

UC Irvine

UC Irvine Previously Published Works

Title

Diurnal profiles of isoprene, methacrolein and methyl vinyl ketone at an urban site in Hong Kong

Permalink

<https://escholarship.org/uc/item/74z5x75j>

Authors

Cheung, K
Guo, H
Ou, JM
[et al.](#)

Publication Date

2014-02-01

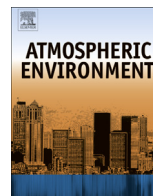
DOI

10.1016/j.atmosenv.2013.11.056

Copyright Information

This work is made available under the terms of a Creative Commons Attribution License, available at <https://creativecommons.org/licenses/by/4.0/>

Peer reviewed



Diurnal profiles of isoprene, methacrolein and methyl vinyl ketone at an urban site in Hong Kong



K. Cheung^a, H. Guo^{a,*}, J.M. Ou^a, I.J. Simpson^b, B. Barletta^b, S. Meinardi^b, D.R. Blake^b

^a Air Quality Studies, Department of Civil and Environmental Engineering, Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong

^b Department of Chemistry, University of California-Irvine, Irvine, CA, USA

HIGHLIGHTS

- Isoprene primarily originated from local biogenic emissions.
- Higher isoprene levels were observed on days when average daily temperature was above 30 °C.
- Traffic emissions and biogenic emissions were the major contributors to MACR/MVK.
- The use of MACR/MVK to represent the isoprene oxidation rate is inappropriate in urban Hong Kong.

ARTICLE INFO

Article history:

Received 26 July 2013

Received in revised form

6 November 2013

Accepted 25 November 2013

Keywords:

Isoprene oxidation products

Methacrolein

Methyl vinyl ketone

Hong Kong

ABSTRACT

Methacrolein (MACR) and methyl vinyl ketone (MVK) are major oxidation products of isoprene, but they also have primary emissions in urban environments, for example from fuel use. To examine whether MACR and MVK could be used as a direct measurement of the oxidation rate of isoprene in an urban setting, the diurnal variations of isoprene, MACR and MVK were characterized at an urban site in Hong Kong from September to November, 2010. Ozone (O₃), carbon monoxide (CO), sulfur dioxide (SO₂), and nitrogen oxides (NO_x) were simultaneously monitored. The average isoprene mixing ratio was 252 ± 204 pptv, with a bell-shaped distribution observed on most sampling days. Higher levels of isoprene were recorded in the beginning of the sampling period, when the temperature was higher. The average mixing ratios of MACR and MVK were 101 ± 85 pptv and 175 ± 131 pptv, respectively. While isoprene, MACR and MVK experienced peak concentrations from 11 a.m. to 3 p.m., increased levels of MACR and MVK during the morning rush hour did not coincide with isoprene. The low associations between isoprene and MACR/MVK suggest that either MACR/MVK were not formed from local isoprene oxidation and/or they could partly originate from primary emissions such as fuel evaporation or combustion. Statistical analyses of linear regression and positive matrix factorization revealed that approximately 20–29% of the measured MACR and MVK was associated with biogenic emissions, and 55–71% was impacted by vehicular emissions, particularly during morning rush hours. Since MACR and MVK originated from both primary emissions and biogenic emissions at this urban site, they can therefore overestimate the actual rate of isoprene oxidation and its contribution to O₃ production in urban areas with strong primary emissions.

© 2013 Elsevier Ltd. All rights reserved.

1. Introduction

Biogenic volatile organic compounds (BVOCs) are emitted in substantial quantities from certain types of terrestrial vegetation, and are believed to play an important role in ozone (O₃) chemistry in forests (Makar et al., 1999), mountains (Dreyfus et al., 2002), semi-rural (Starn et al., 1998) and urban areas (Biesenthal and

Shepson, 1997; Fuentes et al., 2000). Isoprene (2-methyl-1,3-butadiene, C₅H₈), with an annual global emission of about 500–750 Tg, is the single highest VOC emission in the troposphere (Guenther et al., 2006). Based on measurements in 2006, biogenic sources are the biggest emission source category for VOCs in the Pearl River Delta (PRD) region of China, where air pollution has been severe due to the rapid growth of industries and population since the 1980s (Zheng et al., 2009). In particular, isoprene is the single highest VOC contributor to ozone formation potential, accounting for 15%. In Hong Kong, a highly urbanized and densely populated city, BVOCs have been shown to account for 8.8 μg m⁻³

* Corresponding author. Tel.: +852 3400 3962; fax: +852 2334 6389.

E-mail addresses: ceguohai@polyu.edu.hk, hai.guo@polyu.edu.hk (H. Guo).

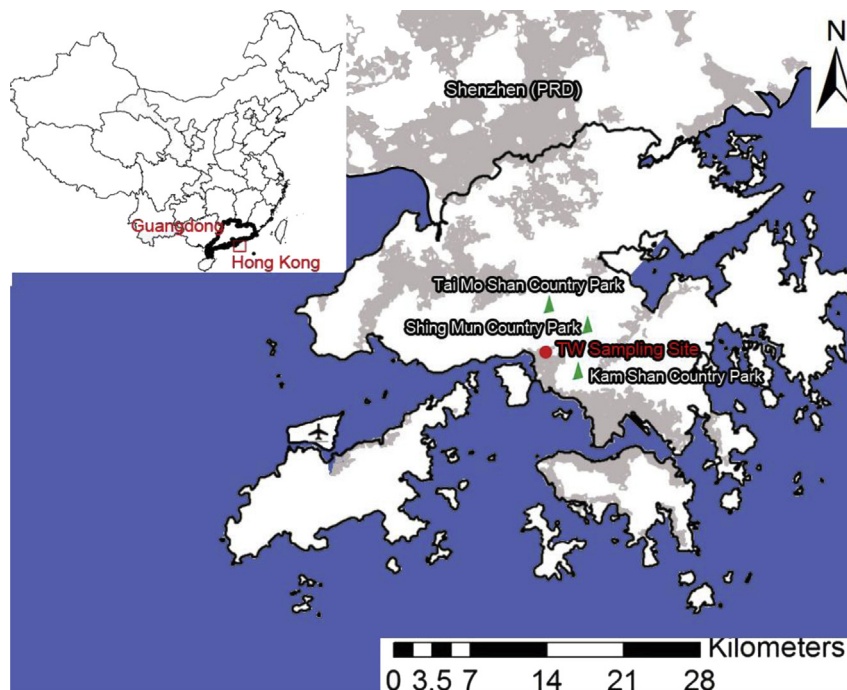


Fig. 1. Map of the sampling site (TW) and its surrounding environments. The highly developed areas are in gray, and Kowloon is located 7–15 km southeast of TW.

(49%) of ambient $PM_{2.5}$ -bounded organic carbon content on days under regional transport influences, compared to $0.99 \mu g m^{-3}$ (21%) on days under mainly local emission influences (Hu et al., 2008). Given the significant contribution of BVOCs to both O_3 and SOA formation in urban areas and on a regional scale, the implications of photochemical oxidation of BVOCs need to be considered and understood for the development of effective air quality regulations.

The main removal pathway of isoprene is reaction with OH radicals during daytime and with O_3 and NO_3 radicals at night (Brown et al., 2009). In high NO_x environments, formaldehyde, MVK and MACR are the major primary oxidation products of isoprene, accounting for more than 50% of the carbon yield (Carter and Atkinson, 1996; Miyoshi et al., 1994; Zhao et al., 2004). Many previous studies have used ratios of isoprene and its oxidation products, such as MVK/MACR and $[MVK + MACR]/isoprene$, to investigate the magnitude and location of isoprene emission sources (Guo et al., 2012; Karl et al., 2007; Barket et al., 2004; Yokouchi, 1994; Stroud et al., 2001). In particular, MVK and MACR have been used to estimate isoprene's contribution to O_3 formation at a semi-rural site in British Columbia, Canada (Biesenthal et al., 1997) and at an urban forested site in Nashville, Tennessee, USA (Starn et al., 1998). The potential use of MVK/MACR as a direct measurement of the actual oxidation rate of isoprene allows the estimation of isoprene's contribution to O_3 production (Guo et al., 2012; Biesenthal and Shepson, 1997). However, MVK and MACR can also originate from primary emission sources including automobile exhaust (Yokouchi, 1994; Biesenthal and Shepson, 1997). Therefore, in urban areas with strong anthropogenic sources, the use of MVK/MACR to represent the isoprene oxidation rate may not be reliable due to the additional contributions of MVK/MACR from primary emissions.

