https://doi.org/10.1016/j.atmosenv.2015.08.083

Re-examination of C_1-C_5 alkyl nitrates in Hong Kong using an observation-based model

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Abstract: The photochemical formation of alkyl nitrates ($RONO_2$) and their impact on ozone (O_3) formation were investigated using a Photochemical Box Model incorporating the Master Chemical Mechanism (PBM-MCM). The model was constrained with field measurement data collected on selected O_3 episode days at Tai O, a rural-coastal site in southwestern Hong Kong, from August 2001-December 2002. The in-situ observations showed that the sum of C_1-C_5 $RONO_2$ varied from 30.7±14.8 pptv in spring to 120.7±10.4 pptv in autumn, of which 2-butyl nitrate dominated with the highest average concentration of 30.8±2.6 pptv. Model simulations indicated that the pathway of CH_3O reacting with NO_2, proposed in our previous study, made minor contributions (11.3±0.7%) to methyl nitrate formation. Indeed, 51.8±3.1% and 36.5±6.3% of the methyl nitrate was attributed to the reaction of CH_3O_2+NO and to oceanic emissions/biomass burning, respectively. For the C_2-C_5 alkyl nitrates, the contribution of photochemical formation increased with increasing carbon number, ranging from 64.4±4.0% for ethyl nitrate ($EtONO_2$) to 72.6±4.2% for 2-pentyl nitrate (2-$PenONO_2$), while the contribution of oceanic emissions/biomass burning decreased from 35.1±6.5% for $EtONO_2$ to 26.8±6.8% for 2-$PenONO_2$. Model simulations of photochemical O_3 levels influenced by $RONO_2$ chemistry showed that the formation of methyl-, ethyl-, *i*-propyl-, *n*-propyl-, 2-butyl-, 2-pentyl-, and 3-pentyl-nitrates led to O_3 reduction of 0.05±0.03, 0.05±0.03, 0.06±0.02, 0.02±0.02, 0.18±0.04,

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0.09±0.02 and 0.06±0.02 ppbv, respectively, with an average reduction rate of 11.0±3.2 ppbv O_3 per 1 ppbv $RONO_2$ formation. The C_1-C_5 $RONO_2$ constituted 18.6±1.9% of the entire $RONO_2$, and had a nitrogen reserve of 4.1±0.2%, implying their potential influence on O_3 production in downwind areas.

Keywords: alkyl nitrate; photochemical formation; O_3 production; PBM-MCM model; field observation

1. Introduction

Photochemical pollution characterized by elevated O_3 in the troposphere (Guo et al., 2013a; Wang et al., 2009) is of increasing concern in megacities, such as the city cluster in the Pearl River Delta (PRD) region, where huge emissions of O_3 precursors, *i.e.,* volatile organic compounds (VOCs) and nitrogen oxides (NO_x) from industries and traffic have caused intense periods of high photochemical O_3 formation (Cheng et al., 2010; Ling et al., 2011) notably in the autumn period. Alkyl nitrates ($RONO_2$) are formed as byproducts in the process of O_3 formation, and are also temporary reservoirs of nitrogen. However, to date there have been few studies on the influence of individual alkyl nitrate on the O_3 budget (Wang et al., 2013; Williams et al., 2014).

There are 5 key gas phase reactions in the troposphere, (1)–(5), for the production and destruction of alkyl nitrates:

$$RO_2 + NO \rightarrow RONO_2, \alpha \quad (1)$$

$$RO + NO_2 \rightarrow RONO_2 \quad (2)$$

$$RO_2 + NO \rightarrow RO + NO_2, (1-\alpha) \quad (3)$$

$$RONO_2 + h\nu \rightarrow RO + NO_2 \quad (4)$$

$$RONO_2 + OH \rightarrow R'C(O)R'' + NO_2 \quad (5)$$

The photochemical formation of $RONO_2$ is mainly attributed to reactions (1) and (2) (Atkinson et al., 1982; Wang et al., 2013). Alternative pathways, *i.e.,* reactions between organic aerosols and particle-phase nitrates, and NO_3 initiated oxidation of RO_2 at nighttime, also contribute to

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photochemical $RONO_2$ production (Worton et al., 2010). Studies (Jenkin et al., 2000; Suarez-Bertoa et al., 2012) indicate that reaction (1) contributes most to ambient $RONO_2$ and becomes increasingly important with increasing carbon number of the RO_2 species, because the decomposition rate of the vibrationally-excited $RONO_2$ decreases with increased complexity of the alkyl (R) group, hence the survival of stabilized $RONO_2$ increases (Atkinson et al., 1983). If the vibrationally-excited $RONO_2$ is not formed, an oxygen atom (O) exchange between RO_2 and NO will occur, *i.e.,* reaction (3). The branching ratio (α) is often used to define the relative reactivity of reaction (1) competing with the reaction (3) (Flocke et al., 1998; Farmer et al., 2011). In contrast to the formation pathway of reaction (1), the production efficiency of $RONO_2$ from reaction (2), *i.e.,* $RO+NO_2$, decreases with increasing carbon number because of the increasing tendency of isomerization and decomposition of RO, and relatively lower abundance of RO compared to the methoxy radical (CH_3O) as the carbon number increases (Atkinson et al., 1982; Williams et al., 2014).

As well as photochemical formation, equatorial oceans (Atlas et al., 1993; Blake et al., 2003) are a primary source of ambient $RONO_2$, particularly for light ($<C_2$) $RONO_2$. Blake et al. (2003) reported that methyl nitrate ($MeONO_2$) was significantly emitted from tropical and subtropical oceans, which was an important source of excess $MeONO_2$ that cannot be explained by photochemical formation. Additionally, biomass burning is also a source of $RONO_2$, for which Simpson et al. (2002) proposed a formation mechanism in the combustion stage involving the combination of RO_2 to generate RO and the reaction of RO with NO_2.

