.* [2003].

3. Results

3.1. Water Types

[8] The alkyl nitrate depth profiles are grouped into four water types, on the basis of the similarity of temperature, salinity, and trace gas depth profiles between stations. Temperature and salinity diagrams for each group of profiles are shown in Figure 2.

[9] Depth profiles taken on the initial southeastward transect of the cruise between 3.3 and 11.2°N (Stations 1–8), are collectively referred to as the Warm Pool profiles. These waters were in an area of high sea-surface temperature (29 – 30°C) and included the North Equatorial Current and North Equatorial Countercurrent. The North Equatorial Current is a westward moving current that forms the southern part of the subtropical gyre in the northern hemisphere. This current is found between 8 – 20°N and moves at 0.1 – 0.3 m/s. The strength and location of eastward flowing North Equatorial countercurrent is determined by the ITCZ [*Glickman*, 2000]. During the summer months, this current is typically found at 5 – 10°N and flows at 0.4 – 0.6 m/s. The depth profiles in this region appear to have sampled Western North Pacific Central water, which is typically found between 150 – 800 m [*Knauss*, 1997; *Glickman*, 2000].

[10] The Equatorial depth profiles were taken between 0 and 2.5°N during the west to east transect (Stations 9–12, 16 and 17). The surface waters in this region were

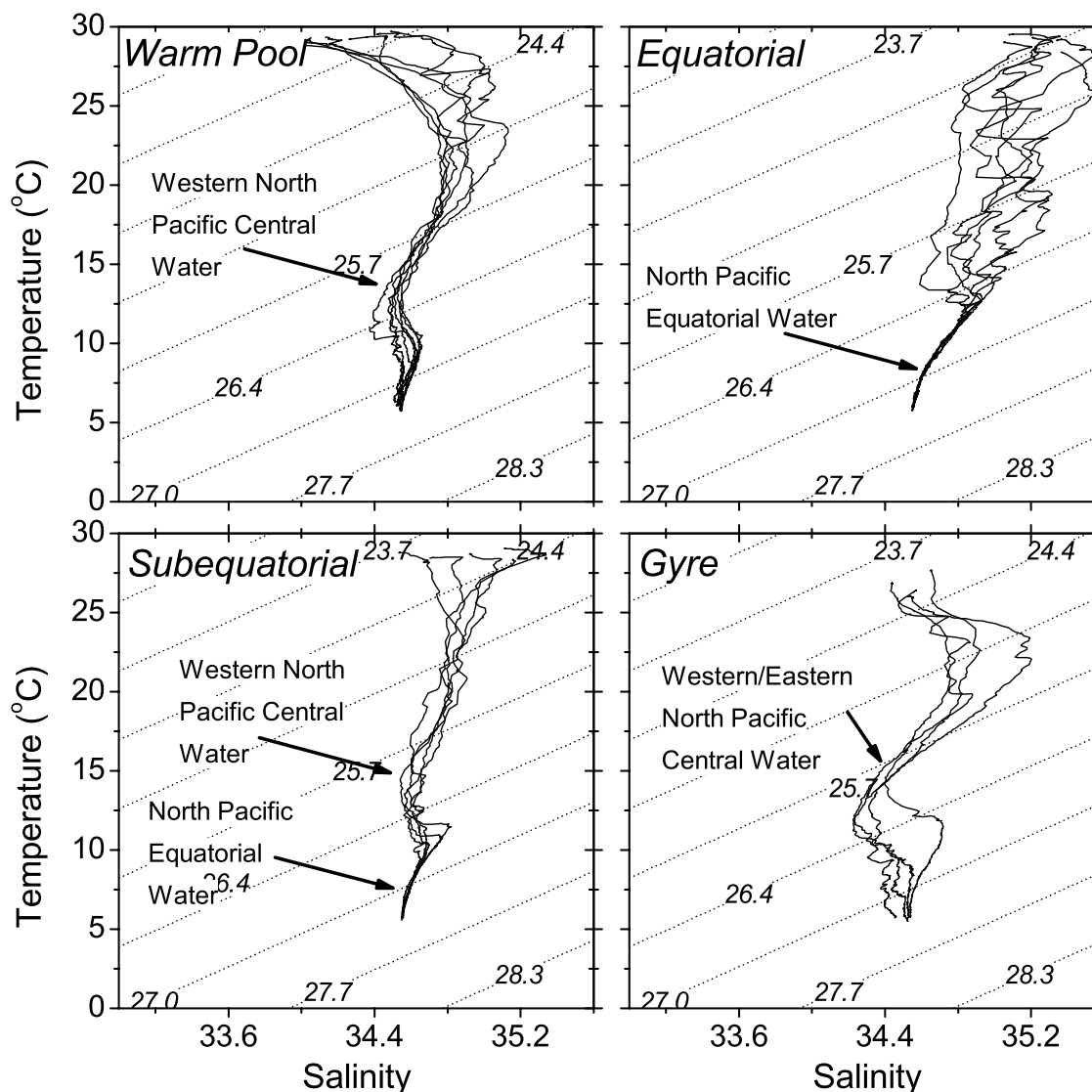


Figure 2. Temperature/salinity diagrams for the water types used for grouping the depth profiles.

~28–30°C, slightly cooler than the Warm Pool. Waters collected during the CTD casts included North Pacific Equatorial water, which is found at 100–600 m in the tropical Pacific. These waters also included the Equatorial Intermediate Current and the Equatorial Undercurrent. The Equatorial Intermediate Current is a westward moving current found below the surface at 300–1000 m [Glickman, 2000] between -2°S and 2°N . The Equatorial Undercurrent moves eastward on the equator at a depth of 200 m [Knauss, 1997; Glickman, 2000].

