Long-term atmospheric measurements of $C_1$–$C_5$ alkyl nitrates in the Pearl River Delta region of southeast China

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Abstract

Mixing ratios of seven $C_1$–$C_5$ alkyl nitrates (RONO$_2$) were measured during a 16-month study (August 2001–December 2002) at Tai O, a coastal site 30 km west of central Hong Kong in the Pearl River Delta, the fastest-growing industrial region in the world. The $C_3$–$C_4$ (rather than $C_1$–$C_2$) RONO$_2$ were most abundant throughout the study, showing the importance of photochemical (rather than marine) RONO$_2$ production in the sampled air. A lack of methyl nitrate (MeONO$_2$) enhancement during summer, when the prevailing winds are from the ocean, indicates that the South China Sea is not a region of strong RONO$_2$ emissions. By contrast, MeONO$_2$ levels during pollution episodes (up to 25 parts per trillion by volume (pptv)) were the highest that our group has recorded during urban photochemical RONO$_2$ production, as opposed to marine emissions or biomass burning. The highest summed RONO$_2$ level of the study (204 pptv) was measured in the afternoon of 7 November 2002, during an intense pollution episode that captured the highest ozone (O$_3$) level ever recorded in Hong Kong (203 ppbv). During pollution episodes, the average ratio of O$_3$ to summed RONO$_2$ was roughly 1000:1 in freshly polluted air (ethyne/CO$_2$/C$_2$H$_3$–5 pptv/ppbv) and 500:1 in very freshly polluted air (ethyne/CO$_2$/C$_2$H$_3$6–8 pptv/ppbv). Ozone and RONO$_2$ share a common photochemical source, and their good correlation in pollution plumes shows that RONO$_2$ can be used as a tracer of photochemical O$_3$ production. Even MeONO$_2$ showed similar diurnal variations as the $C_2$–$C_5$ RONO$_2$, indicating a strong photochemical source despite its very slow photochemical production from methane oxidation. The decomposition of longer-chain alkoxy radicals also does not explain the high MeONO$_2$ levels, and rough calculations show that methoxy radical reaction with NO$_2$ appears to be a viable alternate pathway for MeONO$_2$ production in polluted atmospheres, though further measurements and modeling are required to confirm this mechanism.

Keywords: Alkyl nitrates; Photochemistry; China; Urban pollution; Ozone

1. Introduction

Alkyl nitrates (RONO$_2$) are a reservoir species for tropospheric reactive odd nitrogen (NO$_y$) and they
share a similar photochemical formation pathway as ozone (O\textsubscript{3}) (Flocke et al., 1998a; Talbot et al., 2000). Our understanding of the sources, distribution, and seasonal cycle of RONO\textsubscript{2} has advanced considerably over the past few years. The formation of RONO\textsubscript{2} from the oxidation of parent hydrocarbons (RH) has been known since the 1970s (Darnall et al., 1976; Atkinson et al., 1982):

\[ \text{RH} + \text{OH} \rightarrow R \cdot + \text{H}_2\text{O}, \quad k_1, \quad \alpha_1, \quad (1) \]

\[ R \cdot + \text{O}_2 \rightarrow \text{RO}_2^-, \quad k_2, \quad (2) \]

\[ \text{RO}_2^- + \text{NO} \rightarrow \text{RO}^- + \text{NO}_2, \quad k_3, \quad 1 - \alpha_2, \quad (3a) \]

\[ \text{RO}_2^- + \text{NO} \rightarrow \text{RONO}_2, \quad k_3, \quad \alpha_2, \quad (3b) \]

where \( k_1, k_2 \) and \( k_3 \) are reaction rate constants, and \( \alpha_1 \) and \( \alpha_2 \) are branching ratios that have recently been updated in the literature (Arey et al., 2001 and references therein). In addition to photochemical RONO\textsubscript{2} formation, the oceanic source of RONO\textsubscript{2} has been known for over a decade (Walega et al., 1992; Atlas et al., 1993; Chuck et al., 2002). Thirdly, biomass burning has mostly NH sources associated with urban/industrial hydrocarbon emissions.

Airborne, ground-based and ship-based studies are providing an increasingly comprehensive spatial characterization of tropospheric RONO\textsubscript{2} (e.g. Schneider et al., 1998; Blake et al., 2003a). Most recently, Blake et al. (2003a) documented changes in RONO\textsubscript{2} mixing ratios with latitude, from methyl nitrate (MeONO\textsubscript{2}) and ethyl nitrate (EtONO\textsubscript{2}), which are dominated by equatorial oceanic sources, through 2-propyl nitrate (2-PrONO\textsubscript{2}), which has both significant oceanic and northern hemispheric (NH) sources, to 2-butyl nitrate (2-BuONO\textsubscript{2}), which has mostly NH sources associated with urban/industrial hydrocarbon emissions.

