

A marine source of methyl nitrate

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[1] Methyl nitrate (CH_3ONO_2) is known to be an important source of reactive nitrogen in the remote marine atmosphere, and it has been speculated that its atmospheric distribution might be explained in part by an ocean source. Measurements made in the N. Atlantic show that dissolved CH_3ONO_2 is present at depths up to 600–800 m. Maximum concentrations are typically found in the upper water column, indicative of an *in situ* source. Although we show that CH_3ONO_2 can be produced photochemically in seawater in the presence of nitrite, and that this reaction may account for some production in the uppermost waters of the ocean, the maxima below this zone indicate that an additional production mechanism exists. **INDEX TERMS:** 4820 Oceanography: Biological and Chemical: Gases; 4850 Organic marine chemistry; 4852 Photochemistry; 0312 Atmospheric Composition and Structure: Air/sea constituent fluxes (3339, 4504)

1. Introduction

[2] The relevance of alkyl nitrates in the marine atmosphere lies in their contribution to the reactive nitrogen budget [Atlas *et al.*, 1993], which controls those photochemical reactions dependent on the level of nitrogen oxides. In the marine boundary layer of the South Pacific alkyl nitrates, primarily methyl nitrate, can make up 20–80% of the reactive nitrogen (NO_y). A number of studies have indicated that the alkyl nitrates, and especially methyl nitrate, may have a marine source [Atlas *et al.*, 1993; Blake *et al.*, 1999; Talbot *et al.*, 2000]. The evidence has come primarily from atmospheric measurements which have shown elevated concentrations of these nitrates near the ocean surface, particularly near the equator. These observations prompted us to include methyl nitrate in the suite of gases that were measured in the ocean water column during a number of cruises beginning in the summer of 1997. The prime focus of the work has been a study of the sources, sinks and fluxes of halogenated gases. The methyl nitrate component of this study was exploratory, and no standard was available at the time of the fieldwork. Furthermore, the analytical method employed was optimized for the measurement of the volatile halocarbons and not for methyl nitrate. Nevertheless, the results that have been accumulated can shed some light on the marine origin of CH_3ONO_2 .

2. Methods

[3] The method is essentially that described in Moore *et al.* [1996] in which a filtered 40 ml water sample, held in a water-

jacketed purge vessel at 40°C, is purged with helium and the dried gas stream is passed through an open tube (OD 0.7 mm) held at –150°C. The contents of the tube were thermally desorbed into a GC-MS system in which separation was effected on two DB624 columns (30 m and 70 m) in series. Methyl nitrate was included in the analytical scheme by monitoring mass 46. A check was done of the retention time by preparing a trace sample of CH_3ONO_2 by the action of nitric and sulphuric acids on methanol at 0°C [Boschan *et al.*, 1955]. Since CH_3ONO_2 is not easily purified, standards are difficult to obtain. In order to achieve at least an approximate quantification of the results, a series of laboratory measurements were made of a calibrated air sample provided by E. Atlas (National Center for Atmospheric Research).

[4] A sample of air collected at Hidden Lake, Colorado, which had been analyzed for CH_3ONO_2 , was measured repeatedly using a slightly modified form of the equipment used for the water analyses. The purge vessel was replaced with a 200 ml steel sampling loop and the air sample was analyzed 6 times with volumes of a deuterated methyl halide internal standard added each time. This gave a value for peak area per unit mass of CH_3ONO_2 , permitting an approximate calibration to be made for previously analysed water samples. Variation in instrument sensitivity was detected and corrected for by normalizing to the internal standard. It is not possible to determine the level of uncertainty associated with this approach to calibration.

[5] The gas extraction method used during this work was optimized for methyl halides, and is expected to give a low purge efficiency for gases that have a much higher solubility, such as CH_3ONO_2 . To determine the purge efficiency (and hence a correction factor for methyl nitrate analyses) an experiment was run in which sub-samples of seawater were purged for times varying from 12–60 minutes, and measured the residual methyl nitrate in the sample. A plot of the log (peak area) against purging time yielded a straight line, the slope of which gave a removal efficiency of 32% for a 12 minute purge. The method as used in the field can provide information about the relative concentrations of CH_3ONO_2 with depth. Alternatively it is possible to estimate absolute concentrations by applying a correction factor for the low collection efficiency and by calibrating with the air sample referred to above. In view of the uncertainties resulting from these two steps, the emphasis of these results is the qualitative information they provide on CH_3ONO_2 distributions and sources in the ocean, although estimates have been made of the maximum concentrations of CH_3ONO_2 amongst the Atlantic samples.