[11] The third group of profiles, called Subequatorial, were taken from 2.8 to 8.4°N (Stations 13, 14, 18–22) and included North Equatorial Countercurrent, Pacific Equatorial, and Western North Pacific Central waters. Depth profiles taken from 9.3 – 18.1°N (Stations 23–26) are referred to as the Gyre profiles. Gyre waters included areas of the North Equatorial Current. The depth profiles appear to have included central waters, possibly a mix of Eastern

and Western North Pacific Central waters that are typically found at 150–800 m [Glickman, 2000].

3.2. Alkyl Nitrate Depth Profiles

[12] Warm Pool depth profiles (Stations 1–8) typically had low, relatively constant alkyl nitrate concentrations in the mixed layer (Figure 3). Mixed layer depths in this region were 20–43 m. Mixed layer methyl nitrate concentrations were 0–60 pM. Below the mixed layer, methyl nitrate concentrations decreased at all stations, except for Stations 2 and 8 which showed a slight increase to ~140 pM. Ethyl nitrate concentrations were between 0 and 10 pM in the mixed layer and increased below the mixed layer to up to 3 times the concentrations in the mixed layer. Isopropyl nitrate concentrations were between 0 and 2 pM in the mixed layer. Stations 1, 2, and 8 had an increase in concentration below the mixed layer (up to 5 pM) and decreased with depth to ≤ 1 pM. N-propyl nitrate had concentrations ≤ 4 pM in the warm pool depth profiles.

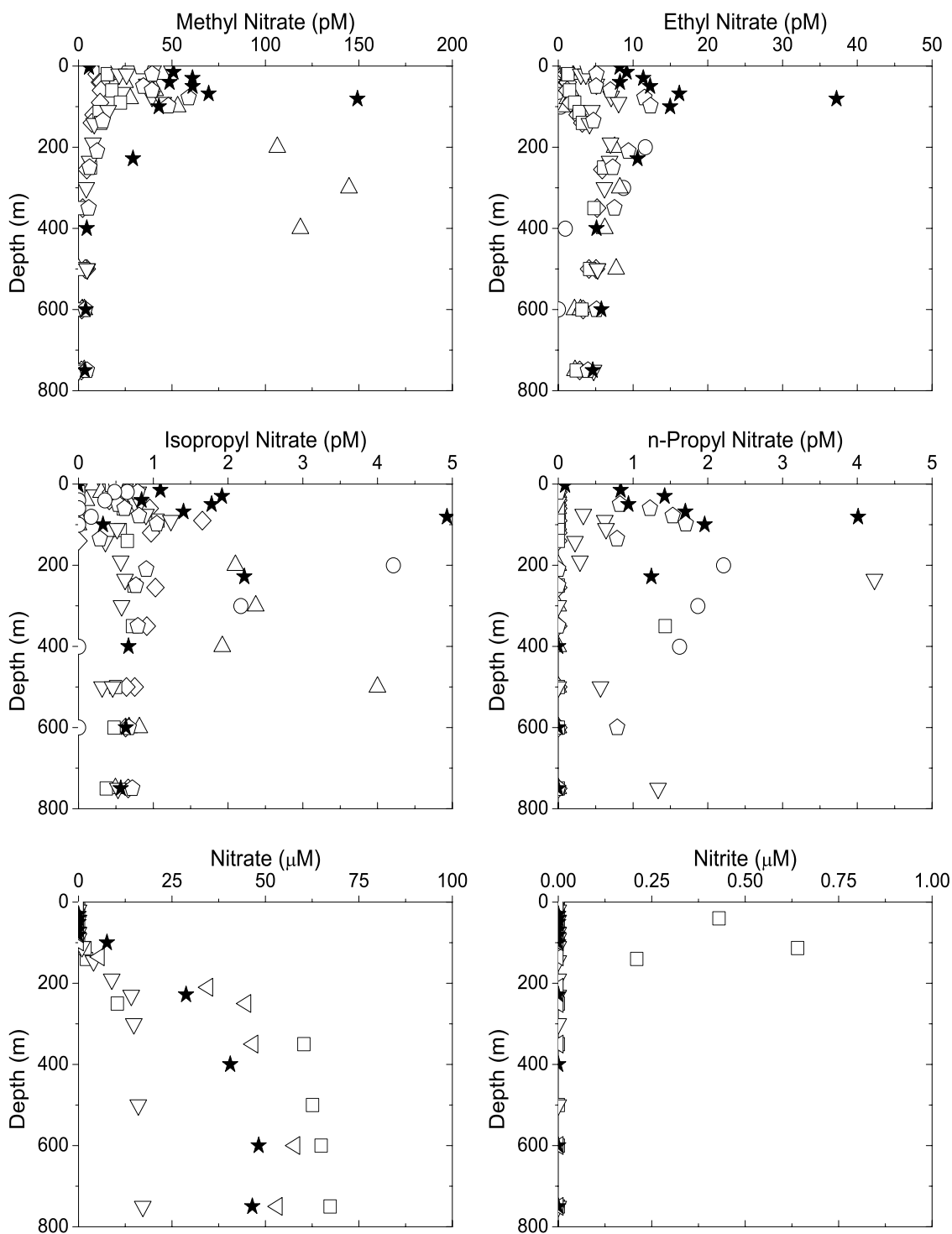


Figure 3. Depth profiles for casts taken in the Warm Pool (3.3–11.2°N). Cast 1 (open circles), Cast 2 (open right-side up triangles), Cast 3 (open diamonds), Cast 4 (open squares), Cast 6 (open upside-down triangles), Cast 7 (open sideways triangles), Cast 8 (solid stars).