Since $RONO_2$ are formed simultaneously with O_3, they are good tracers of photochemical pollution (Simpson et al., 2006; Aruffo et al., 2014). They also affect O_3 production by interfering with the NO_x budget as temporary nitrogen reservoirs (Aruffo et al., 2014). The availability of reactive nitrogen will be reduced through reactions (1) and (2) due to the long atmospheric lifetimes of $RONO_2$ (Atlas, 1988). Moreover, the RO generated from reaction (3) decreases, resulting in the loss of OH and HO_2. These will reduce the potential for O_3 production. On the other hand, the formation of $RONO_2$ competes with the reaction of O_3 titration by NO. As a temporary reservoir of reactive NO_x, $RONO_2$ can also release RO and NO_2 through photolysis (reaction (4)) and OH-initiated oxidation (reaction (5)) (Aschmann et al., 2011; He et al., 2011). The additional NO_2, secondary organic degradation products (*i.e.,* PANs, aldehydes, ketones, etc.)

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and radicals (*i.e.,* RO_2, HO_2, OH, etc.) consequently promote the photochemical production of O_3. During the process of $RONO_2$ degradation, OH and HO_2 are consumed and their recycling is strongly dependent on the reactivity of the carbonyls generated from the oxidation of RO (Derwent et al., 2005). It remains uncertain whether $RONO_2$ make positive or negative contributions to O_3 formation, and what differences there are between individual alkyl nitrate species.

In this study, PBM-MCM model was adapted to investigate the photochemical formation of C_1-C_5 $RONO_2$ and their impacts on O_3 production at Tai O, a rural-coastal site in southwestern Hong Kong. Using the same dataset, Simpson et al. (2006) reported the mixing ratios and seasonal patterns of the observed $RONO_2$, the potential formation pathways of $MeONO_2$ and the correlation between the sum of C_1-C_5 $RONO_2$ and O_3. Here alternative formation pathways of $MeONO_2$ were examined, and the correlations between $RONO_2$ and O_3 were fully developed by quantifying the impacts of the C_1-C_5 $RONO_2$ formation on the net O_3 production.

2. Experimental

2.1 Sample collection and chemical analysis

From 24th Aug. 2001 to 31st Dec. 2002, a multi-pollutant sampling campaign was conducted at Tai O, a rural-coastal site in southwestern Hong Kong. Figure 1 shows the geographical location of the sampling site (22.25°N, 113.85°E). Local emissions are not predominant at this site due to the low traffic and population density. Tai O is located approximately 30 km to the west of the urban center of Hong Kong, 30 km to the east of Macau, and at the mouth of Pearl River Estuary. This site is influenced by air pollution from the PRD region, particularly enhanced in the cooler autumn-winter seasons when northeastern winds passing over the PRD region and Hong Kong urban areas dominate. Conversely, air pollution from the PRD is less evident during the prevailing summer southerly winds bringing in fresh air and diluting the air pollution. Full details about the sampling site and field campaign are available in Wang et al. (2005) and Simpson et al. (2006).

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Figure 1. Geographical location of the Tai O sampling site and environs. The red star = Tai O, orange blocks = urban areas, and pink dots represent the population distributions.

Whole air VOC samples were collected using evacuated 2-L stainless steel canisters, which were preprocessed with 10 Torr of degassed, distilled water to quench the active surface sites of the inner walls. The canisters were cleaned and evacuated following the procedures described in Simpson et al. (2006) prior to sampling. Each whole air sample was collected through a valve for 1 min. to ensure that the canister was fully filled. After sampling, the canisters were shipped to the University of California, Irvine (UCI) for chemical analysis. Totally, mixing ratios of 7 C_1-C_5 $RONO_2$, 42 nonmethane hydrocarbons (NMHCs), 26 halocarbons and 3 reduced sulfur compounds were determined. Details on the analysis techniques, detection limits and quality control strategies are given in Colman et al. (2001) and Simpson et al. (2006). It is important to note that the $RONO_2$ were calibrated with a new scale in 2008 that applied a factor of 2.13, 1.81, 1.24, 1.17 and 1.13 to C_1, C_2, C_3, C_4 and C_5 $RONO_2$. This scale was provided by Atlas (University of Miami), and accepted by the analytical team (UCI) (Simpson et al., 2011).

The measurement techniques for trace gases, *i.e.*, CO, NO, NO_y, SO_2 and O_3 are fully described in Wang et al. (2003a). Briefly, CO was thermally catalyzed to CO_2, and then measured with a gas filter correlation, non-dispersive infrared analyzer (Advanced Pollution Instrumentation, Inc., Model 300); NO and NO_y were detected with a modified commercial MoO/chemiluminescence analyzer (Thermo-Environmental Instruments, Inc. (TEI), Model 42S) that converted NO_y to NO on the surface of MoO, and then NO was quantified by the chemiluminescent analyzer; SO_2 was measured by pulsed UV fluorescence (TEI, Model 43S); and a commercial UV photometric instrument (TEI, Model 49) was used to detect the O_3 mixing ratios. The detection limits of CO, NO, NO_y, SO_2 and O_3 were 30, 0.05, 0.05, 10 and 2 ppbv, respectively.

2.2 Model description

2.2.1 PMF model

Based on the chemical mass balance between measured species concentrations and source profiles, Positive Matrix Factorization (PMF) treats the measured concentration of species, *j,* in sample *i* (x_{ij}) as the sum of contributions from *p* sources, which can be decomposed as

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contribution, G and source profile, F, as shown in the following equation (eqn. 1): (Paatero, 1997):

$$x_{ij} = \sum_{k=1}^{p} g_{ik} f_{kj} + e_{ij} \quad \text{eqn. 1}$$

where g_{ik} is the species contribution of the kth source to the ith sample, f_{kj} is the species fraction in the kth source and e_{ij} is the residual associated with species j in sample i. Details on the PMF operation is provided in Guo et al. (2011).