[6] Photochemical experiments were done using an Oriel 300W solar simulator that uses a xenon arc source to

provide a collimated light beam with a spectral dependence closely matching solar irradiation at sea level, at a solar zenith angle of 40° and an intensity of approximately 1325 W m^{-2} over the window 280–1100 nm [Oriel Corporation, 1993]. Water samples were irradiated either in 100 ml glass syringes, or in quartz tubes. Where indicated, NaNO_2 was added to give a final concentration of $100 \mu\text{M}$. Samples were analysed immediately after irradiation.

3. Results and Discussion

[7] CH_3ONO_2 was included amongst the set of gases measured in seawater during cruises of *R.V. Knorr* in the Western Atlantic in 1997, of *NOAA Vessel Ronald Brown* during Leg 2 of GasEx98 north of the Azores in 1998, and during a North Atlantic cruise of *Poseidon* between Bremerhaven and Halifax in 1999. Figure 1 illustrates typical profiles of this gas which are plotted normalized to the maximum concentration in the water column. As discussed in Methods, this approach has been taken because of a much higher confidence in the relative concentrations than in their absolute values. For the two *Poseidon* cruise profiles (Figure 1), the maxima in the upper water column are estimated as 48 and 62 pM for the profiles of August 23

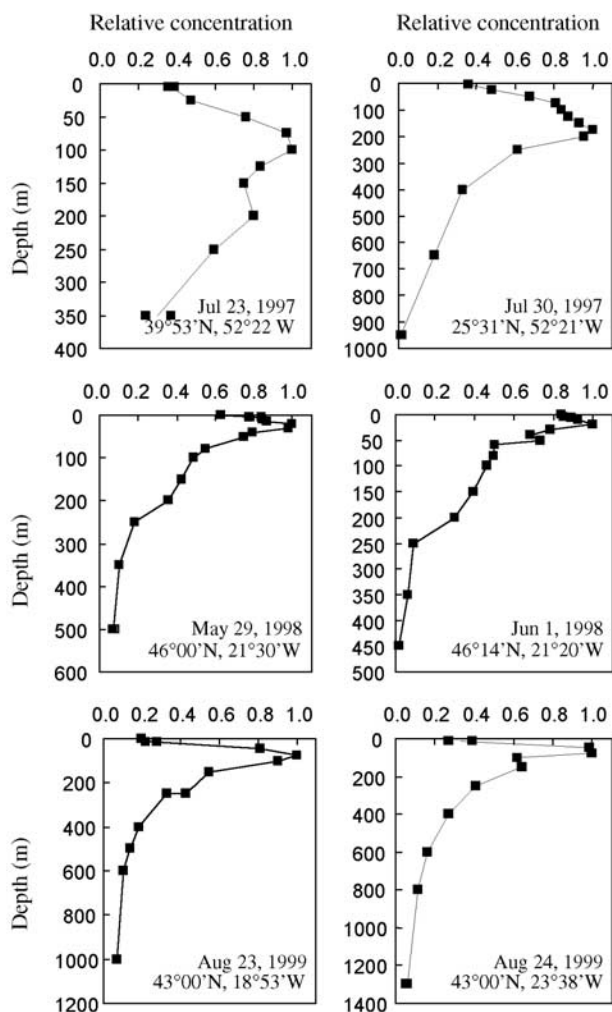


Figure 1. N. Atlantic profiles of methyl nitrate concentrations normalized to the maximum in each profile.