[13] Depth profiles for alkyl nitrates, nitrite, and nitrate in Equatorial waters (Stations 9–12, 16 and 17, 0–2.5°N) are shown in Figure 4. Equatorial alkyl nitrate mixed layer concentrations were generally higher than those in the Warm Pool. Mixed layer depths in this area were between 20–50 m. Methyl nitrate was 200–400 pM in the mixed layer and decreased sharply to 0–50 pM below the mixed

layer. Ethyl nitrate concentrations were 40–80 pM in the mixed layer, and decreased below the mixed layer to ≤ 20 pM. Station 9 had a high concentration, ~ 180 pM, near the base of the mixed layer (100 m). Isopropyl nitrate concentrations were ≤ 2 pM in the mixed layer and ≤ 5 pM below the mixed layer. N-propyl nitrate concentrations were also higher in the mixed layer (3–13 pM) and decreased

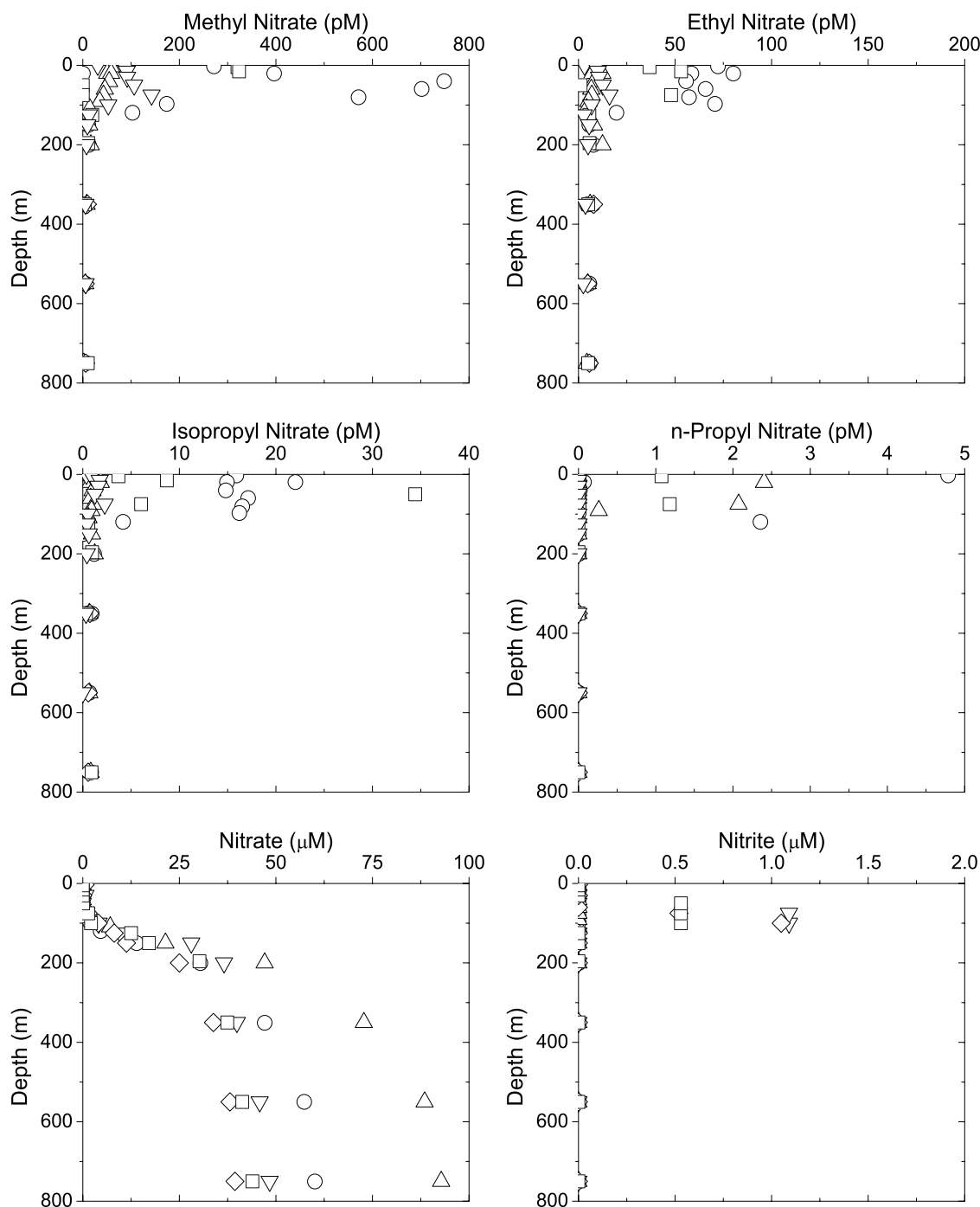


Figure 4. Depth profiles for casts taken in the Equatorial waters ($0\text{--}2.5^\circ\text{N}$). Note the change in the x axes relative to the Warm Pool waters. Cast 9 (open circles), Cast 10 (open right-side up triangles), Cast 11 (open diamonds), Cast 12 (open squares), Cast 16 (open upside-down triangles), Cast 17 (open sideways triangles).

with depth. The ethyl and *n*-propyl nitrate concentrations observed in the profiles in this water type were the highest ever observed in the oceans.