Diurnal variations and species correlations at a particular site can contain information about the dominant local sources and chemical processes. Although many studies have reported time-series profiles of BVOCs in the PRD region (Li and Wang, 2012; Tang et al., 2007), limited information is available on the diurnal

profile of isoprene oxidation products, particularly in urban areas in close proximity to fresh primary emissions. In this paper, the diurnal profiles of isoprene, MVK and MACR are studied at an urban site in Hong Kong and used to identify their sources and formation mechanisms. The goal of the paper is to examine the sources of MVK and MACR, and determine whether MVK/MACR is a reliable tool to represent the oxidation rate of isoprene in an urban area with local primary emissions.

2. Materials and methods

2.1. Sampling description

The Hong Kong Environmental Protection Department (HKEPD) air quality monitoring station at Tsuen Wan (TW) is used to characterize VOCs in an urban area (Fig. 1). Tsuen Wan District, located in the New Territories of Hong Kong, has an area of $60.7 km^2$ with a population of around 300,000 in 2011; it is a mixed residential, commercial and light industrial district. The sampling site ($22.373^\circ N$, $114.112^\circ E$) is adjacent to major roadways and surrounded by residential and industrial blocks. Previous studies have shown that vehicular exhaust is the predominant emission source of polycyclic aromatic hydrocarbons (Sin et al., 2003) and total non-methane hydrocarbons (NMHCs) (Guo et al., 2004b) at this site.

The sampling campaign lasted from September to November 2010, the season when O_3 levels are generally highest due to the long range transport of pollution-laden continental air masses, strong photochemical activity, and/or meteorological conditions that favor the accumulation of atmospheric pollutants (Chan et al., 1998; Leung and Zhang, 2001). In this study, hourly VOC samples were collected on selected O_3 episode days (Oct. 24, 29–31; Nov. 1–3, 9 and 19) and non-episode days (Sep. 28, Oct. 2, 8, 14, 18–19, 27–28; Nov. 20–21). During the sampling period, O_3 levels were predicted based on weather forecasts and meteorological data such as temperature, wind speed and vertical mixing conditions. An episode day was defined when the highest hourly O_3 level

Table 1

Overall statistics of SO₂, O₃, CO and NO, NO₂, isoprene, MVK & MACR at the Tsuen Wan (TW) sampling site for data collected between September and November, 2010. Ozone episode days (see Section 2.1) are highlighted in bold.

	SO ₂ (ppbv)	CO (ppbv)	O ₃ (ppbv)	NO (ppbv)	NO ₂ (ppbv)	Isoprene (pptv)	MACR (pptv)	MVK (pptv)
28-Sep	6.5 ± 5.1	402 ± 95	10.2 ± 5.8	63.7 ± 30	31.9 ± 8.7	579 ± 215	71 ± 35	83 ± 39
2-Oct	3.3 ± 0.2	427 ± 80	20.9 ± 9.3	33.9 ± 8.3	29.9 ± 5.5	556 ± 261	103 ± 44	146 ± 69
8-Oct	5.2 ± 1.1	665 ± 46	34.4 ± 13	21.5 ± 11	34.7 ± 7.1	285 ± 157	121 ± 46	212 ± 94
14-Oct	2.4 ± 0.2	492 ± 64	25.1 ± 9.2	26.3 ± 7.6	28.9 ± 5.6	492 ± 248	148 ± 122	194 ± 130
18-Oct	4.2 ± 0.7	635 ± 86	30.1 ± 18	26.2 ± 19	31.9 ± 11	462 ± 263	91 ± 60	204 ± 163
19-Oct	4.8 ± 0.5	512 ± 35	23.6 ± 4.4	23.1 ± 3.5	25.6 ± 1.8	360 ± 219	86 ± 29	206 ± 116
24-Oct	4.8 ± 2.0	478 ± 33	44.2 ± 23	12.4 ± 10	22.6 ± 2.5	275 ± 127	135 ± 57	207 ± 71
27-Oct	5.4 ± 1.2	487 ± 76	29.7 ± 13	18.8 ± 7.1	20.4 ± 5.5	110 ± 61	57 ± 18	177 ± 52
28-Oct	5.6 ± 0.3	480 ± 43	35.2 ± 8.4	18.7 ± 7.1	25.4 ± 5.8	105 ± 54	68 ± 43	152 ± 80
29-Oct	7.2 ± 0.7	545 ± 32	44.1 ± 16	18.0 ± 9.4	28.6 ± 3.9	149 ± 57	56 ± 32	104 ± 54
30-Oct	9.7 ± 1.0	684 ± 21	46.3 ± 14	16.5 ± 6.9	28.6 ± 4.2	130 ± 50	64 ± 30	89 ± 29
31-Oct	7.3 ± 1.5	668 ± 65	42.8 ± 10	13.5 ± 5.1	30.3 ± 10	144 ± 66	55 ± 38	131 ± 73
1-Nov	6.1 ± 1.3	630 ± 90	39.7 ± 15	21.6 ± 7.0	36.3 ± 9.8	170 ± 54	94 ± 68	154 ± 69
2-Nov	5.9 ± 1.1	661 ± 68	45.2 ± 19	22.0 ± 17	34.9 ± 11	175 ± 64	90 ± 45	181 ± 99
3-Nov	5.9 ± 0.7	673 ± 53	32.7 ± 11	25.9 ± 12	36.0 ± 7.0	140 ± 68	132 ± 85	254 ± 112
9-Nov	8.7 ± 3.3	725 ± 128	30.0 ± 21	37.2 ± 31	42.7 ± 15	230 ± 101	174 ± 181	270 ± 237
19-Nov	7.5 ± 3.2	766 ± 39	27.4 ± 22	21.9 ± 11	41.8 ± 13	300 ± 391	142 ± 68	230 ± 128
20-Nov	3.3 ± 0.4	683 ± 88	17.5 ± 7.1	34.5 ± 17	32.7 ± 3.6	170 ± 55	121 ± 99	137 ± 88
21-Nov	9.4 ± 4.5	519 ± 60	16.0 ± 7.2	34.4 ± 15	33.8 ± 6.0	252 ± 117	146 ± 183	234 ± 317
All days	6.2 ± 2.3	592 ± 121	33.0 ± 17	24.9 ± 17	31.6 ± 9.4	252 ± 204	101 ± 85	175 ± 131

exceeded 100 ppbv on a regional level. VOCs samples were collected using conditioned 2-L electropolished stainless steel canisters. The canisters were developed and prepared by the Rowland/Blake group at the University of California, Irvine (UCI). More details about the design and specification of the canisters can be found in Simpson et al. (2010). A stainless steel flow controlling device was used to control the sampling flow at 0.033 lpm for the collection of 2-L of air in one hour. During O₃ episode days, hourly samples were collected from 9 a.m. to 4 p.m. (one sample every hour) with some additional samples collected at 7 a.m., 6 p.m. and 9 p.m. On non-O₃ episode days, hourly VOC samples were collected from 7 a.m. to 7 p.m. (one sample every two hours). A total of 161 VOC samples were collected at the sampling site.