The primary RONO\textsubscript{2} sinks are photolysis and reaction with the hydroxyl radical (OH):

\[ \text{RONO}_2 + h\nu \rightarrow \text{RO}^- + \text{NO}_2, \quad J_{\text{RONO}_2}, \quad (4) \]

\[ \text{RONO}_2 + \text{OH} \rightarrow \text{products}, \quad k_5, \quad (5) \]

where \( J_{\text{RONO}_2} \) and \( k_5 \) are reaction rate constants for loss by photolysis and OH, respectively. The importance of RONO\textsubscript{2} loss by photolysis decreases with increasing carbon number (Clemitshaw et al., 1997; Talukdar et al., 1997). RONO\textsubscript{2} lifetimes vary with season, latitude and altitude (Clemitshaw et al., 1997), ranging from \( \sim \)1 month for MeONO\textsubscript{2} to several days for pentyl nitrates.

A winter peak and springtime decline of RONO\textsubscript{2} mixing ratios has been observed at remote sites in the high NH (e.g. Beine et al., 1996; Blake et al., 2003b). Similarly, year-round measurements at Mauna Loa (Atlas and Ridley, 1996) and Summit, Greenland (Swanson et al., 2003) show a winter maximum and summer minimum, whereas long-term RONO\textsubscript{2} measurements in Germany distinguished between a summer minimum in clean, photochemically aged air masses, vs. a summer maximum in polluted air masses (Flocke et al., 1998a). Day et al. (2003) also observed a summer maximum in air sampled downwind of Sacramento, CA.

Here, we present a 16-month record of C\textsubscript{1}–C\textsubscript{5} RONO\textsubscript{2} measured at Tai O, in southeast China at the mouth of the Pearl River Delta (PRD), the fastest-growing industrial area in the world (Wang et al., 2003). The Tai O measurements are the first long-term RONO\textsubscript{2} record from Asia, and they are used to investigate the sources of RONO\textsubscript{2} sampled at Tai O; characterize seasonal pollution patterns; investigate seasonally high air pollution episodes; and investigate the relationship between ozone and summed RONO\textsubscript{2} (\( \sum \text{RONO}_2 \)).

2. Experimental

The Tai O experimental station (22°N, 114°E, 168 m elevation) is a coastal site on the west coast of Lantau Island, about 30 km west of central Hong Kong at the mouth of the PRD where it joins the South China Sea (Fig. 1). Northeastery winds prevail during winter, and the site is frequently impacted by urban pollution plumes originating from China, often superimposed with fresh emissions from Hong Kong. During summer, southerly winds prevail and the site receives cleaner air from the tropical Pacific Ocean and South China Sea. Local emissions from Tai O are small because of the sparse population and light traffic to the area. More site details are found in Wang et al. (2003).

Between 24 August 2001 and 31 December 2002, 187 whole air samples were collected at Tai O as part of a multidisciplinary study of air quality in the Hong Kong area that also included measurements of O\textsubscript{3}, NO\textsubscript{y}, nitric oxide (NO), carbon monoxide...
(CO), sulfur dioxide (SO$_2$), and meteorological parameters. Each whole air sample was collected over a 1-min period into a conditioned, evacuated 2-L stainless steel canister. Our sampling strategy emphasized pollution episodes during which samples were taken every 2 h during the daytime (between 7 a.m. and 7 p.m.). These intensive sampling periods occurred on 17–19 October 2001, 29–30 August 2002, 5–6 September 2002, 9–11 October 2002, 25 October 2002, 6–8 November 2002, and 12 November 2002. The 6–8 November episode captured the highest hourly O$_3$ levels ever recorded in Hong Kong (203 ppbv). Samples were taken either daily or every few days throughout the remainder of the study, typically in the mid-afternoon.

The whole air samples were analyzed for seven C$_1$–C$_5$ RONO$_2$, 42 C$_2$–C$_{10}$ nonmethane hydrocarbons (NMHCs), 26 C$_1$–C$_2$ halocarbons and three sulfur compounds at the University of California, Irvine (UCI), using techniques described in Colman et al. (2001) and Simpson et al. (2003). Briefly, the RONO$_2$ were detected using gas chromatography (GC, HP-6890) with electron capture detection (ECD), and the C$_2$–C$_{10}$ NMHCs were detected using GC with flame ionization detection (FID). The trace gases in each sample were preconcentrated by passing 1520 ± 1 cm$^3$ (STP) of canister air through a stainless steel tube filled with glass beads (1/8-inch diameter) and immersed in liquid nitrogen. A mass flow controller with a maximum allowed flow of 500 mL min$^{-1}$ controlled the trapping process. The trace gases were revolatilized using a hot water bath and then reproducibly split into five streams. Each stream was directed to a different column–detector combination, two of which were used to analyze the RONO$_2$ (a Restek-1701 column, and a DB-5 column connected in series to a Restek-1701 column). The mixing ratios determined from both column–detector combinations were averaged to give a single mixing ratio for each sample.