[14] Depth profiles for Subequatorial waters (Stations 13–15 and 18–22, $2.8\text{--}8.4^\circ\text{N}$) are shown in Figure 5. The shapes of the depth profiles were similar to those in Equatorial waters with mixed layer maxima. The mixed layer depths in these waters were 24–86 m. Methyl nitrate

concentrations were relatively constant (50–100 pM) in the mixed layer at Stations 14 and 22. Station 21 had a methyl nitrate level of ~ 320 pM at the surface, but lower levels, 100 pM, within the rest of the mixed layer. The concentration of methyl nitrate in the mixed layer at Station 13 increased from ~ 280 pM at the surface, to ~ 750 pM at 40 m, and then decreased with depth. These are the highest concentrations of methyl nitrate ever observed in the

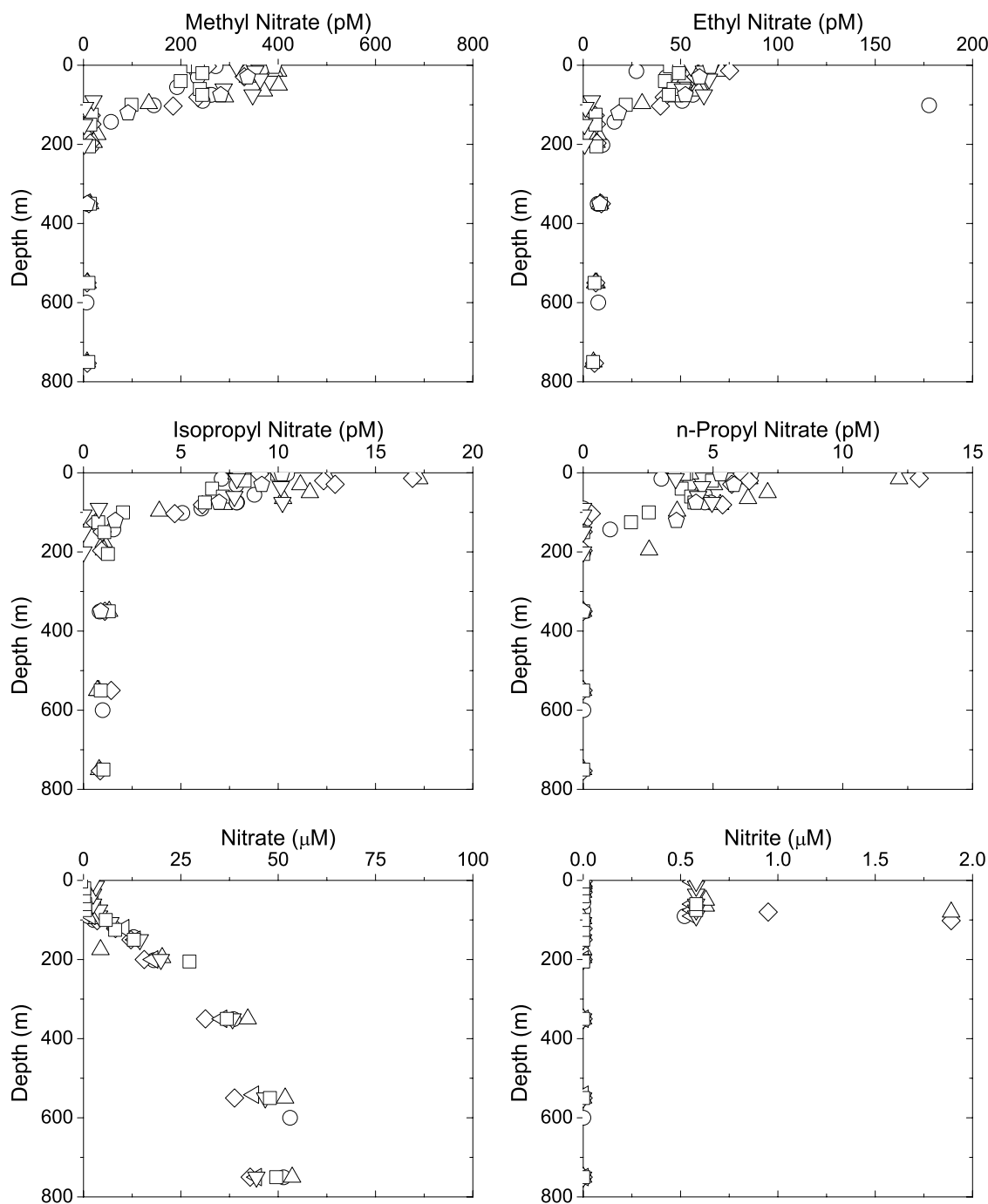


Figure 5. Depth profiles for casts taken between 2.8 and 8.4°N in the Subequatorial waters. Note the change in the x axis of methyl, ethyl, and isopropyl nitrate relative to the Warm Pool waters. Cast 13 (open circles), Cast 14 (open right-side up triangles), Cast 18 (open diamonds), Cast 21 (open squares), Cast 22 (open upside-down triangles).

oceans, and they are accompanied by a high degree of variability within the mixed layer. Ethyl nitrate concentrations at Stations 14 and 22 were between 3 and 16 pM in the mixed layer and did not change much with depth. Concentrations of ethyl nitrate in the mixed layer at Stations 13 and 21 were higher, 36–55 pM and 55–80 pM respectively, and decreased below the mixed layer. Isopropyl and *n*-propyl nitrate depth profiles were similar to those of ethyl nitrate, with relatively little variability with depth at Stations 14

and 22 and a decrease below the mixed layer at Stations 13 and 21. The isopropyl nitrate concentrations in this water type were the highest observed to date in seawater.

