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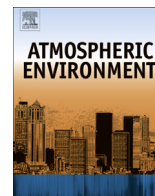
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## VOCs and OVOCs distribution and control policy implications in Pearl River Delta region, China



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### HIGHLIGHTS

- ▶ The first and foremost large spatial–temporal VOCs grid study in the PRD region.
- ▶ More detailed VOCs spatial emission characteristics were identified.
- ▶ High OH concentration in PRD favoured fast reactions and ozone formation.
- ▶ Ozone formation potential of VOCs and OVOCs were analysed.
- ▶ Findings supported further control measures and policies formulation.

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### ABSTRACT

Ambient air measurements of volatile organic compounds (VOCs) and oxygenated volatile organic compounds (OVOCs) were conducted and characterised during a two-year grid study in the Pearl River Delta (PRD) region of southern China. The present grid study pioneered the systematic investigation of the nature and characteristics of complex VOC and OVOC sources at a regional scale. The largest contributing VOCs, accounting over 80% of the total VOCs mixing ratio, were toluene, ethane, ethyne, propane, ethene, butane, benzene, pentane, ethylbenzene, and xylenes. Sub-regional VOC spatial characteristics were identified, namely: i) relatively fresh pollutants, consistent with elevated vehicular and industrial activities, around the PRD estuary; and ii) a concentration gradient with higher mixing ratios of VOCs in the west as compared with the eastern part of PRD. Based on alkyl nitrate aging determination, a high hydroxyl radical (OH) concentration favoured fast hydrocarbon reactions and formation of locally produced ozone. The photochemical reactivity analysis showed aromatic hydrocarbons and alkenes together consisted of around 80% of the ozone formation potential (OFP) among the key VOCs. We also found that the OFP from OVOCs should not be neglected since their OFP contribution was more than one-third of that from VOCs alone. These findings support the choice of current air pollution control policy which focuses on vehicular sources but warrants further controls. Industrial emissions and VOCs emitted by solvents should be the next targets for ground-level ozone abatement.

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### 1. Introduction

Due to rapid economic and industrial development, the Pearl River Delta (PRD) region, situated in southern China, has suffered

from degraded air quality and visibility since the 1990's (Wang et al., 2008a). Hong Kong, as a part of the PRD region, is experiencing an increasing ozone trend and regional photochemical smog problem (Wang et al., 2009), which reduces visibility, adversely affects human health, damages plants and degrades various materials (Finlayson-Pitts and Pitts, 1997; Bashkin, 2003). Hence, this has recently raised public concern and added fresh inputs to scientific interests.

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Volatile organic compounds (VOCs) are important precursors to the formation of ground-level ozone, and hence photochemical smog (IPCC, 2007). VOCs react with hydroxyl radical (OH) through photochemical reactions to produce oxygenated compounds, and subsequently forming ozone (Sillman, 1999; Hofzumahaus et al., 2009). The relation between ozone, nitrogen oxides (NO<sub>x</sub>) and VOCs is driven by complex nonlinear photochemistry. In addition, some VOCs are also considered hazardous pollutants. For example, 1,3-butadiene and benzene, commonly found in industrial and vehicular emissions, are known carcinogens (USEPA, 2009, 2012). Therefore, it is important to identify the VOC sources and photochemical transformation characteristics, in order to formulate appropriate pollution control policies.

Since the 1990s, the recognition of adverse health effects from anthropogenic VOCs has led to various scientific studies and related aspects, including global emission inventory (Piccot et al., 1992), sampling and analytical techniques (Dewulf and Langenhove, 1999), and VOCs speciation characteristics & evolution in different parts of the world (Ciccioli et al., 1993; Watson et al., 2001; Parra et al., 2009; and others). Those studies suggested vehicle exhaust to be the major anthropogenic VOC source. In addition, contributions from gasoline evaporation, leakage of liquefied petroleum gas (LPG), coating and solvent use were also found significant (Watson et al., 2001; Chan et al., 2006; Parra et al., 2009). A number of studies have been carried out to investigate the spatial–temporal characteristics of VOCs and their sources in Hong Kong (Ho et al., 2004; Guo et al., 2007). Many studies have indicated that the origin of photochemical pollution is regional rather than local (Shao et al., 2009; Guo et al., 2009; Wang et al., 2009). Therefore, the coverage of VOC studies has been extended to regional scales (Barletta et al., 2005; Chan et al., 2006; Shao et al., 2009). In particular, the Program of Regional Integrated Experiments on Air Quality over Pearl River Delta of China 2004 (PRIDE-PRD2004) was carried out to proactively coordinate research interests and key findings within the region (Liu et al., 2008a, 2008b; Wang et al., 2008a, 2008b).