2.2.2 PBM-MCM model

The PBM-MCM is a photochemical box model combined with a near-explicit chemical mechanism, which has been successfully applied in previous studies (Lam et al., 2013; Ling et al., 2014). Details on the model construction can be found in Lam et al. (2013) and the mechanism in Saunders et al. (2003) and Jenkin et al. (2003). Briefly, field measurement data, *i.e.*, VOCs, SO_2, CO, NO, NO_2, O_3, temperature and relative humidity, are used to construct the model. The model considers photochemical processes appropriate to the planetary boundary layer (PBL) and comprises the chemical mechanism (MCMv3.2) involving around 5,900 species and 16,500 reactions. The reactions are homogeneous in the boundary layer and no vertical/ horizontal dispersion is considered. To achieve appropriate simulation for the region, the model has been developed and adjusted for Hong Kong (Lam et al., 2013; Ling et al., 2014). For example, the boundary layer is set to vary between 300-1400 m according to actual autumn conditions in Hong Kong, while the photolysis rates are determined using the photon fluxes from the Tropospheric Ultraviolet and Visible Radiation (TUVv5) Model (Madronich and Flocke, 1997) as a function of the location of Hong Kong and time period of the campaign. The concentrations of stable species above the boundary layer, *i.e.*, $RONO_2$, peroxyacetylnitrate-type compounds (PANs) and carbonyls, are set based on the previous application of the model in Hong Kong (Lam et al., 2013). These species exist in the aloft layer (the free troposphere above PBL) and are entrained in PBL during the morning as the boundary layer expands. However, this is a natural mixing process involving molecular movement, but not physical process like wind or vertical exchange. Further details can be found in Lam et al. (2013).

In this study, the field observations of 69 parameters consisting of 2 meteorological factors (*i.e.,* temperature and relative humidity), 5 trace gases (*i.e.,* SO_2, CO, O_3, NO and NO_2), 61 non-

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172 methane VOCs and CH_4 were used to constrain the model. Five O_3 episode days (*i.e.*, 11th and
173 25th Oct., 2002 and 06th-08th Nov. 2002) were selected from the whole sampling campaign, in
174 order to study the photochemical formation of C_1-C_5 $RONO_2$ and their impacts on net O_3
175 production. The hourly data required for the PBM-MCM input were only available on these 5
176 days, and they are representative of autumn conditions when high photochemical pollution
177 frequently occurs. The first hourly (*i.e.*, 07:00) data were used to initiate the model simulations.
178 The model was run in a base case (BC) and two constrained cases (CC_1 and CC_2). Details on the
179 model configuration are provided in Table 1.

180 Table 1 Model configuration of the base case and constrained cases

181

182 It is noteworthy that NO_2 was obtained from the difference between NO and NO_y because NO_y
183 detected by the MoO/chemiluminescence analyzer approximately equals NO_x when the air mass
184 is greatly affected by fresh emissions (Xu et al., 2013). In this study, ~90% of air masses were
185 identified as freshly emitted polluted air, with ethyne/CO > 4 pptv/ppbv according to the method
186 proposed by Smyth (1996). In addition, the ratios of propane/ethane (1.3±0.2), ethene/ethane
187 (0.9±0.1) and toluene/benzene (7.4±0.6) at Tai O on the five episode days were comparable to
188 those at an urban site in Hong Kong (1.0±0.1, 1.1±0.1 and 7.3±1.2 for propane/ethane,
189 ethene/ethane and toluene/benzene, respectively) (Guo et al. 2007), further confirming that Tai O
190 was significantly influenced by fresh emissions during the episodes. Furthermore, PANs and
191 $RONO_2$ were only ~7% of NO_2, as indicated in section 3.3.2 "Nitrogen partitioning". Therefore,
192 the slightly-overestimated NO_2 would not significantly influence $RONO_2$ formation.

193

194 ## 3. Results and discussion

195 ### 3.1 Mixing ratios and seasonal patterns of $RONO_2$

196 Table 2 shows the mean levels of O_3, C_1-C_5 $RONO_2$ and their parent hydrocarbons at Tai O
197 over the whole sampling period, with 95% confidence intervals. It was found that the average
198 mixing ratios of $RONO_2$ ranged from 4.0±0.4 pptv for *n*-$PrONO_2$ to 30.8±2.6 pptv for 2-
199 $BuONO_2$. Inconsistently, the *n*-butane mixing ratio (1893±586 pptv) was the second lowest

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among the parent hydrocarbons, while the parent hydrocarbon of *n*-$PrONO_2$ (*i.e.* propane) ranked the second highest with an average mixing ratio of 2392±740 pptv. This suggested that $RONO_2$ not only relates to the abundance, but also the reaction pathways and reactivity of the parent hydrocarbon (Atlas et al., 1993; Blake et al., 2003), as well as primary emissions.

Similar seasonal patterns were observed for the sum of C_1-C_5 $RONO_2$ and O_3, *i.e.*, higher in autumn and lower in spring, suggesting the importance of photochemical formation of $RONO_2$. The average mixing ratios of the sum of C_1-C_5 $RONO_2$ were 30.7±14.8, 74.9±23.8, 120.7±10.4 and 91.2±8.8 pptv in spring, summer, autumn and winter, respectively. Similar to $RONO_2$, the average mixing ratio of O_3 also peaked in autumn (68.4 ± 8.0 ppbv). Indeed, the sum of C_1-C_5 $RONO_2$ correlated well with O_3 (R^2 = 0.71), and for $MeONO_2$ (R^2 = 0.62). However, inconsistent with the observation that O_3 had lowest mixing ratios in winter (25.1±5.7 ppbv), $RONO_2$ levels in winter were the second highest among the four seasons (91.2±8.8 pptv), implying possible $RONO_2$ sources from oceanic emissions and/or biomass burning. Therefore, the pathway contributions to $RONO_2$ were determined in the following section (3.2).