[15] The alkyl nitrate, nitrite and nitrate depth profiles for Gyre waters (Stations 18–26, 9.3–18.1°N) are shown in Figure 6. The shapes of the depth profiles in these waters were different from the depth profiles in the Equatorial and Subequatorial waters, but similar to the profiles in the Warm Pool. The mixed layer depths were 72–82 m. Methyl nitrate

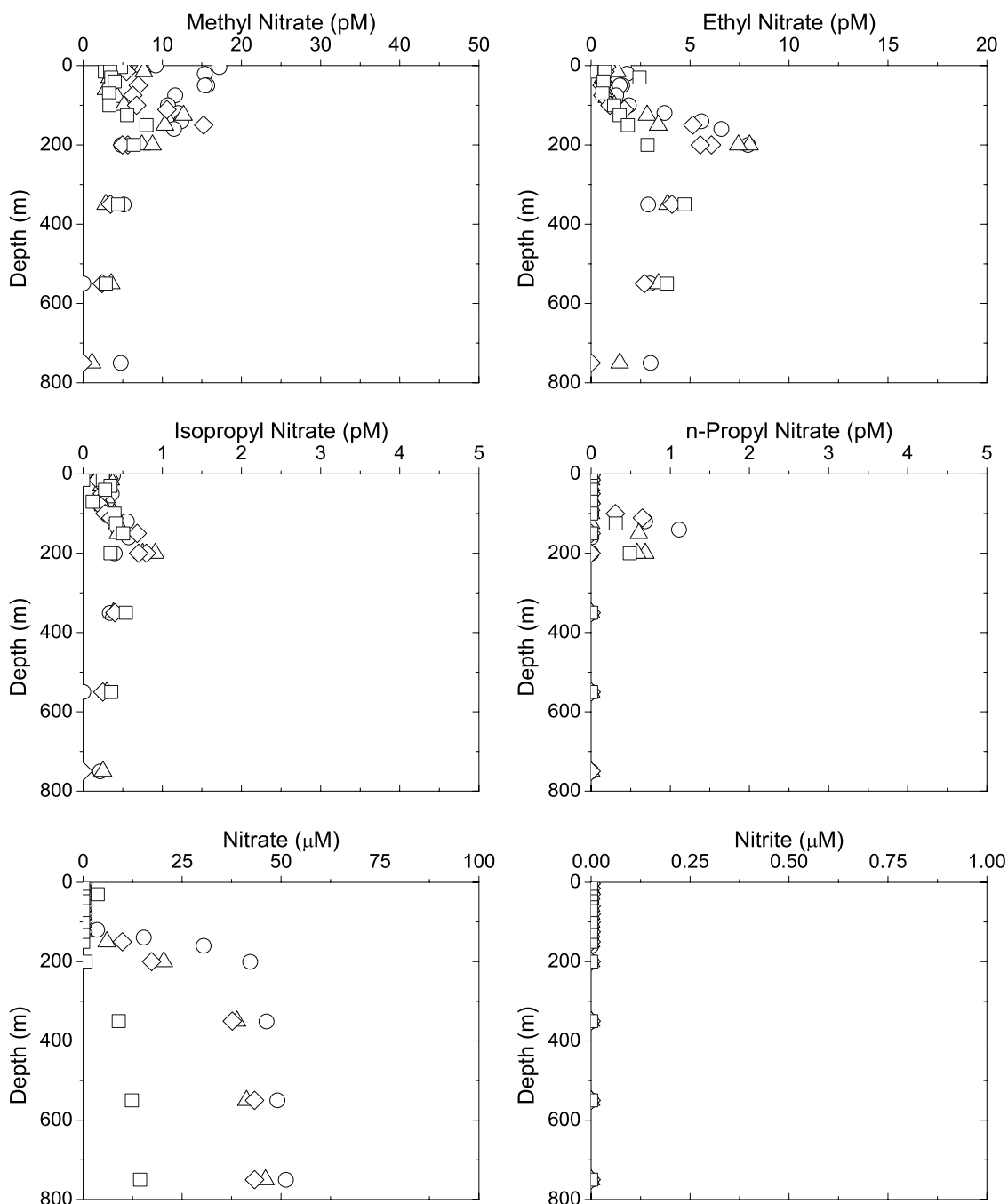


Figure 6. Depth profiles for casts taken between 9.3 and 18.1°N in the Gyre waters. Cast 23 (open circles), Cast 24 (open triangles), Cast 25 (open diamonds), Cast 26 (open squares).

concentrations were low (2–18 pM) in the mixed layer and decreased slightly with depth. Ethyl nitrate concentrations were also low in the mixed layer (0–2.5 pM) and increased with depth to maxima of 5–8 pM at 200–350 m. Isopropyl and n-propyl nitrate concentrations behaved similarly to ethyl nitrate with depth.

3.3. Alkyl Nitrate Ratios

[16] Correlation plots of methyl nitrate, isopropyl nitrate and n-propyl nitrate concentrations versus ethyl nitrate

concentration were used to examine the relationship between the alkyl nitrates in each water type (Figure 7). The concentrations were positively correlated in most of the water mass types.

[17] In the Warm Pool (Figure 7, row A), methyl nitrate and ethyl nitrate concentrations were positively correlated, with different slopes for 0–189 m and 190–750 m. The [Me]/[Et] ratio from 0–189 m was 3.1 ± 0.5 , higher than the [Me]/[Et] ratio of 1.9 ± 0.3 from 190–750 m. Isopropyl nitrate concentrations were positively correlated with ethyl