2.2. Chemical analysis of VOCs

The canister samples were analyzed by the UCI group. 73 VOCs were quantified using multicolumn gas chromatography (GC). The details of the analytical procedures were described in Colman et al. (2001). In brief, for each canister sample, a 1520 cm³ aliquot was introduced into the system's manifold and split into five streams. Each stream was chromatographically separated on an individual column and sensed by a single detector. Two flame ionization detectors (FIDs), two electron capture detectors (ECDs) and a quadrupole mass spectrometer detector (MSD) were used to measure hydrocarbons, halocarbons and sulfur compounds respectively. VOCs were then identified by their retention times and mass spectra. The mixing ratios of target VOCs were quantified using multipoint external calibration curves, National Bureau of Standards, Scott Specialty Gases and UCI-made standards. For quality control and assurance, working standards were analyzed every four samples and absolute standards were analyzed twice a day. The limit of detection is 5 pptv for MVK and MACR, and 3 pptv for NMHCs including isoprene.

2.3. Continuous monitoring of O₃, CO, SO₂ and NO–NO₂–NO_x

The sampling site is one of the 14 air quality monitoring stations maintained and operated by the HKEPD. O₃, CO, SO₂, NO–NO₂–NO_x and meteorological parameters were monitored continuously by the HKEPD, and the hourly data were obtained from their online

database (<http://epic.epd.gov.hk/ca/uid/airdata>). O₃ was measured by UV absorption (Advanced Pollution Instrumentation (API), model 400), whereas CO and SO₂ were monitored by a gas filter correlation, non-dispersive infrared analyzer (API, model 300) and a pulsed UV fluorescence analyzer (API, model 100E), respectively. A commercial chemiluminescence analyzer (API, Model 200A) was used to quantify the levels of NO, NO₂ and NO_x. More details on the sampling instruments, measurement protocols, and quality assurance and control procedures can be found in HKEPD (2012).

3. Results

Table 1 shows overall statistics of SO₂, O₃, CO and NO, NO₂, isoprene, MVK and MACR at TW. The average mixing ratios of SO₂, O₃, CO and NO, NO₂ were calculated using the hourly data which correspond to the hour when VOC canister samples were simultaneously collected. In general, significant levels of SO₂ (overall average = 6.21 ± 2.85 ppbv, hourly maximum = 16.9 ppbv) and NO₂ (overall average = 31.6 ± 9.4, hourly maximum = 66.5 ppbv) were observed. These levels were in line with other urban cities such as Los Angeles and Pittsburgh in the United States (<http://www.epa.gov/airtrends/>), highlighting the impact of anthropogenic emissions at this site. The overall average isoprene mixing ratio was 252 ± 204 pptv, and the overall average MACR and MVK levels were 101 ± 85 pptv and 175 ± 131 pptv, respectively. The average O₃ level during episode days (39.2 ± 7.2 ppbv) was significantly higher than on non-episode days (24.3 ± 8.2 ppbv) ($p < 0.001$). Nonetheless, the maximum hourly O₃ level on any given sampling day at this site was lower than 100 ppbv – the level defining an O₃ episode according to the Ambient Air Quality Standard (Grade II) in China. As mentioned previously, the TW sampling site is located in an urban environment surrounded by major roadways as well as residential and industrial blocks. Due to the proximity to anthropogenic emission sources, the average NO mixing ratio was significant at this site (24.9 ± 17 ppbv). Reaction with NO is known to be the primary removal mechanism of O₃ (NO + O₃ → NO₂ + O₂) in environments with strong primary emissions (Ghim and Chang, 2000; Tan et al., 2009). A strong negative correlation between daily NO and O₃ ($R^2 = 0.64$, $p < 0.001$), together with troughs of O₃ levels during morning traffic hours (6–9 a.m.; Fig. 2), confirm the titration of O₃ by NO at this urban site.

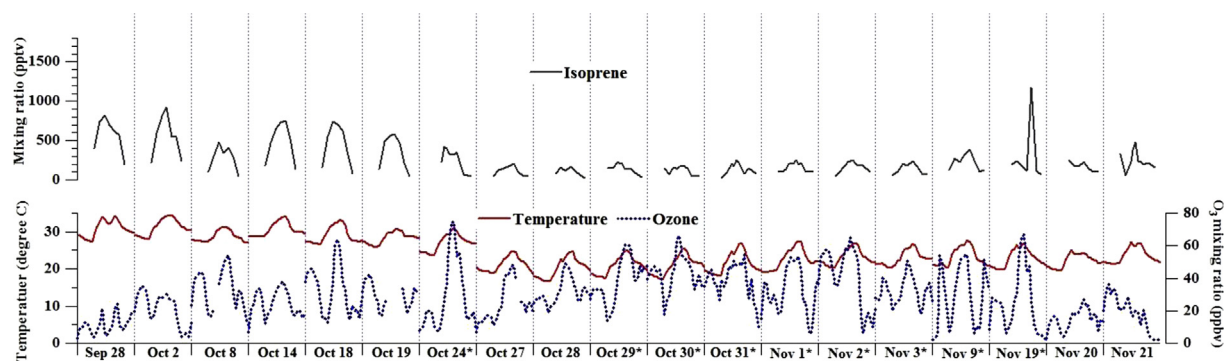


Fig. 2. Diurnal profiles of isoprene (top), ozone and temperature (bottom) at the TW site in autumn, 2010. Ozone episode days are marked with an asterisk.

3.1. Sources of isoprene

The top panel of Fig. 2 shows the diurnal profiles of isoprene on the 19 sampling days. A typical bell-shaped distribution, with peaks occurring between 11 a.m. and 3 p.m., was observed on most days with the exception of Oct. 24, Nov. 20 (peaks at 9 or 10 a.m.) and Nov. 19 (peak at 5 p.m.). On Oct. 24, solar radiation was strongest (daytime maximum = 851 W m^{-2}) of the study, facilitating the photo-oxidation of isoprene. The daytime average solar radiation was 413 W m^{-2} on Oct. 24, compared to an overall average of $297 \pm 68 \text{ W m}^{-2}$ on the rest of the sampling days. This probably led to lower levels of isoprene as the day progressed. The isoprene peak on Nov. 19 coincided with the peaks of limonene and α -pinene, suggesting a common biogenic origin. Higher levels of isoprene ($p < 0.001$) were observed in the beginning of the sampling campaign (Sep. 28 to Oct. 24) compared to the latter part of the sampling period (Oct. 27 to Nov. 21), when the temperature was higher (average daily temperatures of $30.6 \pm 1.6 \text{ }^\circ\text{C}$). From Oct. 27 onwards, the temperature dropped to an average daily value of $23.8 \pm 1.2 \text{ }^\circ\text{C}$. Indeed, the association between isoprene and temperature was fair ($R^2 = 0.54$). The emission rate of isoprene from vegetation largely depends on the ambient temperature. For example, an in-vivo study demonstrated that isoprene emission increases with leaf temperature almost linearly from $15 \text{ }^\circ\text{C}$ to around $40 \text{ }^\circ\text{C}$, with a maximum at $39 \text{ }^\circ\text{C}$ (Rasulov et al., 2010). Therefore, the higher levels of isoprene observed in the beginning of the study are consistent with expectation.

Although isoprene is primarily emitted by vegetation, vehicular exhaust is also a source of isoprene, as demonstrated in several dynamometer, tunnel and city studies (Chiang et al., 2007; Borbon et al., 2001; Dai et al., 2010). Since the sampling site is located adjacent to roadways with a high traffic flow (annual average daily traffic rate = 29,980 vehicles per day in 2010; The Annual Traffic Census (2011)), the assumption that isoprene originated purely from biogenic sources was examined using a linear regression analysis. Highest associations were found with dimethyl sulfide (DMS) ($R^2 = 0.24$, $p < 0.001$), followed by the biogenic tracer limonene ($R^2 = 0.22$, $p < 0.001$). Some correlation was found with the tailpipe exhaust tracers for *n*-decane ($R^2 = 0.15$, $p < 0.001$). Together with the bell-shaped diurnal variation of isoprene, it is suggested that isoprene predominately arose from biogenic emissions at this sampling location during the study period. The specific source contributions to isoprene are quantified using positive matrix factorization (PMF) in Section 3.3.