Table 2 Statistics of C_1-C_5 $RONO_2$ and O_3 at Tai O over the whole sampling period (mean±95% confidence interval) (units: pptv unless otherwise specified)

3.2 Pathways to $RONO_2$

Since the PBM-MCM is a chemical model without the consideration of primary emissions, the primary emission of $RONO_2$ should be eliminated before the model simulation. Here, the hourly C_1-C_5 $RONO_2$ mixing ratios were applied in PMF analysis for source apportionment (Guo et al., 2013b). Figure 2 shows the profiles of three sources extracted by PMF. Factor 1 is distinguished by high loadings of O_3 and $RONO_2$, likely to represent the secondary formation of $RONO_2$. Additionally, moderate percentages of methyl chloride (CH_3Cl) were observed in this factor. Apart from oceanic sources, CH_3Cl can be emitted from biomass burning (Rudolph et al., 1995), another source of $RONO_2$. Although $RONO_2$ is formed secondarily in the combustion stage of biomass burning, its formation mechanism is quite different from that in the normal atmosphere (Simpson et al., 2002). Therefore, CH_3Cl in this factor may indicate $RONO_2$ formation in the stage of plume transport, rather than $RONO_2$ formed in the combustion stage of biomass burning. Factor 2 has high loadings of dimethyl sulfide (DMS) and bromoform ($CHBr_3$), which are typical tracers of marine outflows (Nowak et al., 2001; Atlas et al., 1993). In addition, the

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moderate percentages of CH_3Cl and C_2-C_5 hydrocarbons may indicate $RONO_2$ formed in the combustion stage of biomass burning. Therefore, this factor is assigned to be the source of marine and biomass burning. Factor 3 shows weak associations with $RONO_2$, with the dominance of anthropogenic VOCs. However, DMS also has a high loading in this factor, which may imply the mixture of marine flows with anthropogenic emissions. This is not unreasonable given that Tai O is a coastal site adjacent to the South China Sea (see Figure 1). As such, $RONO_2$ in factor 3 is thought to be associated with oceanic emissions as well as anthropogenic emissions.

Figure 2 Profiles for the sources of $RONO_2$ at Tai O. The errors were estimated with the Bootstrap method integrated in PMF.

With the exclusion of oceanic sources and biomass burning, the secondarily/photochemically formed $RONO_2$ was used to construct and constrain the PBM-MCM model. Figure 3 presents the simulated and observed O_3 and secondary $RONO_2$. It can be seen that the model reasonably simulated the variations of daytime O_3 and $RONO_2$, *i.e.*, the values increased in the morning, peaked in early afternoon and decreased in late afternoon. The simulated results well captured the observed low and high values (standard deviation, SD < ±30%) except for O_3, $MeONO_2$ and *n*-$PrONO_2$ on November 7, 2002 when the simulated maximums were ~ 40%-50% lower than the observations. This may be caused by the source apportionment of $RONO_2$ and O_3 by PMF, which averaged the hourly contributions of each factor, and may underestimate/overestimate the extremely high/low values. In addition, for most cases, the model simulations did not well track the rapid decrease of $RONO_2$ in the afternoon, probably due to the fact that the physical processes, *i.e.*, vertical and horizontal dispersion were not considered in the PBM-MCM model (Lam et al., 2013; Ling et al., 2011).

Figure 3 Simulated and observed O_3 and secondary $RONO_2$ at Tai O on episode days.

To further evaluate the model performance, the index of agreement (IOA) was used to examine the correlation between simulated and observed results (Wang et al., 2015; Jiang et al., 2010). The IOA value is between 0 and 1, and a higher IOA represents better agreement. The IOA is determined as follows (Huang et al., 2005):

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$$\mathrm{IOA} = 1 - \frac{\sum_{i=1}^{n}(O_i - S_i)^2}{\sum_{1i=1}^{n}(|O_i - \bar{O}| + |S_i - \bar{O}|)^2}$$

where O_i, S_i, and $\bar{O}$ refer to the hourly observed value, simulated value, and the average observed value, respectively.

Table 3 summarizes the IOAs for the simulation of O_3 and C_1-C_5 $RONO_2$. Good to moderate agreements were found between the simulated and observed values, indicating the performance of this model was reasonably acceptable.

Table 3 IOAs of O_3 and C_1-C_5 $RONO_2$ between simulated and observed values

Furthermore, the relative contribution of the two reaction pathways, *i.e.* "RO_2+NO" and "RO+NO_2", to the secondary $RONO_2$ can be determined with the model running in BC and CC_1 (see model description, section 2.2.2). Taking $MeONO_2$ as an example, the reaction of "CH_3O_2+NO" and "CH_3O+NO_2" contributed 82.2±2.5% and 17.8±2.5% to the secondary $MeONO_2$, respectively. This contradicts the hypothesis proposed by Simpson et al. (2006) and verified by Archibald et al. (2007), that the reaction of CH_3O and NO_2 may constitute a major part of $MeONO_2$ at Tai O. It is well recognized that the most competitive reaction to "CH_3O+NO_2" is the oxidation of CH_3O by O_2, forming HCHO and HO_2. Here, it was found that the reactivity of CH_3O oxidized by O_2 was approximately four orders of magnitude (*i.e.* ~0.8×10^4) higher than that of CH_3O reacting with NO_2. On the other hand, the production of HCHO only increased by ~0.1% when closing off the reaction of "CH_3O+NO_2", suggesting that the reaction of CH_3O with NO_2 is not competitive with the oxidation of CH_3O. Moreover, inconsistent with the kinetic calculation by Simpson et al. (2006), the model well reproduced the secondary $MeONO_2$. It is noteworthy that the branching ratio (α) of CH_3O_2 reacting with NO to form $MeONO_2$ was 0.001 (Carter and Atkinson, 1989) in MCM protocol, rather than 0.0003 used by Simpson et al. (2006). Additionally, CH_3O_2 considered in the kinetic calculations only involves the OH-initiated oxidation of CH_4. Indeed, the sources of CH_3O_2 are complicated, *e.g.* photolysis of acetaldehyde and oxidation of CH_4 by chloride and OH. Model simulations indicated that OH-initiated oxidation of CH_4 only contributed 46.7±2.9% of CH_3O_2 in the $MeONO_2$ formation. Namely, the production of CH_3O_2 in the kinetic calculation was underestimated, causing the deficit in $MeONO_2$. Archibald et al. (2007) verified the pathway of

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"CH_3O+NO_2", and indicated that it became dominant at NO_2 >35 ppbv. In this study, NO_2 reached 40.1±5.1 ppbv. However, the contribution of "CH_3O+NO_2" to $MeONO_2$ was not the foremost (*i.e.*, 17.8±2.5%). Even when the NO_2 level increased by 10 ppbv, the contribution only increased to 18.7±2.6%. It should be noted that the model Archibald et al. (2007) used was a simplified version of the MCM 2.0 with a carbon bond mechanism, and the inputs were European profiles of VOCs and NO_x, and not the observations in Hong Kong, which may cause the discrepancies.