Aldehydes and ketones, also termed oxygenated volatile organic compounds (OVOCs), are an important fraction of the VOCs. Reactions with OH radicals and photolysis are their major sinks and their lifetimes are in the order of a few hours to 1 day (Atkinson, 2000). Through photolysis, they can produce reactive hydroxyl radicals; thereby play an important role in initiating and sustaining the photochemical radical pool necessary to produce ozone. OVOCs can be emitted from primary sources (vehicles and cooking) or formed through secondary photochemical transformation of VOCs in the atmosphere. The relative importance of primary and secondary formation is compound dependent, and also varies with season, time of day and location. Information on OVOCs is scant in the PRD region (Ho et al., 2002; Yu et al., 2008). Measurements of OVOCs provide further insight into VOC oxidation mechanisms, and thereby enhance the understanding of ozone formation potential.

In 2005, the Governments of the Guangdong Province and the Hong Kong Special Administrative Region (HKSAR) teamed up to address the regional air pollution problem. They jointly established the PRD Regional Air Quality Monitoring Network which aimed at providing quality-assured criteria pollutant data to devise appropriate control measures, to evaluate the effectiveness of such control measures, and to provide the public with the most updated information on the general air quality over the region. For example, the 2006 and 2007 data from this network showed distinct seasonal and diurnal cycles in ground level ozone, which was attributed to the monsoon climate and patterns of human activity, respectively (Zheng et al., 2010).

Despite extensive studies in the past, most were restricted to a few sites, usually comprised of an urban site and a rural site (e.g.

Ho et al., 2002; Guo et al., 2009). In comparison, in an investigation on air quality of Mexico City, Blake and Rowland (1995) demonstrated that a more refined spatial distribution of sampling sites is essential in order to comprehensively identify the pollution problem. Since understanding on VOC and OVOC characteristics over the vast area of the PRD region is still limited, a more systematic and larger scale grid study over the region would fill in the data gap for learning the VOC and OVOC characteristics. This also solidifies the findings and improves the data quality with a high resolution of sampling locations, and more rigorous sample treatment and QA/QC standard. This grid study was the first and foremost large spatial–temporal scale VOCs and OVOCs sampling in the PRD region. The improved spatial coverage of sampling locations has provided representative measurements over the entire study area, including transitional terrains.

## 2. Methodology

### 2.1. Sampling sites and sampling method

The study area covered the whole territory of HKSAR and the PRD Economic Zone (PRDEZ). Previous studies, which focused on a few urban or rural sites in this region, have shown that the major VOC sources were vehicle related emissions, solvent usages and biomass burning (Chan et al., 2006; Guo et al., 2007; Liu et al., 2008a). To extend the investigation, the present study improved the spatial coverage of sampling locations and hence, provided representative VOC measurements over the entire study area. Sampling sites were selected within a total area of 40,000 km<sup>2</sup> (the land area of PRD is about 55,000 km<sup>2</sup>), which was finely divided into 100 square grid cells each at 20 km in length. All sites were selected with the aim of collecting ambient air samples away from immediate influence of localised pollution sources such as roadside vehicle exhausts and industrial emissions. This was to ensure that the measurements are representative for the regional ozone formation characteristics. Samples at sea were not taken, leaving a total of 84 land sites for VOC sampling (Fig. 1).

Whole-air samples (Blake and Rowland, 1995; Simpson et al., 2002) were obtained simultaneously at a designated sampling time at all the selected sites. Each whole-air sample was collected for two minutes using 2-L stainless steel canisters which were each equipped with a stainless steel bellows valve, and were certified as leak-free and clean before use.

For OVOCs measurements, an active sampling method was adopted, for which the species were collected onto 2,4-dinitrophenylhydrazine (DNPH) coated cartridges following the USEPA method TO-11A (USEPA, 1999). Each sample was collected at a flow rate of 1 L min<sup>-1</sup> for 4 h. Due to limited resources, OVOCs sampling was carried out at a subset of 20 sites out of the 84 sites selected for VOCs canister sampling and the 20 sites were uniformly distributed over the entire sampling grid (Fig. 1).