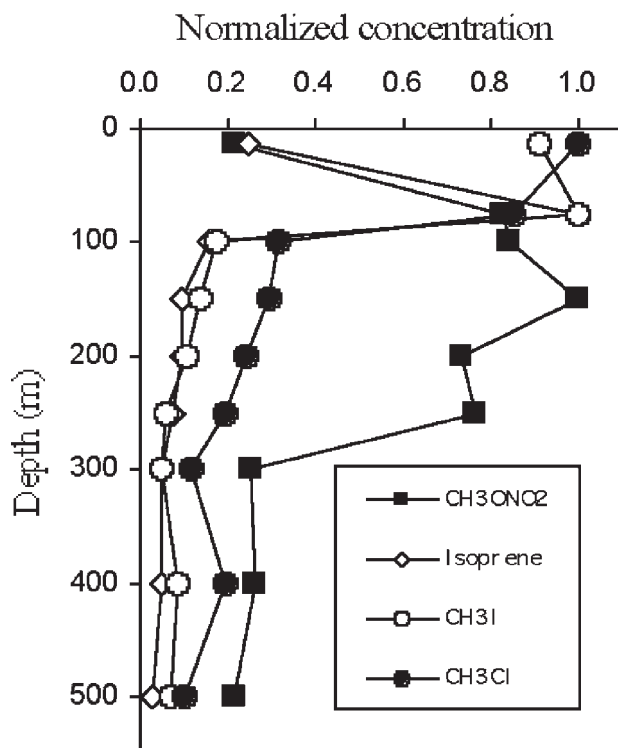


Figure 2. Profiles of CH_3ONO_2 , CH_3Cl , CH_3I and isoprene, in the N. Atlantic at 43°N , 37.3°W (Aug. 27 1999); concentration of each normalized to its maximum in the water column.

and 24, respectively. Using the distilled water solubility of *Kames and Shurath* [1992] the corresponding atmospheric concentrations of CH_3ONO_2 at equilibrium are estimated to be around 22–31 ppt. This range can be compared with reported concentrations in marine air. *Blake et al.* [1999] reported atmospheric CH_3ONO_2 concentrations of around 15–25 ppt at high southern latitudes during the ACE 1 experiment, and as much as 50 ppt in the marine boundary layer near the equator. However, concentrations are commonly lower than these, with typical background values in the Northern Hemisphere being 2–3 ppt, and around 4 ppt in the free troposphere of the S. Pacific [Blake et al., 2002]. Air samples collected near the Azores during GasEx98, close in time and location to profiles shown in Figure 1, had an average methyl nitrate concentration of 4.6 ppt. Therefore the concentration maxima we report in the water column represent strong supersaturation with respect to the local atmosphere. *Atlas et al.* [1994] reported CH_3ONO_2 concentrations in ocean waters near the Antarctic peninsula of $100 \pm 20 \text{ pM}$ which are similar to the maximum values that we report in the water column.

[8] Concentrations increase with depth, reaching a maximum in the upper water column, and then decrease rather gradually with increasing depth. The rate of decrease with depth is clearly slower than that of various biogenic gases such as CH_3Cl and isoprene (Figure 2). One possible explanation is that CH_3ONO_2 has a longer lifetime in the water column than isoprene and the methyl halides. CH_3Cl has been shown to have biological loss processes in addition to hydrolysis, and it is reasonable to suppose that isoprene would experience microbial degradation. Further evidence for a relatively long residence time of CH_3ONO_2 is apparent

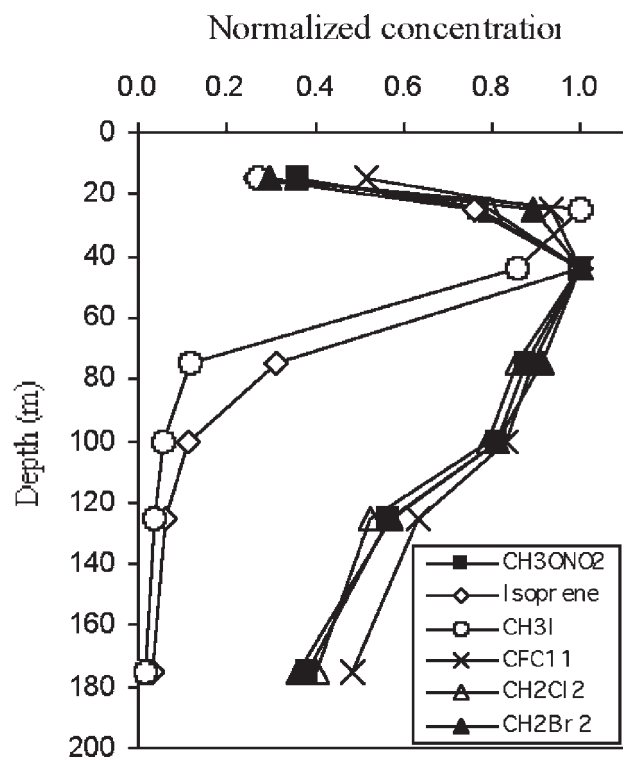


Figure 3. Profiles of a suite of trace gases in the western N. Atlantic, 43.4°N, 60.3°W, (Sept. 2 1999); concentration of each normalized to its maximum in the water column.