Based on the source apportionment and pathway contributions to photochemical $RONO_2$ formation, the relative contributions of oceanic emissions and possible biomass burning, "RO_2+NO" and "$RO+NO_2$" can be determined, as shown in Table 4. It was found that the contribution of oceanic emission and biomass burning decreased from 36.5±6.3% for $MeONO_2$ to 26.8±6.8% for 2-$PenONO_2$, except for *n*-$PrONO_2$ (25.8±6.9%), consistent with the observations in marine outflows. For photochemical formation, the reaction of CH_3O_2+NO was predominant, and the relative contribution increased with increasing carbon number of $RONO_2$ except for *n*-$PrONO_2$. This is mainly due to the increase of branching ratio leading to $RONO_2$ formation from 0.001 for $MeONO_2$ to 0.131 for 3-$PenONO_2$, and to some extent related to the abundance of RO_2. For example, the possibility of hydrogen (H) extraction on the second and third carbon of *n*-pentane is 0.568/0.349 by OH and 0.558/0.220 by chlorine (Cl), causing a higher contribution of "RO_2+NO" to 2-$PenONO_2$ compared to 3-$PenONO_2$, although the branching ratio leading to 2-$PenONO_2$ formation is slightly lower (0.129). Then, the pathway contribution of "$RO+NO_2$" to $MeONO_2$ was much higher than that to C_2-C_5 $RONO_2$. This could be attributable to the abundance of CH_3O originating from the oxidation of CH_4 and decomposition of larger RO_2 radicals.

Table 4 Pathway contributions to C_1-C_5 $RONO_2$ during O_3 episodes at Tai O (unit: %)

3.3 Impact on O_3 formation

3.3.1 Net O_3 production

$RONO_2$ chemistry influences the budget of NO_x and atmospheric radicals, thus influencing the variations in O_3 . With the model simulation of BC and CC_2 (see model description, 2.2.2), the

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net O_3 production induced by $RONO_2$ formation was determined, as shown in Figure 4. Overall, the $RONO_2$ formation made negative contributions to O_3, with the average reduction of 0.05±0.03, 0.05±0.03, 0.06±0.02, 0.02±0.02, 0.18±0.04, 0.09±0.02 and 0.06±0.02 ppbv for the formation of $MeONO_2$, $EtONO_2$, *i*-$PrONO_2$, *n*-$PrONO_2$, 2-$BuONO_2$, 2-$PenONO_2$ and 3-$PenONO_2$, respectively. The average O_3 reduction induced by each $RONO_2$ formation correlated well (R^2=0.93) with the concentrations of photochemically formed $RONO_2$. The average O_3 reduction rate was –11.0±3.2 ppbv/ppbv. Namely, O_3 was reduced by 11.0±3.2 ppbv per ppbv $RONO_2$ formation. Although $RONO_2$ is generally present as a minor constituent (*i.e.* magnitude of pptv), the effect of $RONO_2$ formation on O_3 reduction in urban areas cannot be neglected. For example, on 07 November, 2002, the maximum O_3 reduction caused by the total C_1-C_5 $RONO_2$ reached 2.7 ppbv (~4.4%) at 13:00. On the other hand, not all $RONO_2$ were considered in this study due to analytical limitations. Based on the model simulations, the C_1-C_5 $RONO_2$ contributed only 18.6±1.9% of the entire $RONO_2$ (*i.e.* alkyl and multifunctional nitrates), implying that the potential of $RONO_2$ formation on O_3 reduction was underestimated.

Figure 4 Net O_3 production induced by C_1-C_5 $RONO_2$ formation at Tai O

To explore the mechanism of O_3 reduction induced by $RONO_2$ formation, the variation of NO_x, HO_x and the O_3 were studied in detail. Taking 2-$BuONO_2$ as an example, Figure 5 shows the temporal variation of each species caused by the formation of 2-$BuONO_2$. In general, the OH, HO_2 and O_3 levels decreased with obvious diurnal variations, while no regular variations were found for NO_2 and NO. Moreover, the average O_3 reduction rate increased nearly linearly with the reduction of HO_x (R^2=0.99) and the increase of NO (R^2=0.94), suggesting that O_3 formation was in the VOC-limited regime. Generally, OH consumed by VOC oxidation can be recycled from the oxidation of RO. However, this pathway was constrained due to the formation of $RONO_2$, therefore the HO_2 and OH generated from the oxidation of RO decreased, and subsequently O_3 was reduced.

Figure 5 Variations of NO_2, NO, HO_2, OH and O_3 induced by 2-$BuONO_2$ formation.

3.3.2 Nitrogen partitioning

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As a temporary reservoir of nitrogen, $RONO_2$ contributes to O_3 production in downwind regions through the release of NO_2. Therefore, quantifying the role of $RONO_2$ in the nitrogen budget is essential to estimating its impact on O_3 production in remote areas. Figure 6 shows the mixing ratios of sinks (*i.e.* HNO_3) and temporary reservoirs (*i.e.* PANs, $RONO_2$, N_2O_5 and NO_3) of nitrogen, as simulated by the PBM-MCM model. It is noteworthy that the entire $RONO_2$ included alkyl and multifunctional nitrates here, PANs included the total peroxyacyl nitrates, and HONO was not considered as it decomposes quickly in the daytime. It was found that PANs, $RONO_2$ and HNO_3 increased from the morning and reached their maximums in the afternoon or at dusk. As the most important nitrogen reservoirs, PANs, $RONO_2$ and HNO_3 accounted for 53.0±4.1%, 29.8±4.9% and 12.8±0.5% of the total reserved nitrogen, respectively. For NO_3 and N_2O_5, they began to build up from the late afternoon (*i.e.* 16:00-17:00) due to their poor stabilities in sunlight, constituting 0.5±0.3% and 3.9±2.0% of the total reserved nitrogen, respectively.