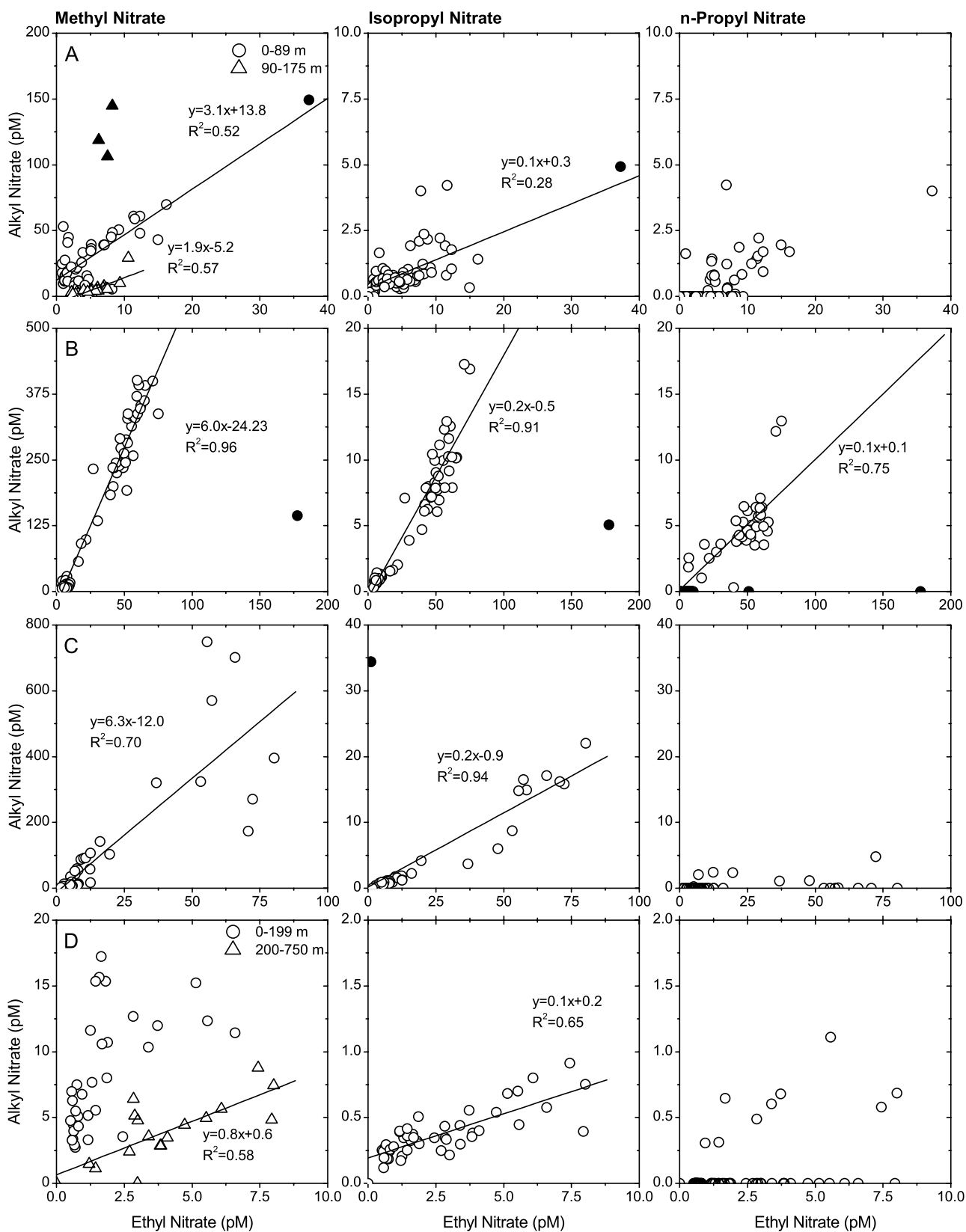


Figure 7. Correlation plots of the alkyl nitrate depth data for the casts taken in the (row A) Warm Pool (3.3–11.2°N), (row B) Equatorial waters (0–2.5°N), (row C) Subequatorial waters (2.8–8.4°N), and (row D) Gyre waters (9.3–18.1°N). Only the regressions with a confidence interval $\geq 95\%$ are shown. The solid symbols represent data that were excluded when determining the fit of the correlation and the confidence intervals.

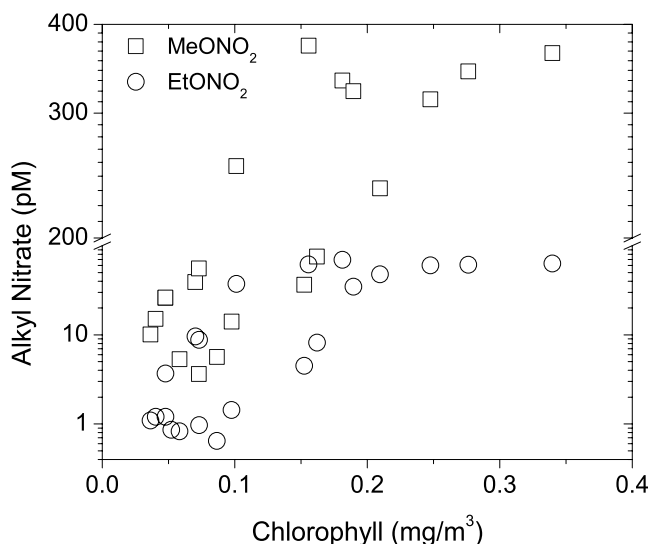


Figure 8. Correlation plot of mixed layer methyl and ethyl nitrate concentrations at each station plotted against June 2004 MODIS average chlorophyll data at each station.

nitrate concentrations with a [iPr]/[Et] ratio of 0.1 ± 0.0 . No significant correlation (i.e. $c.i. \geq 95\%$) was observed between ethyl nitrate and n-propyl nitrate concentrations. This may have been due to detection limit issues since the concentrations of n-propyl nitrate in these waters were often below the 0.25 pM detection limit of the instrument.

[18] At the Equatorial stations ($0-2.5^\circ\text{N}$, Figure 7, row B), methyl and ethyl nitrate concentrations were positively correlated at all depths with an [Me]/[Et] ratio of 6.0 ± 0.2 . This is $\sim 2-3$ times the [Me]/[Et] ratios observed in the Warm Pool. Isopropyl and ethyl nitrate concentrations were also positively correlated at all depths with an [iPr]/[Et] ratio of 0.2 ± 0.0 . This ratio was about twice that in the Warm Pool. N-propyl nitrate was positively correlated with ethyl nitrate with an [nPr]/[Et] ratio of 0.1 ± 0.0 .