in Figure 1 where a number of profiles show that it is measurable down to 600–800 m in the Atlantic.

[9] Strong correlations between methyl nitrate and other trace gases including CH_2Br_2 , CH_2Cl_2 , and CFC11 were observed in a few instances. This is illustrated in Figure 3 with profiles of a suite of gases in the western N. Atlantic (43.4°N, 60.3°W). In view of the solely atmospheric source of CFC11, simplest explanation for the close similarity in the profiles is that they result simply from mixing between cold waters holding high concentrations of the gases, and warmer surface waters depleted in them. For both CFC-11 and CH_2Cl_2 , the high concentrations are likely to have resulted from equilibration with the atmosphere, but for CH_2Br_2 , which is known to have a biological source [Moore *et al.*, 1996], production in the ocean is probable.

[10] A few observations can be made regarding the possibility of a biological source of CH_3ONO_2 . First, it is not inconsistent with the vertical profiles, which have highest concentrations in the upper water column. However, the concentration maxima lie deeper than is typically seen for gases known to have some algal source. For example, the CH_3Cl maximum in the profile shown in Figure 1 for August 23 (N. Atlantic, 1999) was located around 47 m, while the CH_3ONO_2 maximum was at 75 m. In the Knorr profile of July 30 1997, CH_3Cl was maximal at 75 m, and CH_3ONO_2 at 175 m. On the other hand, CH_2Br_2 , which has an algal source, also showed a relatively deep maximum (175 m) at this location. The depth of trace gas maxima would be expected to have some dependence on the lifetime of each gas in seawater, and, as indicated above, this appears to be relatively long for methyl nitrate.

[11] A second source of information regarding the possibility of biological production of CH_3ONO_2 is laboratory

studies of halocarbon production by two species of marine algae, *Prochlorococcus*, and *Nitzschia curvilineata*. The analyses done on the growth media in these experiments did include methyl nitrate. Its concentration was no higher in the cultures than in controls of the culture medium alone. While a positive result from such experiments would be very significant, a negative one does not rule out a biological source. Indeed, it is very common for other biogenic marine trace gases to have production rates which vary greatly from one organism to another [e.g. Scarratt and Moore, 1998].

[12] As also recognized by E. Saltzman (personal communication), CH_3ONO_2 could also be formed photochemically in surface waters [Blough, 2001]. Analogous to the reaction of superoxide (O_2^-) with nitric oxide (NO) to form peroxy-nitrite [Blough and Zafiriou, 1985], organic peroxy radicals react rapidly with NO in aqueous solution to generate organic peroxy-nitrites, which can subsequently rearrange in part to form nitrates [Padmaja and Huie, 1993; Huie, 1995]:



[13] Because methyl peroxy radicals can be produced by the photolysis of chromophoric dissolved organic matter [CDOM; Del Vecchio and Blough, 2002] in surface waters [Blough, 1997; Johnson *et al.*, 1996; Kieber and Blough, 1990], while NO can be generated by the photolysis of nitrite [Zafiriou and McFarland, 1981; Zafiriou and True, 1981], the above reactions could represent a viable path to CH_3ONO_2 .

[14] To test this possibility, 100 μM NO_2^- was added to a seawater sample that was then irradiated in a glass syringe with a solar simulator. A large increase in CH_3ONO_2 was observed in this sample, as compared with an un-irradiated control containing NO_2^- and an irradiated control containing no NO_2^- (Table 1). The production of CH_3ONO_2 in seawaters containing NO_2^- increased in an approximately linear fashion with irradiation time over a 1 h period (Figure 4). Irradiation of a seawater sample containing NO_2^- in a quartz tube increased substantially the production of CH_3ONO_2 (Figure 4), clearly revealing the importance of the shorter wavelengths in the UV-A and UV-B in the production mechanism. Consistent with the above reactions, this increase can be explained by the enhanced formation of CH_3OO at short wavelengths. Blough [1997] previously showed that the quantum yield for production of the methyl radical (the immediate precursor of CH_3OO) rises rapidly below ~ 330 nm for CDOM in near-shore waters.