It is noticeable that variations of the entire $RONO_2$ was consistent with those of the C_1-C_5 $RONO_2$ (see Figure 3), indicating similar formation mechanisms for all $RONO_2$. The C_1-C_5 $RONO_2$ accounted for 18.6±1.9% of the entire $RONO_2$, which means that 4.1±0.2% nitrogen was stored in the C_1-C_5 $RONO_2$. It should be noted that most $RONO_2$ have much longer lifetimes than PANs, causing longer and higher O_3 formation in the remote atmosphere due to the transport of $RONO_2$ and continual release of NO_2. This needs further study, beyond the scope of the present work, for example by undertaking continuous sampling in both the upwind (*i.e.* $RONO_2$ formation) and downwind (*i.e.* $RONO_2$ degradation) regions.

Figure 6 Time series of reserved nitrogen at daytime hours on episode days at Tai O

4. Conclusions

In this study, data from a comprehensive field measurement campaign, conducted from August 2001 to December 2002 at Tai O, a coastal site in Hong Kong, was used to investigate the pathways leading to C_1-C_5 $RONO_2$ and their impacts on O_3 formation. The sum of C_1-C_5 $RONO_2$ were the highest in autumn and correlated well with O_3, suggesting the importance of

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photochemical formation. Evaluation of the Hong Kong PBM-MCM model constrained with the field data gave good to moderate agreement between observed and simulated secondary C_1-C_5 $RONO_2$ and O_3. The model was further applied to quantify the contribution of each pathway to C_1-C_5 $RONO_2$. In contrast with previous suggestions, the reaction of CH_3O with NO_2 was not the major pathway for $MeONO_2$ formation, accounting for only 11.3±0.7% of the total $MeONO_2$, while the pathway of CH_3O_2 reacting with NO and oceanic emission /biomass burning contributed 51.8±3.1% and 36.5±6.3% to the total $MeONO_2$, respectively. From $EtONO_2$ to $PenONO_2$, the contribution to $RONO_2$ made by photochemical formation increased, while that of oceanic/biomass burning emissions decreased. Studies on the relationship between net O_3 production and $RONO_2$ formation indicated that $RONO_2$ formation limited O_3 formation due to the decrease of OH and HO_2. The average O_3 reduction rate was –11.0±3.2 ppbv O_3 per ppbv $RONO_2$. Although $RONO_2$ is a minor component of NO_y, the impact of total $RONO_2$ on O_3 reduction cannot be neglected. Moreover, the nitrogen reserved in $RONO_2$ (4.1±0.2%) may continue to contribute to O_3 formation in downwind areas. These findings enhance our knowledge on the influence of individual $RONO_2$ species on O_3 production.

Acknowledgements

This study was supported by the Research Grants Council of the Hong Kong Special Administrative Region via grants PolyU5154/13E and PolyU152052/14E, and the Hong Kong Polytechnic University Ph.D. scholarships (project #RTUP). This study is partly supported by the Public Policy Research Funding Scheme (2013.A6.012.13A) and the National Natural Science Foundation of China (No. 41405112). We appreciate Prof. Blake's group at the University of California at Irvine for the chemical analysis of the whole air VOC samples.

References

Archibald, A.T., Khan, M.A.H., Watson, L.A., Utembe, S.R., Shallcross, D.E., Clemitshaw, K.C., Jenkin, M.E., 2007. Comment on 'Long-term atmospheric measurements of C_1-C_5 alkyl nitrates in the Pearl River Delta region of southeast China' by Simpson et al.. Atmos. Environ. 41, 7369-7370.

Aruffo, E., Carlo, P.D., Dari-Salisburgo, C., Biancofiore, F., Giammaria, F., Busilacchio, M., Lee, J., Moller, S., Hopkins, J., Punjabi, S., Bauguitte, S., O'Sullivan, D., Percival, C., Breton, M.L., Muller, J., Jones, R., Forster, G., Reeves, C., Heard, D., Walker, H., Ingham, T., Vaughan, S., Stone, D., 2014.

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405 Aircraft observations of the lower troposphere above a megacity: Alkyl nitrate and O_3 chemistry.
406 Atmos. Environ. 94, 479-488.

407 Aschmann, S.M., Tuazon, E.C., Arey, J., Atkinson, R., 2011. Products of the OH radical-initiated
408 reactions of 2-propyl nitrate, 3-methyl-2-butyl nitrate and 3-methyl-2-pentyl nitrate. Atmos. Environ.
409 45, 1695-1701.

410 Atkinson, R., Aschmann, S.M., Carter, W.P.L., Winer, A.M., Pitts, J.N., 1982. Alkyl nitrate formation
411 from the nitrogen oxide (NO_x)-air photooxidations of C_2-C_8 n-alkanes. J. Phys. Chem. 86, 4563-4569.

412 Atkinson, R., Carter, W.P.L., Winer, A.M., 1983. Effects of Temperature and Pressure on Alkyl Nitrate
413 Yields in the NO_x Photooxidations of +Pentane and n-Heptane. J. Phys. Chem. 87, 2012-2018.

414 Atlas, E., 1988. Evidence for $\geq C_3$ alkyl nitrates in rural and remote atmospheres. Nature 331, 426-428.

415 Atlas, E., Pollock, W., Greenberg, J., Heidt, L., Thompson, A.M., 1993. Alkyl nitrates, nonmethane
416 hydrocarbons, and halocarbon gases over the equatorial Pacific Ocean during SAGA-3, J. Geophys.
417 Res. 98, 16933-16947.