Based on a consecutive reaction scheme of isoprene oxidation by OH radicals under NO_x -rich environments, Stroud et al. (2001) developed an expression for the time rate of change in the MACR/isoprene and MVK/isoprene ratios as a function of the rate

coefficients, processing time and average OH concentrations. Since then, the ratios of MACR/isoprene and MVK/isoprene have been widely used to estimate the photochemical age of isoprene in an air mass (Apel et al., 2002; Guo et al., 2012; Roberts et al., 2006). Fig. 3 shows MACR/isoprene versus MVK/isoprene, based on daytime data from 9 a.m. to 4 p.m. ($n = 104$), when isoprene photochemistry was strong. Theoretical ratios were calculated using an average daytime OH concentration of $8 \times 10^6 \text{ molecules cm}^{-3}$, as obtained in a rural area about 60 km northwest of Guangzhou in the PRD in July 2006 (Hofzumahaus et al., 2009). As seen in the Figure, the measured data fit the predicted line well, with most data points corresponding to isoprene photochemical ages between 12 and 42 min, averaging to around 25 min. With an average wind speed of $2.1 \pm 0.9 \text{ m s}^{-1}$ from 9 a.m. to 4 p.m., the average distance between the center of the isoprene emitting source and the sampling site was about 3.2 km. Three large country parks, namely Tai Mo Shan Country Park, Kam Shan Country Park and Shing Mun Country Park are located 2–5 km from the sampling site (Fig. 1). With wind originating from southeast or east half of the sampling time, these country parks could be the dominant emission source of isoprene measured at TW. Note that the isoprene transport time calculated using this method is very sensitive to the assumed OH levels, which could vary spatially and temporally. Nonetheless, it is reasonable to conclude that the isoprene measured at TW is not significantly impacted by regional air mass transport from the PRD region of China, where the nearest city (Shenzhen) is located $>20 \text{ km}$ away

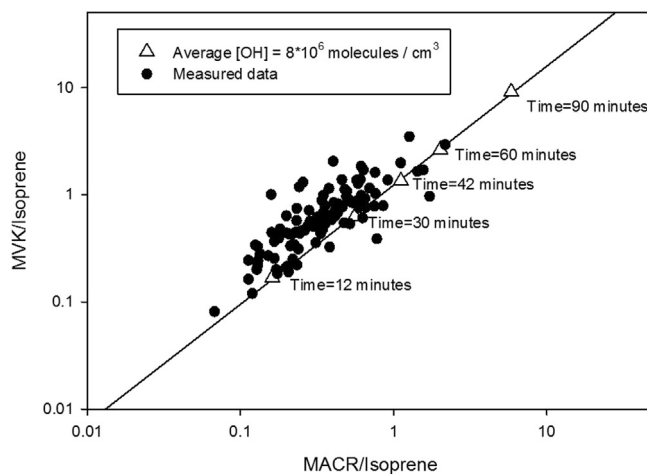


Fig. 3. Measured ratios of MVK/isoprene versus MACR/isoprene (black circles) together with calculated ratios (white triangles) based on a consecutive reaction scheme model (see text).

from the sampling site, and an air mass originating from Shenzhen would take 1.9 h to arrive the sampling site even at a wind speed of 3 m s^{-1} (average wind speed + one standard deviation). On the other hand, most of the measured data fall above the predicted line, consistent with some previous observations, suggesting that in addition to the photochemical oxidation of isoprene, anthropogenic sources could contribute to the daytime levels of MVK (Apel et al., 2002; Guo et al., 2012; Stroud et al., 2001). The correlation between MVK and MACR is $R^2 = 0.70$, suggesting predominant common origins but also the presence of additional, uncorrelated sources. The specific sources of MACR and MVK during the study period are discussed and quantified below.

3.2. Sources of MACR and MVK

Fig. 4 shows the time-series plot of MACR and MVK. The diurnal profiles of MACR and MVK followed each other fairly well, with the exception of Oct. 29–31 and Nov 2. As stated in Section 3.1, the association between MACR and MVK was good ($R^2 = 0.70$), suggesting their common origins. Most of the time, levels of MVK were higher than MACR; in only 12 of the 161 sampling hours were the levels of MACR higher than those of MVK. The peaks of MACR and MVK usually occurred between 11 a.m. and 3 p.m., except on Nov. 9 (peak at 9 a.m.) and Nov. 21 (peak at 7 a.m.). This is consistent with the isoprene peaks observed from 11 a.m. to 3 p.m., suggesting that the peak concentrations of MACR and MVK in the middle of the day were the results of photo-degradation of isoprene. On 8 out of 19 sampling days (Oct. 8, 14, 30, 31, and Nov. 2, 3, 9, 21), morning levels of MACR/MVK were comparable to/higher than the afternoon ones. Increased levels of MACR/MVK were also observed in the morning rush hours on 7 additional days (Oct. 2, 27, 28, 29, and Nov. 1, 19 and 20), although their levels were not necessarily as high as their respective afternoon peaks. Low levels of MACR/MVK were observed on 4 sampling days (Sep. 28 and Oct. 18, 19 and 24) during the morning sampling hours. On three of these days (Sep. 28, Oct. 18 and Oct. 19) northeasterly to northwesterly wind prevailed in the early morning. As seen in Fig. 1, to the north of the site is Tai Mo Shan Country Park. The northerly wind likely brought air masses that were relatively free of primary emissions to the site. On the fourth day (Oct. 24), westerly/northwesterly wind dominated from midnight until early afternoon. Also, of the 19 sampling days, the strongest solar radiation was observed on Oct. 24, reaching 111 and 577 W m^{-2} at 7 and 9 a.m. respectively. This strong solar radiation likely resulted in a higher mixing depth, which might account for the lower levels of anthropogenic MACR/MVK in the morning rush hour on Oct. 24. While increased levels of MACR and MVK in both

morning and midday were not observed in previous studies in rural or forested sampling sites (Apel et al., 2002; Montzka et al., 1995; Jordan et al., 2009; Nouaime et al., 1998; Spaulding et al., 2003), such diurnal trends were observed in metropolitan Houston, Texas and the morning peak was attributed to tail-pipe emission sources in the morning rush hour (Park et al., 2011). Given the low levels of isoprene in the early morning on all sampling days in this study (Fig. 2), it is possible that there were additional morning emission sources of MACR and MVK.

The top panel of Fig. 4 shows the ratio of the sum of [MACR + MVK] to [isoprene]. In areas where the three species originate from biogenic emissions, this ratio is mainly driven by the dominant oxidant chemistry that destroys isoprene and produces and destroys MACR and MVK during daytime. The ratio also depends on the degree of atmospheric mixing, distance from isoprene emitters, and the concentration of NO_x (Biesenthal et al., 1998). In this study, the average [MACR + MVK]/[isoprene] ratio was 1.69 ± 1.58 , which is higher than those reported in other studies (0.23–1.0) (Montzka et al., 1995; Yokouchi, 1994; Apel et al., 2002; Biesenthal et al., 1998). Note that higher ratios are expected when the sampled air mass has aged under high NO_x conditions (Biesenthal et al., 1998), which could be our case because NO_x levels were relatively high (Section 3) with an average photochemical age time of $\sim 25 \text{ min}$ (Fig. 3). Even higher ratios (>6) were observed in the sampling hours of 7 a.m., 5 p.m. or 9 p.m., which further suggests the direct emissions of MACR and MVK at this site.