[15] While these experiments do support the notion that CH_3ONO_2 may be produced photochemically in seawater, they do not demonstrate that this is a major source. Indeed, the photochemically-effective wavelengths for the formation of CH_3OO and NO (from NO_2^- photolysis) are limited to the UV-A and UV-B spectral regions, where the irradiance is rapidly attenuated with depth due to absorption by CDOM [Blough and Del Vecchio, 2002; Nelson and Siegel,

Table 1. Effect on Methyl Nitrate Signal of Irradiating Seawater with and without Addition of Nitrite

Sample	Peak Area (10^6)
Untreated seawater	1.52
Untreated seawater	1.57
Irradiated seawater	1.58
Seawater + nitrite (100 μmolar) irradiated	20.2

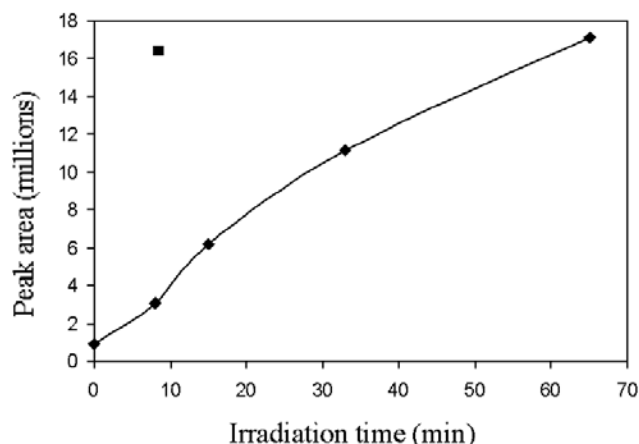
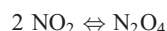


Figure 4. Change in concentration with time of CH_3ONO_2 in samples irradiated in glass syringes. Single point (square) shows the result of using a quartz irradiation vessel.

2002]. Thus, the production of CH_3ONO_2 by this mechanism would be limited to the very near-surface waters, most likely to depths <25 m depending on CDOM content. The depths of the observed maxima (Figure 1) make it rather unlikely that photochemical processes could solely be responsible for CH_3ONO_2 production in Atlantic waters.

[16] Photochemical production may, however, be important in upwelling regions such as the central equatorial Pacific, where both NO_2^- (and NO_3^-) and CDOM are increased in surface waters [Nelson and Siegel, 2002]. Additional NO could potentially be generated in these regions indirectly by the photolysis of nitrate; this reaction produces NO_2 , which could be converted in part to nitrite through one-electron reduction or the following reactions [Blough, 1997]:



[17] Interestingly, Blake *et al.* [1999] reported maximum concentrations of atmospheric methyl nitrate (up to 50 ppt) in the central equatorial Pacific.

[18] While NO is also produced biologically as an intermediate in nitrification and denitrification [Naqvi and Noronha, 1991] this is not expected to occur in surface waters because nitrification is inhibited by light [Ward and Zafiriou 1988]. In subsurface waters where this source of NO is feasible, the CH_3OO radical would not be formed photochemically.

3.1. Summary

[19] It is shown that CH_3ONO_2 occurs in Atlantic waters and that there must be a source supplying the ubiquitous maxima seen at depths ranging from 25 to 200 m. It is measurable at depths of 600–800 m, suggesting either production at depth or a lifetime that is long in comparison with such trace gases as CH_3Cl , CH_3I , and isoprene, probably on the order of months.

[20] Laboratory studies have shown that seawater containing high levels of NO_2^- does yield CH_3ONO_2 on irradiation with simulated sunlight. While there is no convincing evidence at present that this reaction could account for the observed profiles, it may contribute to the high levels reported in upwelling regions where water containing

enhanced NO_2^- , NO_3^- and CDOM is present at shallow depths, especially in regions of high solar irradiance.

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