A primary RONO$_2$ standard was prepared at NCAR from commercially purchased or laboratory-synthesized RONO$_2$ diluted into humidified zero air. Secondary standards of whole air were run every four samples during the analysis and were...
compared to quantitative flow dilutions of the primary RONO$_2$ standard. Assignment of the RONO$_2$ mixing ratios in the primary standard was based on a combination of FID response and GC with atomic emission detection. The standard scale is currently being re-evaluated against several newly prepared RONO$_2$ mixtures. For each RONO$_2$, the mixing ratios obtained from either column showed excellent correlation ($r^2 = 0.94–0.99$). The RONO$_2$ mixing ratios obtained from the Restek-1701 column were on average 5–12% higher than those from the DB-5/Restek-1701 column, and the standard measurements were used to adjust any deviation from a 1:1 slope during the final calibration. The RONO$_2$ measurement precision is 3% for mixing ratios above 5 parts per trillion by volume (pptv) and 5% for mixing ratios below 5 pptv. The measurement accuracy is 5–10% for MeONO$_2$, EtONO$_2$ and 2-PrONO$_2$, and 10–20% for 1-propyl nitrate (1-PrONO$_2$), 2-BuONO$_2$, 2-pentyl nitrate (2-PeONO$_2$) and 3-pentyl nitrate (3-PeONO$_2$). The detection limit is 0.01 pptv.

The sampling inlets, instrumentation and calibration for O$_3$, NO, NO$_y$ and CO measurements are described in Wang et al. (2003). Briefly, O$_3$ was measured using a commercial UV photometric instrument (Thermo-Environmental Instruments (TEI), Model 49), and NO and NO$_y$ were detected using a modified commercial MoO/chemiluminescence analyzer (TEI, Model 42S). Data were collected every second and averaged to 1-min values. Carbon monoxide was measured with a gas filter correlation, nondispersive infrared analyzer (API, Model 300) with a heated catalytic scrubber to convert CO to carbon dioxide (CO$_2$) for baseline determination. The O$_3$ analyzer has a detection limit of 2 ppbv and a 2σ precision of 2 ppbv for a 2-min average. The NO/NO$_y$ analyzer has a detection limit of 0.05 ppbv, a 2σ precision of 4%, and an uncertainty of about 10%.

3. Results and discussion

3.1. General features

The general features of the Tai O RONO$_2$ and their parent hydrocarbons are summarized in Table 1. Each reported RONO$_2$ was present at levels above its detection limit in every sample. As expected, minimum values were larger for the longer-lived RONO$_2$ (MeONO$_2$ and EtONO$_2$) compared to the shorter-lived species. Even though RONO$_2$ have a strong marine source, the maximum values were sampled during air pollution episodes (Section 3.2).

The C$_3$–C$_4$ RONO$_2$ were the most abundant in the Tai O air samples (Table 1). In photochemical RONO$_2$ production, the branching ratios leading to RONO$_2$ formation increase with increasing carbon number (Atkinson et al., 1982; Arey et al., 2001), but the ambient mixing ratios of parent n-alkanes decrease with increasing carbon number. The net effect of these two factors is maximum photochemical production of C$_3$–C$_4$ RONO$_2$, in particular 2-PrONO$_2$ and 2-BuONO$_2$. By contrast, oceans are the dominant source of MeONO$_2$ and, to a lesser extent, EtONO$_2$ (e.g. Blake et al., 2003a). Here the relative abundance of C$_3$–C$_4$ RONO$_2$ at Tai O indicates the importance of photochemical (rather than marine) RONO$_2$ production in air masses transported to this site.

The range of RONO$_2$ mixing ratios measured at Tai O was similar to that measured by our group between 0 and 2 km in early spring 2001 during the Transport and Chemical Evolution over the Pacific (TRACE-P) field campaign, flown off the Asian coast (Simpson et al., 2003). The mean and median RONO$_2$ mixing ratios were 1.6–2.1 times higher at Tai O than during TRACE-P, which is not unexpected given the closer proximity to urban
sources at Tai O and a bias towards sampling during pollution episodes. The similar maximum and minimum values at Tai O and during TRACE-P suggest that both field studies captured the full range of RONO₂ mixing ratios that are typical along the southeast Asian coast.

3.2. Seasonal pattern

The RONO₂ measured at Tai O show a winter maximum and summer minimum (Fig. 2). This pattern is opposite to that observed for polluted air masses at temperate sites in North America and Europe, and happens to match the RONO₂ seasonality that has been observed in photochemically aged air (Section 1). At the subtropical Tai O site, the RONO₂ seasonality is explained by the seasonal wind pattern, which brings polluted air from the east and north in winter, and cleaner marine air from the south in summer (Section 2). Also due to local wind patterns, Flocke et al. (1998a) observed a summer maximum in polluted air masses in Germany, which were transported to the sampling site more frequently during summer than in winter. The seasonal pattern for the RONO₂ is similar to that for other trace gases measured at the Tai O site such as CO, NMHCs, NOₓ, and SO₂ (Wang et al., 2005).