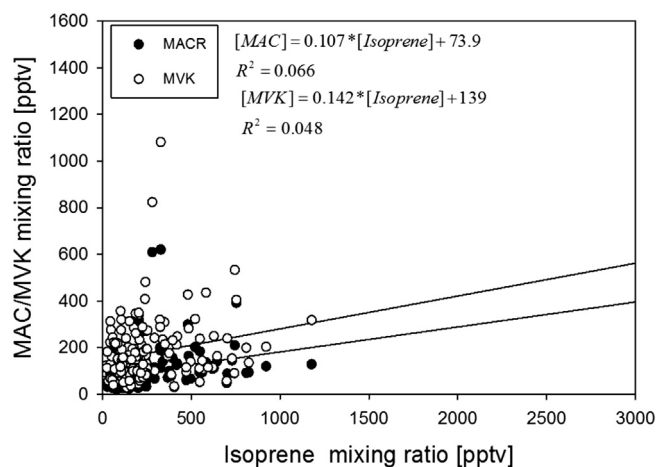


Fig. 5. Linear regressions between MACR/MVK and isoprene.

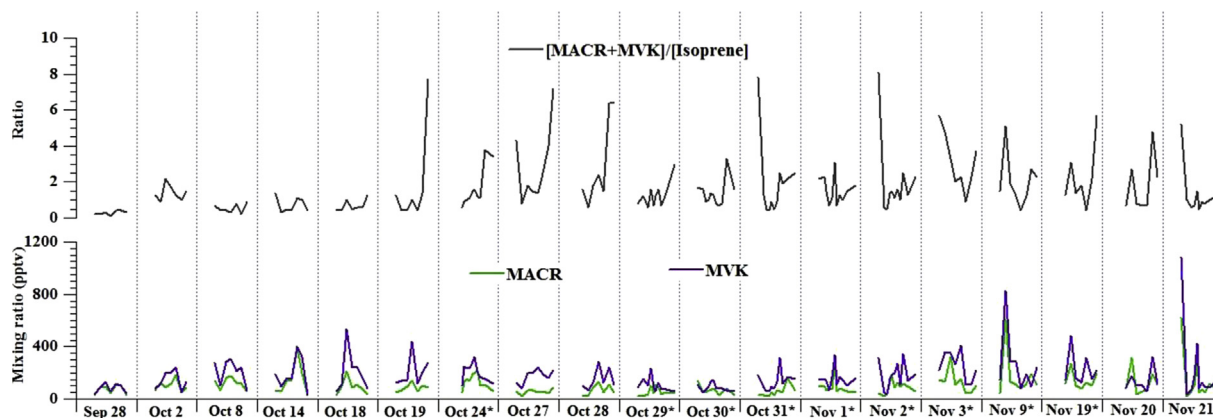


Fig. 4. Diurnal profiles of the ratio of [MACR + MVK]/[Isoprene] (top), and of MACR and MVK (bottom).

In contrast to the fair association between isoprene and temperature ($R^2 = 0.54$), there was no clear relationship for MACR and MVK with temperature ($R^2 = 0.027$ and 0.009 , respectively). Fig. 5 shows the linear regression between the mixing ratios MACR/MVK and isoprene. The very low correlation coefficients ($R^2 = 0.066$ for MACR and $R^2 = 0.048$ for MVK) suggest that local isoprene was not responsible for all of the measured MACR and MVK; that MACR and MVK could be formed at a distance and transported to the site; and/or that local primary MACR and MVK emissions might be present. The fact that the associations were not improved after lagging the isoprene concentrations relative to MACR and MVK ($R = 0.036$ and 0.020 respectively), coupled with the generally low wind speeds in the early morning (average = $1.21 \pm 0.38 \text{ m s}^{-1}$ from 5 to 8 a.m.), suggest that the transport of the isoprene oxidation products might not explain the MACR and MVK levels in the early morning.

A linear regression analysis was performed to better understand the sources of MACR and MVK. For MVK, its highest association was found with acetaldehyde ($R^2 = 0.39$, $p < 0.001$) followed by HCFC-141b ($R^2 = 0.38$, $p < 0.001$) (Fig. 6a, b). MACR experienced some correlation with acetaldehyde ($R^2 = 0.49$) and 1-butene ($R^2 = 0.42$) (Fig. 6c, d). HCFC-141b is used in metal degreasing and dry cleaning agents in Hong Kong (Guo et al., 2009). Previous studies at TW and in other urban parts of Hong Kong have associated acetaldehyde and 1-butene with vehicular emissions (Ho et al., 2002b, 2002a; Guo et al., 2004a). In a tunnel study conducted in California, MVK was identified in the emission of light-duty gasoline vehicles (emission factor = $0.67 \pm 0.13 \text{ mg kg}^{-1}$ in 2001 and $0.26 \pm 0.02 \text{ mg kg}^{-1}$ in 2006), as well as mid-duty and heavy-duty diesel trucks (emission factor = $3.0 \pm 1.2 \text{ mg kg}^{-1}$ in 2006) (Ban-Weiss et al., 2008). MVK is also listed as a constituent of gasoline exhaust in the USEPA Master

List of Mobile Source Air Toxics (<http://www.epa.gov/OMSWWW/toxics.htm>). Similarly, MACR was identified in a study of gasoline exhaust emissions using different fuels, with emission rates of $0.001 \text{ mg mile}^{-1}$, $0.03 \text{ mg mile}^{-1}$ and $0.001 \text{ mg mile}^{-1}$ for gasoline, 10% ethanol blend and 15% ethanol blend, respectively (Fanick, 2011). City studies have also associated MACR and MVK with vehicular emissions in Toronto and Houston (Biesenthal and Shepson, 1997; Park et al., 2011). Thus, the moderate correlations between MACR and MVK with acetaldehyde, HCFC-141b and 1-butene suggest anthropogenic contributions to the measured MACR and MVK levels. To examine the impact of vehicular exhaust, a restricted analysis was conducted using data from morning rush hours (7 a.m. and 9 a.m., $n = 34$). Indeed, improved associations were observed using this data subset ($R^2 > 0.77$ for all regressions, Fig. 6a–d), further suggesting a significant contribution of traffic emissions to the observed MACR and MVK levels.

3.3. Source apportionment

To quantitatively apportion the sources of isoprene, MACR and MVK, the U.S. Environmental Protection Agency (EPA) PMF model was applied to the dataset. PMF is a multivariate factor analysis tool based on the explicit least-squares technique, and it has been widely used to apportion the source contributions of ambient VOCs in various environments (Anderson et al., 2001; Pindado and Perez, 2011; Kim et al., 2005). More details about PMF modeling can be found in the literature (Paatero, 1997). Based on the calculated statistical parameters and prior knowledge about the known emission source profiles, a five-factor model best reproduced the observed VOC concentrations (Table 2). The first factor has high