418 Blake, N.J., Blake, D.R., Swanson, A.L., Atlas, E., Flocke, F., Rowland, F.S., 2003. Latitudinal, vertical
419 and seasonal variations of the C_1-C_4 alkyl nitrates in the troposphere over the Pacific Ocean during
420 PEM-Tropics A and B: Oceanic and continental sources. J. Geophys. Res. 108, 8284,
421 http://dx.doi.org/10.1029/2001JD001444.

422 Cheng, H.R., Guo, H., Saunders, S.M., Lam, S.H.M., Jiang, F., Wang, X.M., Simpson, I.J., Blake, D.R.,
423 Louie, P.K.K., Wang, T.J., 2010. Assessing photochemical O_3 formation in the Pearl River Delta with a
424 photochemical trajectory model. Atmos. Environ. 44, 4199-4208.

425 Colman, J.J., Swanson, A.L., Meinardi, S., Sive, B.C., Blake, D.R., Rowland, F.S., 2001. Description of
426 the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-
427 Tropics A and B. Anal. Chem. 73, 3723-3731.

428 Derwent, R.G., Jenkin, M.E., Saunders, S.M., Pilling, M.J., Passant, N.R., 2005. Multi-day O_3 formation
429 for alkenes and carbonyls investigated with a master chemical mechanism under European conditions.
430 Atmos. Environ. 39, 627-635.

431 Farmer, D.K., Perring, A.E., Wooldridge, P.J., Blake, D.R., Baker, A., Meinardi, S., Huey, L.G., Tanner,
432 D., Vargas, O., Cohen, R.C., 2011. Impact of organic nitrates on urban O_3 production. Atmos. Chem.
433 Phys. 11, 4085-4094.

434 Flocke, F., Volz-Thomas, A., Buers, H.J., Patz, W., Garthe, H.J., Kley, D., 1998. Long-term
435 measurements of alkyl nitrates in southern Germany 1. General behavior and seasonal and diurnal
436 variation. J. Geophys. Res. 103, 5729-5746.

437 Guo, H., Cheng, H.R., Ling, Z.H., Louie, P.K.K., Ayoko, G., 2011. Which emission sources are
438 responsible for the volatile organic compounds in the atmosphere of Pearl River Delta?. J. Hazard.
439 Mater. 188, 116-124.

440 Guo, H., Ling, Z.H., Cheung, K., Jiang, F., Wang, D.W., Simpson, I.J., Barletta, B., Meinardi, S., Wang,
441 T.J., Wang, X.M., Saunders, S.M., Blake, D.R., 2013a. Characterization of photochemical pollution at
442 different elevations in mountainous areas in Hong Kong. Atmos. Chem. Phys. 13, 3881-3898.

*Corresponding author. Tel: 852 3400 3962; Fax: 852 2334 6389; Email: ceguohai@polyu.edu.hk

443 Guo, H., Ling, Z.H., Cheung, K., Wang, D.W., Simpson, I.J., Blake, D.R., 2013b. Acetone in the
444 atmosphere of Hong Kong: Abundance, sources and photochemical precursors. Atmos. Environ. 65,
445 80-88.

446 Guo, H., So, K.L., Simpson, I.J., Barletta, B., Meinardi, S., Blake, D.R., 2007. C_1-C_8 volatile organic
447 compounds in the atmosphere of Hong Kong: Overview of atmospheric processing and source
448 apportionment. Atmos. Environ. 41, 1456-1472.

449 He, S.Z., Chen, Z.M., Zhang, X., 2011. Photochemical reactions of methyl and ethyl nitrate: a dual role
450 for alkyl nitrates in the nitrogen cycle. Environ. Chem. 8, 529-542.

451 Huang, J.P., Fung, J.C.H., Lau, A.K.H., Qin, Y., 2005. Numerical simulation and process analysis of
452 typhoon-related O_3 episodes in Hong Kong. J. Geophys. Res. 110,
453 http://dx.doi.org/10.1029/2004JD004914.

454 Jenkin, M.E., Clemitshaw, K.C., 2000. Ozone and other secondary photochemical pollutants: chemical
455 processes governing their formation in the planetary boundary layer. Atmos. Environ. 34, 2499-2527.

456 Jenkin, M.E., Saunders, S.M., Wagner, V., Pilling, M.J., 2003. Protocol for the development of the
457 Master Chemical Mechanism, MCM v3 (Part B): tropospheric degradation of aromatic volatile organic
458 compounds. Atmos. Chem. Phys. 3, 181-193.

459 Jiang, F., Guo, H., Wang, T.J., Cheng, H.R., Wang, X.M., Simpson, I.J., Ding, A.J., Saunders, S.M., Lam,
460 S.H.M., Blake, D.R., 2010. An O_3 episode in the Pearl River Delta: Field observation and model
461 simulation. J. Geophys. Res. 115, http//dx.doi.org/10.1029/2009JD013583.

462 Lam, S.H.M., Saunders, S.M., Guo, H., Ling, Z.H., Jiang, F., Wang, X.M., Wang, T.J., 2013. Modelling
463 VOC source impacts on high ozone episode days observed at a mountain summit in Hong Kong under
464 the influence of mountain-valley breezes. Atmos. Environ. 81, 166-176.

465 Ling, Z.H., Guo, H., Cheng, H.R., Yu, Y.F., 2011. Sources of ambient volatile organic compounds and
466 their contributions to photochemical O_3 formation at a site in the Pearl River Delta, southern China.
467 Environ. Pollut. 159, 2310-2319.

468 Ling, Z.H., Guo, H., Lam, S.H.M., Saunders, S.M., Wang, T., 2014. Atmospheric photochemical
469 reactivity and ozone production at two sites in Hong Kong: Application of a Master Chemical
470 Mechanism-photochemical box model. J. Geophys. Res. Atmos. 119, 10567-10582.