The seasonal RONO₂ pattern at Tai O shows considerable day-to-day variability depending on the intensity of pollution episodes (Fig. 2). The magnitudes of the summer minima at Tai O are similar to those measured at the remote Summit, Greenland site, ranging from 1 to 2 pptv and 0.5 to 1 pptv for 2-PrONO₂ and 2-BuONO₂, respectively (Table 1; Swanson et al., 2003). These low values reflect the clean marine air sampled at Tai O during summer. The maximum RONO₂ mixing ratios at Tai O are within the range of maxima that have been measured at other urban sites. The respective peak 2-PrONO₂ and 2-BuONO₂ mixing ratios at Tai O were 53 and 77 pptv, compared to 34 and 45 pptv in urban samples collected in Karachi, Pakistan during winter (Barletta et al., 2002), and 67 and 79 pptv in fresh Asian outflow measured downwind of Shanghai during the springtime TRACE-P mission (Simpson et al., 2003). Flocke et al. (1998a) measured a higher 2-PrONO₂ maximum of 79 pptv downwind of Freiburg and the Rhine Valley, Germany during summer.

Interestingly MeONO₂ shows the same seasonal pattern as the higher RONO₂, despite the much slower reaction of its parent hydrocarbon methane (CH₄) with OH, compared to parent n-alkanes ≥ C₂. The photochemical production of MeONO₂ at this site is discussed in Section 3.3.2. Blake et al. (2003a) observed high MeONO₂ mixing ratios (up to 50 pptv) in the equatorial Pacific as a result of marine emissions, and lower values (< 6 pptv) to the north of the equatorial enhancements. At Tai O, the lack of MeONO₂ enhancements during the summer (median = 5 pptv between April and August 2002) indicates that the marine air transported to this site was not strongly influenced by oceanic MeONO₂ emissions. Consistent with this, Blake et al. (2003a) found that in the Pacific south of 10°N, marine RONO₂ were emitted in the following ratios: MeONO₂/EtONO₂, 3:1; MeONO₂/2-PrONO₂, 10:1; MeONO₂/2-BuONO₂, 50:1. Here, the average ratios for the summer samples were MeONO₂/ EtONO₂, 2:1; MeONO₂/2-PrONO₂, 1:1; MeONO₂/ 2-BuONO₂, 2:1. These much lower Tai O ratios are typical of NH air masses influenced by urban/industrial emissions (Blake et al., 2003a) and they confirm a lack of strong marine RONO₂ emissions in the Tai O samples.

The C₁–C₅ RONO₂ measured at Tai O comprise a small fraction of NOₓ (0.3–8% during winter and 1–6% during summer; see Table 1). RONO₂ typically comprise less than 10% of NOₓ in continental air masses (e.g. Buhr et al., 1990; Shepson et al., 1993; Talbot et al., 2003)—with reports of 10–20% of NOₓ using a more broad definition of total RONO₂ (Day et al., 2003)—compared to 20–80% in the equatorial marine boundary layer over the Pacific (Talbot et al., 2000; Blake et al., 2003a). At Tai O the low RONO₂ fraction is explained by the wintertime sampling of polluted continental air masses, and the summertime sampling of oceanic air that was not strongly influenced by marine RONO₂ sources.

3.3. Pollution episodes

3.3.1. Maximum O₃ and RONO₂ mixing ratios

The strongest pollution episode of the 16-month study was sampled from 6 to 8 November 2002, with very high levels of parent n-alkanes and high rates of daughter RONO₂ production, especially on 7 November (Fig. 3). The prevailing winds on 7 November were from the east and northeast, and a cold front pushed continental air to the Tai O site. The ratio of ethyne/CO reflects the amount of atmospheric processing (photochemical reaction...
Fig. 2. Alkyl nitrate mixing ratios (pptv) measured at Tai O between August 2001 and December 2002: (A) methyl nitrate; (B) ethyl nitrate; (C) 1-propyl nitrate; (D) 2-propyl nitrate; (E) 2-butyl nitrate; (F) 2-pentyl nitrate; and (G) 3-pentyl nitrate.
Fig. 3. Parent $n$-alkane mixing ratios (circles and solid line) and daughter alkyl nitrate mixing ratios (triangles and dashed line) measured during pollution episode of 6–8 November 2002: (A) methane and methyl nitrate; (B) ethane and ethyl nitrate; (C) propane and 1-propyl nitrate; (D) propane and 2-propyl nitrate; (E) $n$-butane and 2-butyl nitrate; (F) $n$-pentane and 2-pentyl nitrate; and (G) $n$-pentane and 3-pentyl nitrate.
and dynamic mixing) within an air mass (Smyth et al., 1996), decreasing from 4 to 5 pptv/ppbv for freshly polluted air to <1 pptv/ppbv for very processed air (E. Browell, pers. comm., 2002). On 7 November the ethyne/CO ratio decreased from 11.4 pptv/ppbv at 7 a.m. to 2.8 pptv/ppbv at 7 p.m., indicating that the air masses sampled early in the morning were very freshly polluted, whereas those sampled later in the day were increasingly processed.