[19] Methyl and ethyl nitrate were also positively correlated at all depths in the Subequatorial waters ($2.8-8.4^\circ\text{N}$; Figure 7, row C). The ratio of [Me]/[Et] in the Subequatorial waters was 6.9 ± 0.6 , $2-3.5$ times that observed in the Warm Pool waters. Isopropyl nitrate concentrations were also positively correlated with ethyl nitrate with an [iPr]/[Et] ratio of 0.2 ± 0.0 . This ratio was about twice that in the Warm Pool waters and similar to that observed in Equatorial waters. N-propyl nitrate concentrations showed no significant correlation with ethyl nitrate concentrations.

[20] In Gyre waters ($9.3-18.1^\circ\text{N}$; Figure 7, row D), methyl nitrate concentrations were not as well correlated with ethyl nitrate as in the tropical waters. No significant correlation of methyl nitrate and ethyl nitrate concentrations was observed from 0–200 m. A positive correlation with an [Me]/[Et] ratio of 0.8 ± 0.2 was observed at depths from 200–750 m. The [Me]/[Et] ratio was $\sim 1/2$ that observed at similar depths in the Warm Pool waters. Ethyl and isopropyl nitrate concentrations were positively correlated, with an [iPr]/[Et] ratio of 0.1 ± 0.0 . This ratio was approximately half the [iPr]/[Et] ratios observed in the Equatorial and Subequatorial waters and equal to the ratio observed in the

Warm Pool. N-propyl nitrate concentrations and ethyl nitrate concentrations had no significant correlation.

3.4. Relationship of Alkyl Nitrates to Chlorophyll

[21] Positive correlations were seen between surface concentrations of methyl, ethyl, and isopropyl nitrate and chlorophyll concentrations (Figure 8). The correlations are driven by the differences between the low chlorophyll, low alkyl nitrate waters (Warm Pool and Gyre) and the high chlorophyll, high alkyl nitrate waters (Equatorial and Subequatorial). Within either the low or high chlorophyll waters there was no correlation of alkyl nitrates with chlorophyll. The areas with highest chlorophyll (Equatorial and Subequatorial) tended to have high alkyl nitrate concentrations in the mixed layer.

3.5. Relationship of Alkyl Nitrates to Nitrite and Nitrate

[22] Alkyl nitrate depth profiles did not appear to be related to nitrite concentration, as suggested by *Dahl et al.* [2003], except possibly at Stations 21 and 22, which had alkyl nitrate maxima near the nitrite maxima. The ethyl, isopropyl, and n-propyl nitrate concentrations did increase with increasing nitrate in the Gyre waters to about 200 m, but no relationship was seen between nitrate and alkyl nitrates depth profiles in the other water types.

[23] Northward of the high chlorophyll areas, in the Gyre waters (Stations 23–26), alkyl nitrate concentrations were low in the surface ocean and increased with depth to about 200 m. This is similar to the increase with depth seen for nitrate. The concentrations in the Gyre waters were also significantly lower, by more than a factor of 5, than the concentrations in the other water types.

4. Discussion

4.1. Inferring Source Mechanisms

[24] The goal of this study was to document the spatial variability of alkyl nitrates in hopes of obtaining insight into the processes controlling their production and surface ocean concentration. *Chuck et al.* [2002] suggested that alkyl nitrates in seawater are produced by algae and *Dahl et al.* [2003] proposed a photochemical mechanism. *Ballschmiter* [2002] also suggested catalyzed reaction of nitrate with alkyl halides, alkylation of nitrate ions, and methyltransferase-catalyzed biochemical methylation of nitrate. To date, only the photochemical mechanism has been studied in natural waters [*Moore and Blough*, 2002; *Dahl et al.*, 2003]. *Moore and Blough* [2002] carried out seawater

Table 1. Estimated Lifetimes of Alkyl Nitrates in Seawater Due to Chloride Substitution and Hydrolysis

Temperature, °C	Lifetime, years			
	Methyl Nitrate	Ethyl Nitrate	Isopropyl Nitrate	n-Propyl Nitrate
0	142.25	115.19	19.56	50.60
10	19.65	17.55	2.58	8.97
15	7.77	7.26	0.99	3.99
20	3.19	3.11	0.40	1.83
25	1.36	1.38	0.16	0.87
30	0.60	0.63	0.07	0.43

irradiations and demonstrated that methyl nitrate is formed photochemically in the presence of nitrite. *Dahl et al.* [2003] demonstrated that the yield of alkyl nitrates from the reaction of alkyl peroxy radicals with nitric oxide ($\text{ROO} + \text{NO}$) is high in aqueous solution, and that this reaction occurs in natural waters. In the oceans, the rate of this reaction should reflect: 1) the abundance and photochemical reactivity of colored dissolved organic matter (CDOM) as the precursor of organic peroxy radicals, and 2) the abundance of nitrite, which photolyzes in sunlight to generate nitric oxide. *Dahl et al.* [2003] carried out sunlight incubations of seawater and obtained alkyl nitrate formation rates on the order of $\mu\text{M}/\text{hr}$,