A total of four sampling campaigns for VOCs and OVOCs were conducted for two different seasons (winter and summer) in two consecutive years (2008 and 2009). It is noted that, due to the mode of economic and industrial activities in this region, the variations in pollutant emissions (Zheng et al., 2009) as well as the ambient pollutant levels (Zheng et al., 2010) between weekday and weekend were generally insignificant. On the other hand, meteorology was found to be the more influential factor to the pollutant levels (Wang et al., 2008b). As a result, the specific sampling day was selected based on a forecast of meteorological conditions and air quality, which primarily aimed at capturing a photochemical pollution event that was prone to producing elevated ozone concentrations. Moreover, Zheng et al. (2009) also showed that there were significant increases in traffic emission during 6 am–9 am on both

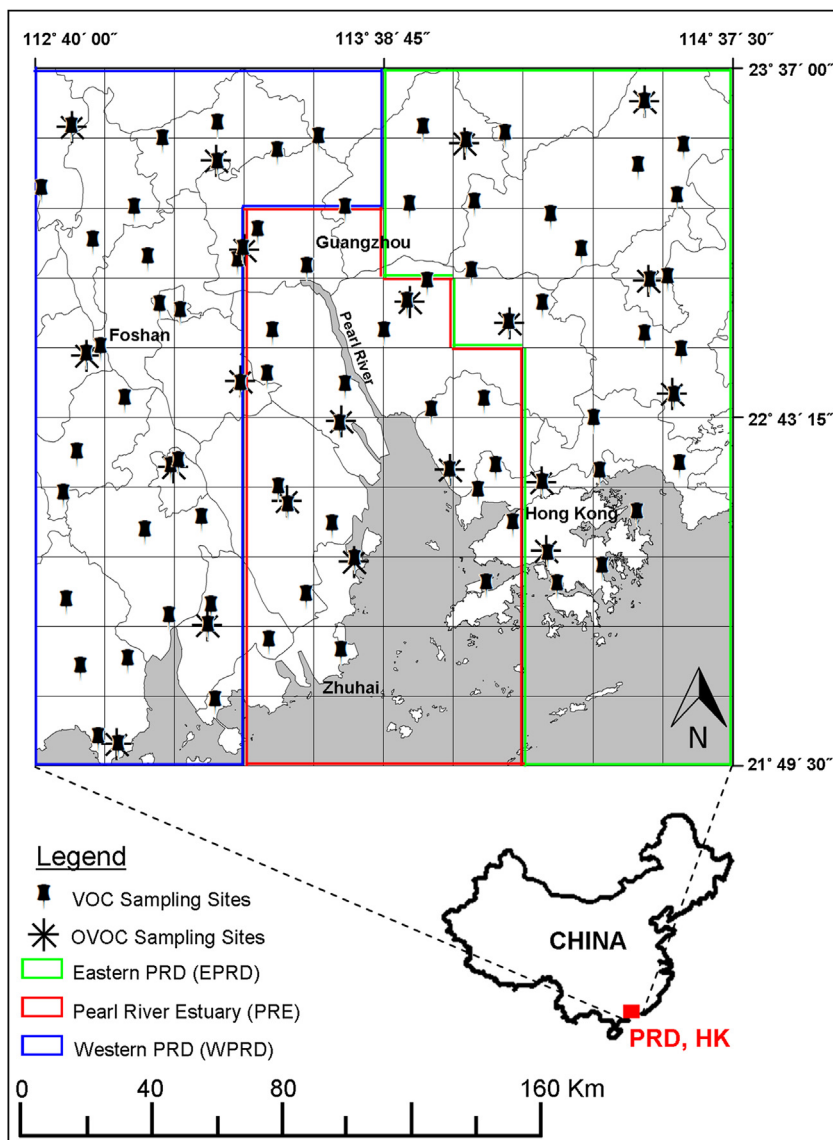


Fig. 1. The Study Area in PRD, China; VOC and OVOC sampling sites.

weekday and weekend. This could be an indicator for the start of human activities of the day and hence, a change in emission intensity. Therefore, in each campaign, one sample was taken at 5 am to capture the ambient VOCs characteristics before the start of human activities at night; and a second sample was taken at 10 am after the start of human activities at daytime. In considerations of limited resources and the large numbers of sampling sites for analysing the spatial VOCs distribution in this region, sampling at two time slots per day was considered appropriate for representing ambient VOCs characteristics of the day under different emissions and day–night conditions. OVOC samples were also collected at two time slots but for longer duration, i.e., 5–9 am and 9 am–1 pm. The details of the sampling campaigns were shown in Table 1.