The highest hourly O₃ level ever recorded in Hong Kong (203 ppbv) was measured during this pollution episode, on 7 November at 4 p.m. The highest 1-PrONO₂ and 2-PrONO₂ mixing ratios of the study (12 and 53 pptv, respectively; Table 1) were also measured on 7 November, at 3 p.m. The mixing ratios of MeONO₂, EtONO₂, 2-BuONO₂, 2-PrONO₂ and 3-PrONO₂ (19, 17, 69, 19 and 16 pptv, respectively) were also strongly elevated in this sample. Whole air samples were collected every 2 h during pollution episodes, whereas O₃ was averaged every minute (Section 2). Therefore, it is possible that the actual RONO₂ maxima occurred closer to 4 p.m. rather than 3 p.m. On the other hand, during a summertime study in Texas, Rosen et al. (2004) observed that the daily total RONO₂ maximum occurred earlier in the afternoon than the O₃ maximum.

Propane mixing ratios were 13.0 ppbv at 7 a.m. on 7 November, and decreased throughout the day to 1.2 ppbv by 7 p.m. (Fig. 3C). By comparison, propane mixing ratios over the western Pacific typically range from 0.5 to 2 ppbv at latitudes comparable to Tai O (Blake et al., 1997). The measured n-butane levels decreased by 94% during the same 12-h period, from 12.8 to 0.8 ppbv (Fig. 3E), and the measured n-pentane levels decreased by 80%, from 1.9 to 0.4 ppbv (Fig. 3F). Daughter RONO₂ are photochemically produced as the parent n-alkane is oxidized (Eqs. (1)–(3)). On 7 November, the 2-PrONO₂, 2-BuONO₂ and 2-PeONO₂ mixing ratios increased at respective average rates of about 4.7, 6.5 and 1.9 pptv h⁻¹ between 7 a.m. and 3 p.m., with maximum increases of 6.0, 7.5 and 2.2 pptv h⁻¹ between 11 a.m. and 3 p.m. Very strong O₃ increases also occurred on 7 November, at an average rate of 25 ppbv h⁻¹ between 7 a.m. and 3 p.m., and 45 ppbv h⁻¹ between 11 a.m. and 3 p.m.

The measured n-alkane decreases on 7 November are much larger than can be accounted for by OH-chemistry alone, which was roughly predicted for the air mass sampled at 7 a.m. using:

\[
[RH] = [RH]_0 e^{-k_A t},
\]

where \( t \) is the elapsed time between parent n-alkane emission and air sampling, and \( k_A \) is \( k_1[OH] \) (Table 2). Although we could not follow this air mass for a Lagrangian analysis, we perform this calculation to test what alkane changes we might have expected for this air mass due to OH oxidation, and whether or not these changes are similar to those observed for upwind air masses that were sampled throughout the day on 7 November.

### Table 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>( k_1 )</th>
<th>( k_2 )</th>
<th>( z_1 )</th>
<th>( z_2 )</th>
<th>( J )</th>
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<tbody>
<tr>
<td>2-BuONO₂</td>
<td>2.44</td>
<td>0.92</td>
<td>0.872</td>
<td>0.084</td>
<td>0.47</td>
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<tr>
<td>2-PrONO₂</td>
<td>4.0</td>
<td>1.85</td>
<td>0.568</td>
<td>0.106</td>
<td>0.46</td>
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<tr>
<td>3-PrONO₂</td>
<td>4.0</td>
<td>1.12</td>
<td>0.349</td>
<td>0.126</td>
<td>0.44</td>
</tr>
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</table>

Units for \( k \): \( \times 10^{-12} \text{cm}^3 \text{molec}^{-1} \text{s}^{-1} \); for \( J \): \( \times 10^{-6} \text{s}^{-1} \).

\( ^a \)Atkinson (1997).

\( ^b \)Atkinson (1990), Atkinson et al. (1997).

\( ^c \)Kwok and Atkinson (1995).


\( ^e \)1 April, 40°N, diurnal \( J \)-value.