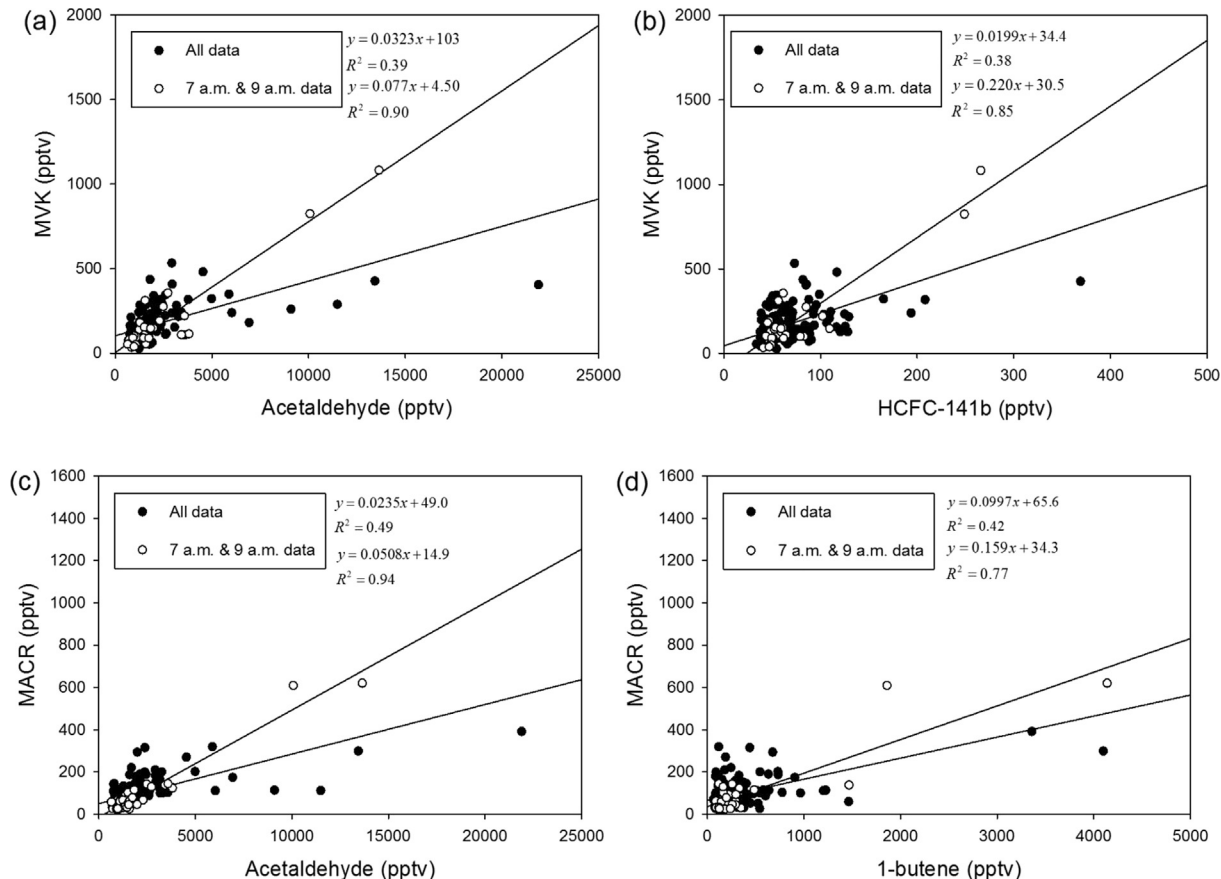


Fig. 6. Linear regressions between MVK and (a) acetaldehyde and (b) HCFC-141b. Linear regressions between MACR and (c) acetaldehyde and (d) 1-butene.

Table 2Positive Matrix Factorization (PMF) extracted source profiles for air samples collected at Tsuen Wan (TW) from September to November, 2010 ($n = 161$) (unit: % of species).

	Factor 1: fuel evaporation	Factor 2: LPG + diesel emission	Factor 3: gasoline emission	Factor 4: biogenic emission	Factor 5: solvent use
CO	1.2	54.6	35.8	7.8	0.6
Ethane	0.0	45.1	50.9	0.0	4.0
Ethene	5.5	59.3	20.5	12.5	2.2
Ethyne	0.3	52.2	39.5	7.2	0.7
Propane	12.5	54.2	22.1	8.9	2.3
Propene	11.4	63.7	7.6	16.2	1.0
<i>i</i> -Butane	22.5	50.6	15.5	11.4	0.0
<i>n</i> -Butane	12.4	59.5	15.3	12.6	0.2
<i>i</i> -Pentane	46.7	23.5	13.2	12.6	4.0
<i>n</i> -Pentane	45.3	22.3	17.2	9.6	5.6
Isoprene	0.0	6.1	24.3	69.4	0.2
<i>n</i> -Hexane	30.7	3.9	36.5	0.0	28.9
<i>n</i> -Heptane	22.0	12.3	35.8	5.7	24.1
<i>n</i> -Nonane	15.9	38.6	0.0	25.2	20.2
<i>n</i> -Decane	13.4	35.0	11.5	20.7	19.4
2-Methylpentane	36.7	10.0	31.7	4.6	17.1
Benzene	1.2	37.3	55.6	0.2	5.7
Toluene	15.0	15.4	50.9	0.0	18.7
Ethylbenzene	0.3	0.0	43.2	0.2	56.3
<i>m</i> -Xylene	3.7	8.3	14.9	5.6	67.4
<i>p</i> -Xylene	0.0	4.5	35.0	4.6	55.9
<i>o</i> -Xylene	2.3	5.9	26.9	5.1	59.8
MACR	12.8	0.0	54.6	28.7	3.9
MVK	8.2	2.5	68.9	20.4	0.0

loadings of *i*- and *n*-pentane, as well as *n*-hexane and *n*-heptane, and is attributed to fuel evaporation. For both MACR and MVK, 8–13% was associated with this factor. Factor 2, with a dominance of propene, *i/n*-butane, as well as *n*-nonane and *n*-decane, was likely derived from liquefied petroleum gas (LPG) and diesel emissions. Around 2.5% of MVK lay in this factor. The factor with high loadings of benzene, toluene, ethylbenzene, and xylenes (BTEX) (Factor 3) was thought to be associated with gasoline emissions, and MACR and MVK respectively contributed 55 and 69% to this factor. Previous studies have identified both MACR and MVK in the composition of fuel and lubricating oil, and in tunnel studies (Ban-Weiss et al., 2008; Magnusson et al., 2002). The significant contribution of MACR and MVK from vehicular emissions observed in this study is consistent with the observations in other urban environment (Park et al., 2011). Note that approximately one-fourth of isoprene was associated with this factor, suggesting a non-trivial influence of vehicular emissions on isoprene levels at TW. The factor with dominant isoprene presence (69%; Factor 4) was identified as biogenic emissions. The associated MACR and MVK contributions were 29 and 20% respectively, suggesting a significant fraction of the measured MACR and MVK arose from isoprene oxidation. Note that reactive species including isoprene, ethylene, and 1,3-butadiene have short lifetimes, typically a few hours. Yet, due to their usefulness, and sometimes exclusiveness in source identification, they have been included in many previous source apportionment studies (Brown et al., 2007; Kim et al., 2005; Xie and Berkowitz, 2006). Since reactive compounds are degraded on the way from the source to the receptor, the concentrations used in the PMF analysis can be considered the lower limit of the concentrations that would be measured at the sources. Therefore, although the sources of isoprene were likely emissions from nearby (~ 3.2 km at the wind speed of 2.1 m s^{-1} ; Section 3.1) country parks, the results of the PMF analysis should be interpreted with caution considering the possibility of underestimation due to the depletion from source to receptor. Factor 5, which contained most of the measured ethylbenzene and xylenes, was identified as solvent use emissions. 4% of MACR was associated with this factor. Thus, gasoline exhaust and biogenic emission were the two most

important contributors to the observed MACR and MVK at the sampling site, with minor contributions from fuel evaporations.

4. Conclusions

In summary, the diurnal profiles of isoprene and its oxidation products (MACR and MVK) were examined at an urban site with close proximity to vehicular and industrial emissions. Isoprene, which primarily originated from local biogenic emissions at this site, showed a typical bell-shaped diurnal distribution with higher levels on days when average temperature was above 30°C . Levels of MACR and MVK, on the other hand, were not correlated with temperature or isoprene concentrations. Although MACR and MVK usually peaked from noontime to early afternoon, high levels were often observed in the morning or afternoon rush hours. The low correlations between isoprene and MACR and MVK, together with high (MVK + MACR)/isoprene ratios during rush hour, suggested either that MACR and MVK were not formed from local isoprene oxidation, and/or that vehicular emissions potentially contributed. Furthermore, high associations were found between MACR and MVK and tracers of anthropogenic emissions (acetaldehyde, 1-butene, HCFC-141b, etc), particularly when the analysis was restricted to morning rush hour data. Positive matrix factorization analysis showed that traffic-related emissions and biogenic emissions were the two dominant contributors to MACR and MVK. As a result, we conclude that the use of MACR and MVK to represent the oxidation rate of isoprene is inappropriate in areas impacted by strong local anthropogenic emissions.

Acknowledgments

The authors thank the Research Grant Committee of the Hong Kong Special Administrative Region for their support via grants PolyU5179/09E and N_PolyU545/09. This study is also partly supported by the Hong Kong Polytechnic University (internal grant A-PL65).