## 2.2. Laboratory analytical systems

The VOCs air sampling canisters were sent to laboratories at University of California, Irvine (UCI), Guangzhou Institute of Geochemistry (GIG) and Peking University (PKU) for the analysis of carbon monoxide (CO), methane (CH<sub>4</sub>) and VOCs. The three

laboratories adopted the same VOCs analytical and quality assurance system (Simpson et al., 2010) in order to reduce analytical uncertainty and enhance data comparability. Briefly, CO and CH<sub>4</sub> were analysed by gas chromatography (GC) with a flame ionization detector (FID). Other VOC species were analysed after preconcentration by GCs with a multi-detector system (consisting of a mass spectrometer detector (MSD), two flame ionization detectors (FIDs) and two electron capture detectors (ECDs)).

For OVOCs, the cartridge samples were sent to the Hong Kong University of Science and Technology (HKUST) for analysis, and to GIG for QA/QC. The OVOCs analytical procedure was based on the USEPA method TO-11A (1999). In brief, the DNPH cartridges were eluted with acetonitrile and the eluent was injected into a high pressure liquid chromatograph (HPLC) for separation and detection by a photodiode array detector (Ho and Yu, 2004). A total of 17 OVOCs were quantified, including C<sub>1</sub>–C<sub>6</sub> aldehydes, acetone, methyl ethyl ketone, benzaldehyde, o-, m-, p-tolualdehyde, 2,5-dimethylbenzaldehyde, glyoxal and methylglyoxal. Two unsaturated carbonyls, acrolein and crotonaldehyde, were detected but not quantified due to known decomposition problem of their DNPH derivatives (Ho et al., 2011).

**Table 1**  
Details of sampling campaigns.

		1st sampling campaign	2nd sampling campaign	3rd sampling campaign	4th sampling campaign
	Date	29 Sep 2008	1 Mar 2009	26 Sep 2009	5 Dec 2009
	Season <sup>a</sup>	Summer	Winter	Summer	Winter
VOCs	Time	Sample 1: 5 am Sample 2: 10 am	Sample 1: 5 am Sample 2: 10 am	Sample 1: 5 am Sample 2: 10 am	Sample 1: 5 am Sample 2: 10 am
	Number of samples analysed successfully	Field: 167 Duplicated <sup>b</sup> : 12 Blank <sup>b</sup> : 9	Field: 171 Duplicated: 12 Blank: 8	Field: 184 Duplicated: 14 Blank: 8	Field: 181 Duplicated: 14 Blank: 9
	OVOCs	Time	Sample 1: 5 am–9 am Sample 2: 9 am–1 pm	Sample 1: 5 am–9 am Sample 2: 9 am–1 pm	Sample 1: 5 am–9 am Sample 2: 9 am–1 pm
	Number of samples analysed successfully	Field: 39 Duplicated: 3 Blank: 4	Field: 39 Duplicated: 4 Blank: 4	Field: 60 Duplicated: 6 Blank: 4	Field: 60 Duplicated: 6 Blank: 6
Meteorological conditions	Prevailing wind direction Details	North to northeast Under the influence of Typhoon Jangmi	Northeast to east Approach of a cold front	Northeast Under the influence of Typhoon Ketsana	North to northeast The passage of a cold air mass

<sup>a</sup> Generally, the four seasons spring, summer, autumn and winter are defined as from March to May, June to August, September to November and December to February, respectively. However, since the PRD is in the tropics, its seasonal variation is characteristic of monsoon climate, which has longer summer and winter and shorter transition seasons of spring and autumn. Therefore, the present study defined two seasons (i.e. summer and winter) for a year instead of four. The specific sampling date in each season was selected based on real-time forecast of meteorological conditions conducive to elevated ozone concentrations (e.g. presence of tropical cyclone near Taiwan Strait in the summer or before arrival of cold front in the winter).

<sup>b</sup> Duplicated and Blank samples were taken for quality assurance/quality control (QA/QC) analysis.

2.3. QA/QC system

In order to ensure data quality, a rigorous QA/QC system was implemented. Each component in the present study, including field sampling, laboratory analysis and result interpretation and reporting, followed a set of comprehensive standard operating procedure (SOP) and all the analysis were well documented in order to maintain traceability. In term of laboratory analytical performance, a Data Quality Objectives (DQO) was established. The

required accuracy was set to within 20% for VOCs, alkyl nitrates and Dimethyl sulphide (DMS), whereas the accuracy for CO and CH<sub>4</sub> was 10% and 1%, respectively. The required precision was within 4 ppbv for CO; 2% or 1.5 pptv (whichever is larger) for alkanes and alkynes; and 3% or 3 pptv for alkenes and aromatics. The detection limit for most VOCs was 5 pptv except benzene (3 pptv). All these parameters were verified by standard samples, prepared by UCI, with known mixing ratios before the analysis of field samples for each campaign.