The measured RONO₂ mixing ratios of MeONO₂, EtONO₂, 2-BuONO₂, 2-PrONO₂ and 3-PrONO₂ (4.0, 1.12, 0.349, 0.126, 0.44, respectively) were also strongly elevated in this sample. Whole air samples were collected every 2 h during pollution episodes, whereas O₃ was averaged every minute (Section 2). Therefore, it is possible that the actual RONO₂ maxima occurred closer to 4 p.m. rather than 3 p.m. On the other hand, during a summertime study in Texas, Rosen et al. (2004) observed that the daily total RONO₂ maximum occurred earlier in the afternoon than the O₃ maximum.

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\( ^e \)1 April, 40°N, diurnal \( J \)-value.
3.3.2. Photochemical MeONO2 production

In addition to a similar seasonal pattern as the higher RONO2 (Section 3.2), MeONO2 also displayed a similar diurnal pattern. For example, during the 6–8 November pollution episode its daily variations were almost identical to those of the C2–C5 RONO2 (Fig. 3). The highest MeONO2 mixing ratio of the study (24.5 pptv) was measured at 11 a.m. on 6 September 2002 (Table 1). By comparison, Barletta et al. (2002) measured a much lower MeONO2 maximum of 13.3 pptv in urban Karachi, Stroud et al. (2001) measured a MeONO2 maximum of 6.5 pptv over rural Colorado, and Roberts et al. (1998) measured a maximum of 6.5 pptv in Nova Scotia. Global background MeONO2 mixing ratios vary little with latitude in the Northern Hemisphere, and year-round values range from about 3 to 5 pptv (Blake, 2004). Therefore, of the 24.5 pptv MeONO2 measured on 6 September, about 20 pptv is in excess of background values.

Although our group has measured larger MeONO2 mixing ratios in samples influenced by biomass burning or marine RONO2 sources (Simpson et al., 2002; Blake et al., 2003a), the MeONO2 levels at Tai O are the largest that we have measured in urban pollution plumes. Despite very high CH4 levels measured on 6 September at 11 a.m. (3.28 ppmv), CH4 oxidation accounts for only a small fraction of the MeONO2 produced in this air mass. Methane is very long-lived (~8 years; Lelieveld et al., 1998; Karlsdóttir and Isaksen, 2000) compared to the C2–C5 alkanes (days–months), and the photochemical production of its daughter RONO2 is limited in part by the slow production of CH3 during CH4 oxidation:

\[
\text{CH}_4 + \text{OH} \rightarrow \text{CH}_3 \cdot + \text{H}_2\text{O} , \quad k_7 \times x_7, \quad (7)
\]

where \( k_7 = 6.18 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) at 298 K (Atkinson, 1997) and \( x_7 = 1 \) (Kwok and Atkinson, 1995). Applying Eq. (6) using \( [\text{CH}_4]_0 = 3280000 \text{ pptv} \), \( t = 24 \text{ h} \) and assuming a diurnal OH value of \( 2 \times 10^6 \text{ molec cm}^{-3} \) gives CH4 loss of about 3500 pptv after 1 day of photochemical processing. (Ethyne/CO was 5.4 pptv/ppbv in the 11 a.m. air mass—indicating freshly polluted air—and therefore 3.28 ppmv is a good approximation of \([\text{CH}_4]_0\). The reaction described by Eq. (2) is fast and the 3500 pptv of CH3 radicals will be quickly converted to 3500 pptv of CH3O2 radicals. For tropospheric conditions, Flocke et al. (1998b) estimate an upper limit of 0.0003 for the branching ratio \( x_2 \) that leads to MeONO2 formation. Therefore, 3500 pptv of CH3O2 radicals are expected to give rise to no more than about 1 pptv of MeONO2 in 1 day and 7 pptv in 7 days (of which some will be consumed by photolysis). As a result, most of the 20 pptv of excess MeONO2 measured in this pollution plume was formed via alternative photochemistry. A similar calculation for EtONO2 shows that ethane oxidation is not sufficient to explain the 13 pptv of EtONO2 that was measured (ethane oxidation yields roughly 4 pptv of EtONO2 after 1 day and 8 pptv after 7 days). In their German study, Flocke et al. (1998a) also observed higher levels of MeONO2 and EtONO2 than could be explained by Eq. (3b).