471 Madronich, S., Flocke, S., 1997. Theoretical estimation of biologically effective UV radiation at the
472 Earth's surface. In: Zerefos, C. (Ed.), Solar Ultraviolet Radiation-Modeling, Measurements and Effects,
473 NATO ASI Series, vol. I52. Springer-Verlag, Berlin.

474 Nowak, J.B., Davis, D.D., Chen, G., Eisele, F.L., Mauldin III, R.L., Tanner, D.J., Cantrell, C., Kosciuch,
475 E., Bandy, A., Thornton, D., Clarke, A., 2001. Airborne observations of DMSO, DMS, and OH at
476 marine tropical latitudes. Geophys. Res. Lett. 28, 2201-2204.

477 Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. Chemom. Intell. Lab.
478 Sys. 37, 23-35.

479 Saunders, S.M., Jenjin, M.E., Derwent, R.G., Pilling, M.J., 2003. Protocol for the development of the
480 Master Chemical Mechanism, MCM v3 (Part A): tropospheric degradation of non-aromatic volatile
481 organic compounds. Atmos. Chem. Phys. 3, 161-180.

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Simpson, I.J., Akagi, S.K., Barletta, B., Blake, N.J., Choi, Y., Diskin, G.S., Fried, A., Fuelberg, H.E., Meinardi, S., Rowland, F.S., Vay, S.A., Weinheimer, A.J., Wennberg, P.O., Wiebring, P., Wisthaler, A., Yang, M., Yokelson, R.J., Blake, D.R., 2011. Boreal forest fire emissions in fresh Canadian smoke plumes: C_1-C_{10} volatile organic compounds (VOCs), CO_2, CO, NO_2, NO, HCN and CH_3CN. Atmos. Chem. Phys. 11, 6445-6463.

Simpson, I.J., Meinardi, S., Blake, D.R., Blake, N.J., Rowland, F.S., Atlas, E., Flocke, F., 2002. A biomass burning source of C_1-C_4 alkyl nitrates. Geophys. Res. Lett. 29(24), 2168, http://doi:10.1029/2002GL016290.

Simpson, I.J., Wang, T., Guo, H., Kwok, Y.H., Flocke, F., Atlas, E., Meinardi, S., Rowland, F.S., Blake, D.R., 2006. Long-term atmospheric measurements of C_1-C_5 alkyl nitrates in the Pearl River Delta region of southeast China. Atmos. Environ. 40, 1619-1632.

Symth, S., Bradshaw, J., Sandholm, S., Liu, S., Mckeen, S., Gregory, G., Anderson, B., Talbot, R., Blake, D., Rowland, S., Browell, E., Fenn, M., Merrill, J., Backmeier, S., Sachse, G., Collins, J., Thornton, D., Davis, D., Singh, H., 1996. Comparison of free trospheric western Pacific air mass classification schemes for the PEM-West A experiment. J. Geophys. Res. 101, 1743-1762.

Suarez-Bertoa, R., Picquet-Varrault, B., Tamas, W., Pangui, E., Doussin, J.F., 2012. Atmospheric Fate of a Series of Carbonyl Nitrates: Photolysis Frequencies and OH-Oxidation Rate Constants. Environ. Sci. Technol. 46, 12502-12509.

Wang, M., Shao, M., Chen, W.T., Lu, S.H., Wang, C., Huang, D.K., Yuan, B., Zeng, L.M., Zhao, Y., 2013. Measurements of C_1–C_4 alkyl nitrates and their relationships with carbonyl compounds and O_3 in Chinese cities. Atmos. Environ. 81, 389-398.

Wang, N., Guo, H., Jiang, F., Ling, Z.H., Wang, T., 2015. Simulation of O_3 formation at different elevations in mountainous area of Hong Kong using WRF-CMAQ model. Sci. Total Environ. 505, 939-951.

Wang, T., Guo, H., Blake, D.R., Kwok, Y.H., Simpson, I.J., Li, Y.S., 2005. Measurements of Trace Gases in the Inflow of South China Sea Background Air and Outflow of Regional Pollution at Tai O, Southern China. J. Atmos. Chem. 52, 295-317.

Wang, T., Poon, C.N., Kwok, Y.H., Li, Y.S., 2003. Characterizing the temporal variability and emission patterns of pollution plumes in the Pearl River Delta of China. Atmos. Environ. 37, 3539-3550.

Wang, T., Wei, X.L., Ding, A J., Poon, C.N., Lam, K.S., Li, Y.S., Chan, L.Y., Anson, M., 2009. Increasing surface O_3 concentrations in the background atmosphere of Southern China, 1994–2007. Atmos. Chem. Phys. 9, 6217-6227.

Williams, J.E., Bras, G.L., Kukui, A., Ziereis, H., Brenninkmeijer, A.M., 2014. The impact of the chemical production of methyl nitrate from the NO + CH_3O_2 reaction on the global distributions of alkyl nitrates, nitrogen oxides and tropospheric O_3: a global modelling study. Atmos. Chem. Phys. 14, 2363-2382.

Worton, D.R., reeves, C.E., Penkett, S.A., Sturges, W.T., Slemr, J., Oram, D.E., Bandy, B.J., Bloss, W.J., Carslaw, N., Davey, J., Emmerson, K.M., Gravestock, T.J., Hamilton, J.F., Heard, D.E., Hopkins, J.R., Hulse, A., Ingram, T., Jacob, M.J., Lee, J.D., Leigh, R.J., Lewis, A.C., Monks, P.S., Smith, S.C., 2010. Alkyl nitrate photochemistry during the tropospheric organic chemistry experiment. Atmos. Environ. 44, 773-785.

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523 Xu, Z., Wang, T., Xue, L.K., Louie, P.K.K., Luk, C.W.Y., Gao, J., Wang, S.L., Chai, F.H., Wang, W.X.,
524 2013. Evaluating the uncertainties of thermal catalytic conversion in measuring atmospheric nitrogen
525 dioxide at four differently polluted sites in China. Atmos. Environ. 76, 221-226.

*Corresponding author. Tel: 852 3400 3962; Fax: 852 2334 6389; Email: ceguohai@polyu.edu.hk