[25] The depth profiles obtained in this study exhibit systematic differences between low and high chlorophyll waters. The high chlorophyll Equatorial and Subequatorial waters had the highest levels of alkyl nitrates, a mixed layer maximum, and a high $[\text{Me}]/[\text{Et}]$ ratio of 6–7. This ratio is similar to ratios of the photochemical production of methyl/ethyl nitrate observed during this study [*Dahl*, 2005; E. E. Dahl and E. S. Saltzman, manuscript in preparation, 2006]. This similarity in ratios suggests that aqueous photochemistry may be an important source of alkyl nitrates to the oceans. The lower chlorophyll waters of the Warm Pool and Gyre had much lower alkyl nitrate levels, a maximum below or near the base of the mixed layer, and a lower Me/Et ratio of <3 , decreasing with depth. These differences do not clearly discriminate between biological and photochemical sources. For example, the high alkyl nitrate waters had mixed layer nitrite concentrations of several hundred nM in the photic zone. Because the Equatorial and Subequatorial waters are affected by equatorial upwelling, it is expected that nitrite and nitrate concentrations should be higher than the other regions in the study area. Higher levels of these nutrients could result in greater production of NO radicals leading to the high observed concentrations of alkyl nitrates. This region may also be influenced by the upwelling of photochemically active CDOM from deeper waters. As demonstrated by *Dahl et al.* [2003], such waters could photochemically generate alkyl nitrates at rates sufficient to explain the observed levels. In contrast, the low chlorophyll surface waters had undetectable nitrite levels, and photochemical production in the surface waters should be very low. The depth profile of the photochemical production rate should reflect the product of the photon flux in the actinic regions, and the depth profiles of nitrite and CDOM. Since the nitrite maximum is typically below the mixed layer, the production rate might be greatest near the base of the mixed layer where nitrite is concentrated.

4.2. Lifetime of Alkyl Nitrates in Seawater

[26] One of the complicating issues in the interpretation of these field measurements is the lack of information about the lifetime of alkyl nitrates in seawater. *Dahl et al.* [2005] used the estimated air/sea flux of ethyl nitrate in the Pacific equatorial mixed layer to calculate an average loss rate of approximately $0.06 \mu\text{M}/\text{hr}$ for a 32.5 m mixed layer. For a concentration of 50 μM , this gives a partial lifetime of about a month.

[27] Hydrolysis and chloride substitution are likely mechanisms for chemical loss of alkyl nitrates in the oceans

(Table 1). *McKinley-McKee and Moelwyn-Hughes* [1951] gave the following rate expression for the temperature dependent hydrolysis rate of methyl nitrate in water:

$$\log k(\text{s}^{-1}) = 75.32 - 21.43 * \log T - \frac{9229.03}{T} \quad (1)$$

[28] *Zafirou* [1974] determined the reactivity of various nucleophiles in seawater relative to that of water, and assigned a value of 9.4 to chloride at a salinity of 35. Hence, the rate of chloride substitution in seawater should be approximately 10 fold faster than hydrolysis.

[29] The nucleophilic substitution reaction rates of other alkyl nitrates can be estimated from those of methyl nitrate, by scaling them according to the relative hydrolysis rates of various alkyl bromides [*Mabey and Mill*, 1978] as follows:

$$\frac{k_{\text{RBr}}}{k_{\text{MeBr}}} = \frac{k_{\text{RONO}_2}}{k_{\text{MeONO}_2}} \quad (2)$$

where R is ethyl, isopropyl, or n-propyl.

[30] This approach yields partial lifetimes of C_1 – C_3 alkyl nitrates with respect to nucleophilic substitution ranging from weeks to more than 100 years. With the possible exception of isopropyl nitrate, these lifetimes are considerably longer than the time scale for removal of gases (days to weeks) from the mixed layer via air/sea exchange, and are not likely to influence mixed layer alkyl nitrate concentrations.

4.3. Alkyl Nitrates in the Deep Ocean

[31] One of the most interesting results of this study is the presence of alkyl nitrates at measurable levels at depths well below the surface mixed layer, similar to observations by *Chuck et al.* [2002] and *Moore and Blough* [2002]. The ventilation times for these waters are considerably longer than the chemical lifetimes calculated above, indicating that there must be an in situ source of these compounds below the photic zone. According to World Ocean Experiment, Pacific Ocean Atlas data, waters in the equatorial Pacific below 600 m have virtually no CFC-12 or CFC-11, indicating that the waters have not been in contact with the surface for at least 50 years [*Talley*, 2004]. Model estimates suggest that the ventilation age of these waters may be even older (i.e. 100s of years) [*Primeau*, 2005]. At the temperature of these waters ($<10^\circ\text{C}$), the estimated chemical lifetime of ethyl nitrate in seawater is on the order of 20 years. If there are no additional loss pathways for alkyl nitrates, the production rate needed to maintain the observed levels is small. However, the actual lifetime of alkyl nitrates at these depths is not known, and their presence may indicate an active nitrogen chemistry that has not previously been observed.

[32] The source of these deep water alkyl nitrates is unknown. One possibility is production by bacterial activity, related to the degradation of sinking organic material. Another source is free radical chemistry involving the reaction $\text{ROO} + \text{NO}$. Such reactive compounds are not normally associated with deep water chemistry, but there are several sources of energy capable of generating free radicals

transients such as OH and NO. These sources include the production of high energy alpha and beta particles via radioactive decay of uranium and potassium [Swallow, 1969], as well as cosmic rays [Swallow, 1969; Gaisser, 1990].

5. Summary and Conclusions

[33] Depth profiles of C₁-C₃ alkyl nitrates were measured for the first time in the equatorial Pacific Ocean. The results demonstrate a large regional variability in alkyl nitrate levels, and vertical distribution, between high chlorophyll, high nitrite Equatorial and Subequatorial waters and the low chlorophyll, low nitrite waters of the Warm Pool and Gyre. The results are consistent with photochemical production from ROO + NO, but do not unambiguously discriminate between biological and photochemical mechanisms. The high alkyl nitrate waters are characterized by high methyl:ethyl nitrate ratios. This must either reflect the composition of dissolved organic matter giving rise to peroxy radicals, or reflect the metabolic processes involved in alkyl nitrate formation.

[34] Alkyl nitrates are present at significantly high levels in intermediate waters well below the photic zone. Estimated rates of chemical loss due to nucleophilic substitution reactions suggest that these compounds must be generated in situ, perhaps as a result of radioactive decay and cosmic ray-induced photochemistry.

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