For RONO2 \( \leq \text{C}_4 \), oxidation of the parent hydrocarbon is not the only source of daughter RO2 radicals, and instead a significant RO2 fraction is formed from the decomposition of larger alkoxy radicals (Bertman et al., 1995; Flocke et al., 1998a). However, at Tai O this mechanism is insufficient for MeONO2 because of the extremely small \( x_2 \) branching ratio for MeONO2 formation (0.0003), which requires the mixing ratio of CH3O2 radicals to be unreasonably large. A possible alternate pathway for the excess MeONO2 formation is via:

\[
\text{CH}_3\text{O} \cdot + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{ONO}_2 + \text{M}, \quad k_8, \quad (8)
\]

where \( k_8 = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) at 298 K (DeMore et al., 1997). This mechanism is independent of the very small CH4 + OH rate constant and very small CH3O2 + NO branching ratio. Although Eq. (8) is a minor RONO2 formation pathway under normal conditions, Flocke et al. (1998a, b) postulated that a possible exception may be the formation of MeONO2 under very polluted conditions. Because the excess MeONO2 at Tai O is not explained by marine emissions, CH4 oxidation or the decomposition of larger alkoxy radicals, reaction of the methoxy radical with NO2 appears to be the most likely source of MeONO2 in the heavily polluted plumes that were sampled at Tai O. This pathway requires significant amounts of NO2 because of the competing reaction of CH3O with O2 to form formaldehyde (HCHO):

\[
\text{CH}_3\text{O} \cdot + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2, \quad k_9, \quad (9)
\]

where \( k_9 = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \) at 298 K (DeMore et al., 1997). Because the CH3O required for MeONO2 formation also yields HCHO, additional data on chemical composition and conditions at the source, as well as chemical box modeling, are required in order to fully verify whether this
3.3.3. RONO2 relationships with O3

Reactions (1–3), which form RONO2, also produce NO2 and lead to tropospheric O3 formation:

\[
\begin{align*}
\text{NO}_2 + h\nu & \rightarrow \text{NO} + \text{O}, \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}.
\end{align*}
\]

During the seven intensive pollution episodes sampled at Tai O (Section 2, \(n = 79\)), the median O3 mixing ratio was 66 ppbv; the median summed RONO2 mixing ratio \(\sum \text{RONO}_{2,i}\) was \(\text{MeONO}_2 + \text{EtONO}_2 + 1\text{-PrONO}_2 + 2\text{-PrONO}_2 + 2\text{-BuONO}_2 + 2\text{-PeONO}_2 + 3\text{-PeONO}_2\) was 78 pptv, and the median ratio of \(O_3/\sum \text{RONO}_{2,i}\) was 830 pptv/ppbv. Similarly, the average mixing ratio (±1 standard error) was 69±8 ppbv for O3 and 89±10 pptv for \(\sum \text{RONO}_{2,i}\), and their average ratio was 810 pptv/ppbv. A plot of O3 vs. \(\sum \text{RONO}_{2,i}\) during these pollution episodes shows considerable scatter (\(r^2 = 0.46\), though this improves when the seven episodes are considered separately) and, for a linear fit, gives a slope of 655 pptv/ppbv and an intercept of about 11 ppbv O3 for zero RONO2 \(i\) (Fig. 4A).

During the seven pollution episodes, the O3 and \(\sum \text{RONO}_{2,i}\) mixing ratios were lowest in the morning and peaked in the mid-afternoon (e.g. Fig. 5), as expected in response to daytime photochemistry and despite the expansion of the daytime boundary layer. The O3/\(\sum \text{RONO}_{2,i}\) ratio increased during the day, with a wide range of morning values (95–845 pptv/ppbv at 9 a.m.) depending largely on variations in O3 levels. By 3 p.m., when O3 and RONO2 values approached their daily maxima, O3/\(\sum \text{RONO}_{2,i}\) ranged from 520 to 1550 pptv/ppbv. During these pollution episodes the mean O3/\(\sum \text{RONO}_{2,i}\) ratio (±1 standard error) was 440±50 pptv/ppbv at 9 a.m., and 1030±115 pptv/ppbv at 3 p.m. Consistent with our results, O3/\(\sum \text{RONO}_{2,i}\) vs. ethyne/CO shows considerable scatter but an overall negative relationship (Fig. 4B). (From Section 3.3.2, the ratio of ethyne/CO decreases as an air mass becomes increasingly photochemically processed.) Using thermal dissociation-laser-induced fluorescence (TD-LIF), Rosen et al. (2004) also observed an increasing slope for O3 vs. total RONO2 from morning to afternoon. However, because the TD-LIF measurements include other RONO2 species not measured in our canisters (i.e. total RONO2 > \(\sum \text{RONO}_{2,i}\)), they observed a smaller O3/RONO2 ratio. Bearing in mind the scatter in our data, these results suggest a
rough O$_3$/RONO$_2$ ratio of 500:1 in very freshly polluted plumes (ethyne/CO~6–8 pptv/ppbv), and a higher O$_3$/RONO$_2$ ratio on the order of 1000:1 in freshly polluted plumes (ethyne/CO~3–5 pptv/ppbv). Though the O$_3$/RONO$_2$ ratios show a large range, the similar diurnal variations of O$_3$ and RONO$_2$ during pollution episodes show that RONO$_2$ can be used as indicators of photochemical O$_3$ production.