References

- Anderson, M.J., Miller, S.L., Milford, J.B., 2001. Source apportionment of exposure to toxic volatile organic compounds using positive matrix factorization. *J. Expos. Anal. Environ. Epidemiol.* 11 (4), 295–307.
- Apel, E.C., Riemer, D.D., Hills, A., Baugh, W., Orlando, J., Faloon, I., Tan, D., Brune, W., Lamb, B., Westberg, H., Carroll, M.A., Thornberry, T., Geron, C.D., 2002. Measurement and interpretation of isoprene fluxes and isoprene, methacrolein, and methyl vinyl ketone mixing ratios at the PROPHET site during the 1998 Intensive. *J. Geophys. Res. Atmos.* 107 (D3).
- Ban-Weiss, G.A., McLaughlin, J.P., Harley, R.A., Kean, A.J., Grosjean, E., Grosjean, D., 2008. Carbonyl and nitrogen dioxide emissions from gasoline- and diesel-powered motor vehicles. *Environ. Sci. Technol.* 42 (11), 3944–3950.
- Barket, D.J., Grossebacher, J.W., Hurst, J.M., Shepson, P.B., Olszyna, K., Thornberry, T., Carroll, M.A., Roberts, J., Stroud, C., Bottenheim, J., Biesenthal, T., 2004. A study of the NO_x dependence of isoprene oxidation. *J. Geophys. Res. Atmos.* 109 (D11).
- Biesenthal, T.A., Bottenheim, J.W., Shepson, P.B., Brickell, P.C., 1998. The chemistry of biogenic hydrocarbons at a rural site in eastern Canada. *J. Geophys. Res. Atmos.* 103 (D19), 25487–25498.
- Biesenthal, T.A., Shepson, P.B., 1997. Observations of anthropogenic inputs of the isoprene oxidation products methyl vinyl ketone and methacrolein to the atmosphere. *Geophys. Res. Lett.* 24 (11), 1375–1378.
- Biesenthal, T.A., Wu, Q., Shepson, P.B., Wiebe, H.A., Anlauf, K.G., Mackay, G.I., 1997. A study of relationships between isoprene, its oxidation products, and ozone, in the Lower Fraser Valley, BC. *Atmos. Environ.* 31 (14), 2049–2058.
- Borbon, A., Fontaine, H., Veillerot, M., Locoge, N., Galloo, J.C., Guillermo, R., 2001. An investigation into the traffic-related fraction of isoprene at an urban location. *Atmos. Environ.* 35 (22), 3749–3760.
- Brown, S.G., Frankel, A., Hafner, H.R., 2007. Source apportionment of VOCs in the Los Angeles area using positive matrix factorization. *Atmos. Environ.* 41 (2), 227–237.
- Brown, S.S., Degouw, J.A., Warneke, C., Ryerson, T.B., Dube, W.P., Atlas, E., Weber, R.J., Peltier, R.E., Neuman, J.A., Roberts, J.M., Swanson, A., Flocke, F., McKeen, S.A., Brioude, J., Sommariva, R., Trainer, M., Fehsenfeld, F.C., Ravishankara, A.R., 2009. Nocturnal isoprene oxidation over the Northeast United States in summer and its impact on reactive nitrogen partitioning and secondary organic aerosol. *Atmos. Chem. Phys.* 9 (9), 3027–3042.
- Carter, W.P.L., Atkinson, R., 1996. Development and evaluation of a detailed mechanism for the atmospheric reactions of isoprene and NO_x. *Int. J. Chem. Kinet.* 28 (7), 497–530.
- Chan, L.Y., Chan, C.Y., Qin, Y., 1998. Surface ozone pattern in Hong Kong. *J. Appl. Meteorol.* 37 (10), 1153–1165.
- Chiang, H.L., Hwu, C.S., Chen, S.Y., Wu, M.C., Ma, S.Y., Huang, Y.S., 2007. Emission factors and characteristics of criteria pollutants and volatile organic compounds (VOCs) in a freeway tunnel study. *Sci. Total Environ.* 381 (1–3), 200–211.
- Colman, J.J., Swanson, A.L., Meinardi, S., Sive, B.C., Blake, D.R., Rowland, F.S., 2001. Description of the analysis of a wide range of volatile organic compounds in whole air samples collected during PEM-Tropics A and B. *Anal. Chem.* 73 (15), 3723–3731.
- Dai, T.Y., Wang, W., Ren, L.H., Chen, J.H., Liu, H.J., 2010. Emissions of non-methane hydrocarbons from cars in China. *Sci. China Chem.* 53 (1), 263–272.
- Dreyfus, G.B., Schade, G.W., Goldstein, A.H., 2002. Observational constraints on the contribution of isoprene oxidation to ozone production on the western slope of the Sierra Nevada, California. *J. Geophys. Res. Atmos.* 107 (D19).
- Fanick, R.E., 2011. Combustion Emission Characterization of E0, E10 and E15 in Support of the Fuel and Fuel Additive Registration of E15. Renewable Fuels Association and Growth Energy.
- Fuentes, J.D., Lerdau, M., Atkinson, R., Baldocchi, D., Bottenheim, J.W., Ciccioli, P., Lamb, B., Geron, C., Gu, L., Guenther, A., Sharkey, T.D., Stockwell, W., 2000. Biogenic hydrocarbons in the atmospheric boundary layer: a review. *Bull. Am. Meteorol. Soc.* 81 (7), 1537–1575.
- Ghim, Y.S., Chang, Y.S., 2000. Characteristics of ground-level ozone distributions in Korea for the period of 1990–1995. *J. Geophys. Res. Atmos.* 105 (D7), 8877–8890.
- Guenther, A., Karl, T., Harley, P., Wiedinmyer, C., Palmer, P.I., Geron, C., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.* 6, 3181–3210.
- Guo, H., Ding, A.J., Wang, T., Simpson, I.J., Blake, D.R., Barletta, B., Meinardi, S., Rowland, F.S., Saunders, S.M., Fu, T.M., Hung, W.T., Li, Y.S., 2009. Source origins, modeled profiles, and apportionments of halogenated hydrocarbons in the greater Pearl River Delta region, southern China. *J. Geophys. Res. Atmos.* 114.
- Guo, H., Lee, S.C., Louie, P.K.K., Ho, K.F., 2004a. Characterization of hydrocarbons, halocarbons and carbonyls in the atmosphere of Hong Kong. *Chemosphere* 57 (10), 1363–1372.
- Guo, H., Ling, Z.H., Simpson, I.J., Blake, D.R., Wang, D.W., 2012. Observations of isoprene, methacrolein (MAC) and methyl vinyl ketone (MVK) at a mountain site in Hong Kong. *J. Geophys. Res. Atmos.* 117.
- Guo, H., Wang, T., Louie, P.K.K., 2004b. Source apportionment of ambient non-methane hydrocarbons in Hong Kong: application of a principal component analysis/absolute principal component scores (PCA/APCS) receptor model. *Environ. Pollut.* 129 (3), 489–498.
- Ho, K.F., Lee, S.C., Chiu, G.M.Y., 2002a. Characterization of selected volatile organic compounds, polycyclic aromatic hydrocarbons and carbonyl compounds at a roadside monitoring station. *Atmos. Environ.* 36 (1), 57–65.
- Ho, K.F., Lee, S.C., Louie, P.K.K., Zou, S.C., 2002b. Seasonal variation of carbonyl compound concentrations in urban area of Hong Kong. *Atmos. Environ.* 36 (8), 1259–1265.
- Hofzumahaus, A., Rohrer, F., Lu, K.D., Bohn, B., Brauers, T., Chang, C.C., Fuchs, H., Holland, F., Kita, K., Kondo, Y., Li, X., Lou, S.R., Shao, M., Zeng, L.M., Wahner, A., Zhang, Y.H., 2009. Amplified trace gas removal in the troposphere. *Science* 324 (5935), 1702–1704.
- Hu, D., Bian, Q., Li, T.W.Y., Lau, A.K.H., Yu, J.Z., 2008. Contributions of isoprene, monoterpenes, beta-caryophyllene, and toluene to secondary organic aerosols in Hong Kong during the summer of 2006. *J. Geophys. Res. Atmos.* 113.
- Jordan, C., Fitz, E., Hagan, T., Sive, B., Frinak, E., Haase, K., Cottrell, L., Buckley, S., Talbot, R., 2009. Long-term study of VOCs measured with PTR-MS at a rural site in New Hampshire with urban influences. *Atmos. Chem. Phys.* 9 (14), 4677–4697.
- Karl, T., Guenther, A., Yokelson, R.J., Greenberg, J., Potosnak, M., Blake, D.R., Artaxo, P., 2007. The tropical forest and fire emissions experiment: emission, chemistry, and transport of biogenic volatile organic compounds in the lower atmosphere over Amazonia. *J. Geophys. Res. Atmos.* 112 (D18).
- Kim, E., Brown, S.G., Hafner, H.R., Hopke, P.K., 2005. Characterization of non-methane volatile organic compounds sources in Houston during 2001 using positive matrix factorization. *Atmos. Environ.* 39 (32), 5934–5946.
- Leung, D.Y.C., Zhang, D.N., 2001. Characteristics of urban ozone level in Hong Kong. *J. Environ. Sci. China* 13 (1), 1–7.
- Li, L.F., Wang, X.M., 2012. Seasonal and diurnal variations of atmospheric non-methane hydrocarbons in Guangzhou, China. *Int. J. Environ. Res. Public Health* 9 (5), 1859–1873.
- Magnusson, R., Nilsson, C., Andersson, B., 2002. Emissions of aldehydes and ketones from a two-stroke engine using ethanol and ethanol-blended gasoline as fuel. *Environ. Sci. Technol.* 36 (8), 1656–1664.
- Makar, P.A., Fuentes, J.D., Wang, D., Staebler, R.M., Wiebe, H.A., 1999. Chemical processing of biogenic hydrocarbons within and above a temperate deciduous forest. *J. Geophys. Res. Atmos.* 104 (D3), 3581–3603.
- Miyoshi, A., Hatakeyama, S., Washida, N., 1994. Om radical-initiated photooxidation of isoprene – an estimate of global co production. *J. Geophys. Res. Atmos.* 99 (D9), 18779–18787.
- Montzka, S.A., Trainer, M., Angevine, W.M., Fehsenfeld, F.C., 1995. Measurements of 3-methyl furan, methyl vinyl ketone, and methacrolein at a rural forested site in the southeastern United States. *J. Geophys. Res. Atmos.* 100 (D6), 11393–11401.
- Nouaime, G., Bertman, S.B., Seaver, C., Elyea, D., Huang, H., Shepson, P.B., Starn, T.K., Riemer, D.D., Zika, R.G., Olszyna, K., 1998. Sequential oxidation products from tropospheric isoprene chemistry: MACR and MPAN at a NO_x-rich forest environment in the southeastern United States. *J. Geophys. Res. Atmos.* 103 (D17), 22463–22471.
- Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. *Chemom. Intell. Lab. Syst.* 37 (1), 23–35.
- Park, C., Schade, G.W., Boedeker, I., 2011. Characteristics of the flux of isoprene and its oxidation products in an urban area. *J. Geophys. Res. Atmos.* 116.
- Pindado, O., Perez, R.M., 2011. Source apportionment of particulate organic compounds in a rural area of Spain by positive matrix factorization. *Atmos. Pollut. Res.* 2 (4), 492–505.
- Rasulov, B., Huve, K., Bichele, I., Laisk, A., Niinemets, U., 2010. Temperature response of isoprene emission in vivo reflects a combined effect of substrate limitations and isoprene synthase activity: a kinetic analysis. *Plant Physiol.* 154 (3), 1558–1570.
- Roberts, J.M., Marchewka, M., Bertman, S.B., Goldan, P., Kuster, W., de Gouw, J., Warneke, C., Williams, E., Lerner, B., Murphy, P., Apel, E., Fehsenfeld, F.C., 2006. Analysis of the isoprene chemistry observed during the New England Air Quality Study (NEAQS) 2002 intensive experiment. *J. Geophys. Res. Atmos.* 111 (D23).
- Simpson, I.J., Blake, N.J., Barletta, B., Diskin, G.S., Fuelberg, H.E., Gorham, K., Huey, L.G., Meinardi, S., Rowland, F.S., Vay, S.A., Weinheimer, A.J., Yang, M., Blake, D.R., 2010. Characterization of trace gases measured over Alberta oil sands mining operations: 76 speciated C-2–C-10 volatile organic compounds (VOCs), CO₂, CH₄, CO, NO, NO₂, NO_y, O-3 and SO₂. *Atmos. Chem. Phys.* 10 (23), 11931–11954.
- Sin, D.W.M., Wong, Y.C., Choi, Y.Y., Lam, C.H., Louie, P.K.K., 2003. Distribution of polycyclic aromatic hydrocarbons in the atmosphere of Hong Kong. *J. Environ. Monit.* 5 (6), 989–996.
- Spaulding, R.S., Schade, G.W., Goldstein, A.H., Charles, M.J., 2003. Characterization of secondary atmospheric photooxidation products: evidence for biogenic and anthropogenic sources. *J. Geophys. Res. Atmos.* 108 (D8).
- Starn, T.K., Shepson, P.B., Bertman, S.B., White, J.S., Splawn, B.G., Riemer, D.D., Zika, R.G., Olszyna, K., 1998. Observations of isoprene chemistry and its role in ozone production at a semirural site during the 1995 Southern Oxidants Study. *J. Geophys. Res. Atmos.* 103 (D17), 22425–22435.
- Stroud, C.A., Roberts, J.M., Goldan, P.D., Kuster, W.C., Murphy, P.C., Williams, E.J., Hereid, D., Parrish, D., Sueper, D., Trainer, M., Fehsenfeld, F.C., Apel, E.C., Riemer, D., Wert, B., Henry, B., Fried, A., Martinez-Harder, M., Harder, H., Brune, W.H., Li, G., Xie, H., Young, V.L., 2001. Isoprene and its oxidation products, methacrolein and methylvinyl ketone, at an urban forested site during the 1999 Southern Oxidants Study. *J. Geophys. Res. Atmos.* 106 (D8), 8035–8046.
- Tan, P.H., Chou, C., Liang, J.Y., Chou, C.K., Shiu, C.J., 2009. Air pollution "holiday effect" resulting from the Chinese New Year. *Atmos. Environ.* 43 (13), 2114–2124.