The O$_3$/RONO$_2$ relationships measured at Tai O were compared with those measured during an encounter with a fresh, well-defined pollution plume over the East China Sea at an altitude of 330 m during the springtime TRACE-P mission. Backward trajectories showed that the air mass had encountered Shanghai 18 h prior to sampling, and a high ethyne/CO ratio (5.0–9.4 pptv/ppbv) confirmed that the plume had been very recently polluted (Simpson et al., 2003). A plot of O$_3$ vs. RONO$_2$ showed excellent correlation ($r^2 = 0.96; n = 7$) with a slope of 496 pptv/pptv and an intercept of 25 ppbv O$_3$ for zero RONO$_2$. This slope agrees remarkably well with that measured in the most freshly polluted plumes at Tai O (ethyne/CO~6–8 pptv/ppbv). That
is, the O\textsubscript{3} vs. \(\sum\text{RONO}_{2,j}\) relationship shows robustness for young air masses collected in a similar region during different seasons. Rosen et al. (2004) also found remarkably similar agreement for \(\text{O}_x = (\text{O}_3 + \text{NO}_2)\) vs. \(\sum\text{RONO}_{2,j}\) measured in Texas and in Germany (Flocke et al., 1998a). By contrast, we expect a poorer agreement in other instances. For example, at Tai O there were several cases of high \(\sum\text{RONO}_{2,j}\) at low \(\text{O}_3\) (Fig. 4A), which we believe is due to titration of \(\text{O}_3\) by \(\text{NO}\):

\[
\text{O}_3 + \text{NO} \rightarrow \text{O}_2 + \text{NO}_2.
\]  

In other environments, \(\text{O}_3\) formation from biogenic hydrocarbon emissions (e.g. isoprene) is expected to greatly affect the measured \(\text{O}_3\) vs. total \(\text{RONO}_2\) ratios (Day et al., 2003). Therefore, despite the good agreement between Tai O and TRACE-P, we do not suggest applying the \(\text{O}_3/\sum\text{RONO}_{2,j}\) relationships measured at Tai O quantitatively to other studies before preliminary \(\text{O}_3\) vs. \(\sum\text{RONO}_{2,j}\) comparisons are made.

4. Conclusions

Mixing ratios of seven C\textsubscript{1}–C\textsubscript{5} RONO\textsubscript{2} were recorded during a 16-month study (August 2001–December 2002) at Tai O, a coastal site in southeast China located about 30 km west of central Hong Kong. Prevailing northeasterly winds during autumn and winter often brought polluted continental air from Hong Kong and mainland China to the site, whereas prevailing southerly winds during spring and summer transported cleaner marine air to Tai O. Photochemical (rather than marine) production is the dominant RONO\textsubscript{2} source at this site.

MeONO\textsubscript{2} is a tracer of marine RONO\textsubscript{2} production, and a lack of MeONO\textsubscript{2} enhancement during summer indicates that the South China Sea is not a region of strong RONO\textsubscript{2} emission. Interestingly, MeONO\textsubscript{2} showed a similar diurnal and seasonal pattern to the higher RONO\textsubscript{2}. MeONO\textsubscript{2} levels during pollution episodes reached 25 pptv and were the highest we have measured during urban photochemical RONO\textsubscript{2} production. Marine emissions, methane oxidation and the decomposition of longer-chain alkoxy radicals do not fully account for the high MeONO\textsubscript{2} levels. Rough calculations, which require confirmation from modeling studies, show that methoxy radical reaction with NO\textsubscript{2} appears to be a viable alternate pathway for MeONO\textsubscript{2} production in polluted atmospheres.

The strongest pollution episode of the study was measured on 7 November 2002, during which ozone reached the highest level ever recorded in Hong Kong (203 ppbv). The maximum 2-PrONO\textsubscript{2} and 2-BuONO\textsubscript{2} mixing ratios on 7 November were 53 and 69 pptv, respectively, and the 2-PrONO\textsubscript{2} and 2-BuONO\textsubscript{2} levels increased by 6 and 7.5 pptv h\textsuperscript{-1}, respectively, between 11 a.m. and 3 p.m. Ozone and summed RONO\textsubscript{2} showed similar diurnal variations during pollution episodes, indicating that RONO\textsubscript{2} can be used as tracers of photochemical \(\text{O}_3\) production from anthropogenic precursors. We observed an \(\text{O}_3/\sum\text{RONO}_{2,j}\) ratio on the order of 500:1 in very freshly polluted air (ethyne/CO\textsuperscript{~}6–8 pptv/ppbv) and 1000:1 in freshly polluted air (ethyne/CO\textsuperscript{~}3–5 pptv/ppbv). However, we do not recommend applying these relationships quantitatively elsewhere, in cases where either \(\text{O}_3\) or RONO\textsubscript{2} measurements are not available, without a better understanding of how \(\text{O}_3/\sum\text{RONO}_{2,j}\) varies in different environments.

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