- Tang, J.H., Chan, L.Y., Chan, C.Y., Li, Y.S., Chang, C.C., Liu, S.C., Wu, D., Li, Y.D., 2007. Characteristics and diurnal variations of NMHCs at urban, suburban, and rural sites in the Pearl River Delta and a remote site in South China. *Atmos. Environ.* 41 (38), 8620–8632.
- Xie, Y., Berkowitz, C.M., 2006. The use of positive matrix factorization with conditional probability functions in air quality studies: an application to hydrocarbon emissions in Houston, Texas. *Atmos. Environ.* 40 (17), 3070–3091.
- Yokouchi, Y., 1994. Seasonal and diurnal-variation of isoprene and its reaction-products in a semirural area. *Atmos. Environ.* 28 (16), 2651–2658.
- Zhao, J., Zhang, R.Y., Fortner, E.C., North, S.W., 2004. Quantification of hydroxycarbonyls from OH-isoprene reactions. *J. Am. Chem. Soc.* 126 (9), 2686–2687.
- Zheng, J.Y., Shao, M., Che, W.W., Zhang, L.J., Zhong, L.J., Zhang, Y.H., Streets, D., 2009. Speciated VOC emission inventory and spatial patterns of ozone formation potential in the Pearl River Delta, China. *Environ. Sci. Technol.* 43 (22), 8580–8586.