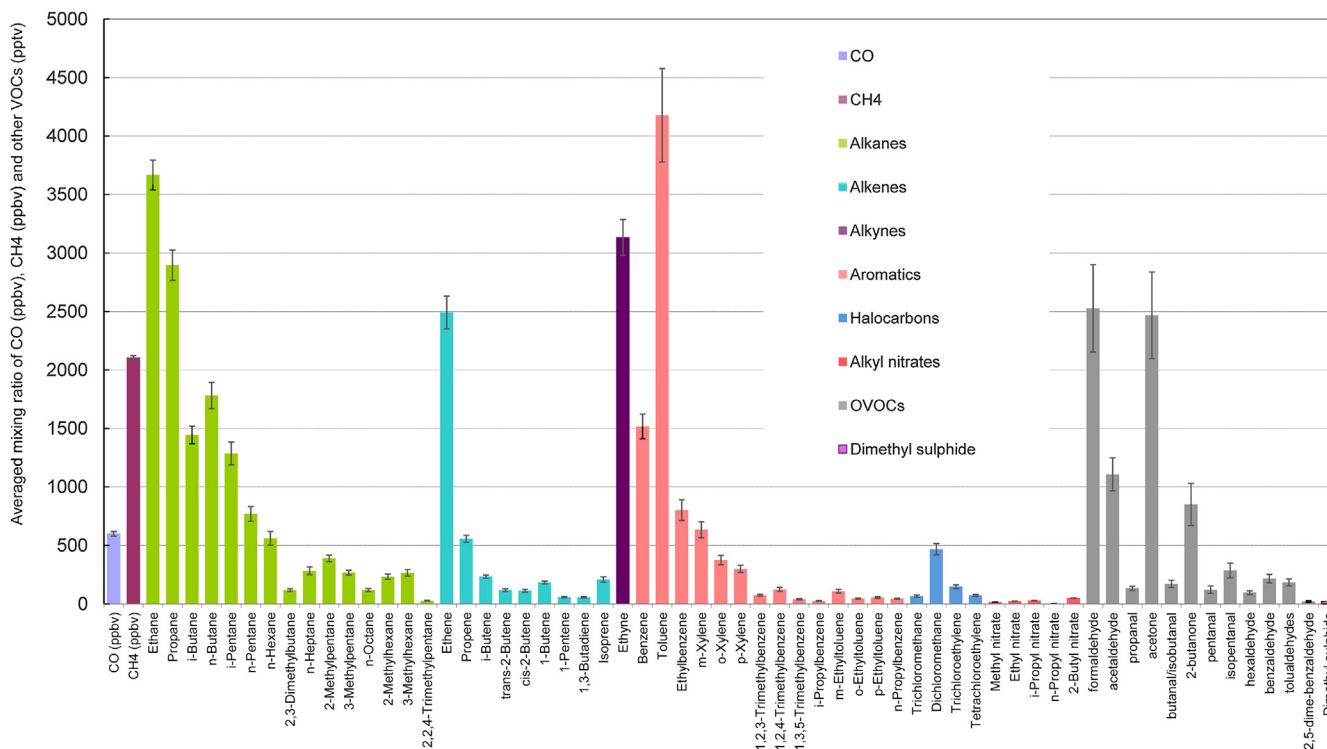


Fig. 2. Averaged VOCs and OVOCs mixing ratios (Error bars showing ±95% confidence interval).

Furthermore, inter-laboratory comparisons of the VOCs analytical system among UCI, GIG and PKU were carried out prior and during the sampling campaigns. This was to investigate and ensure the performance of each laboratory in accordance with the DQO and QA/QC system indicated above. The inter-comparison focused on the assessment of the analytical systems and performance status of various laboratories as infrastructure and experience varied among them. This also involved the exchange of calibration equipment for cross-checking and standardised the calibration scale in order to improve the consistency of the analytical process. The inter-comparison not only ensured the data quality but also served as an important platform for exchange of knowledge and technologies among different institutions.

All laboratories could accurately quantify the significant VOCs (e.g. alkanes, alkenes, aromatics, etc.). However, some other VOCs (e.g. alkyl nitrates, dimethyl sulphide) required more efforts to harmonize the analytical performance. On the whole, all laboratories put in serious efforts to ensure the data quality of the VOCs samples.

The DQO for OVOCs, assessed through recoveries of spiked cartridges at three spiked levels, was set to be better than  $80 \pm 10\%$ , and was achieved. Nine blind spiked cartridge samples were exchanged between the HKUST and GIG laboratories. The results determined by the HKUST lab were in agreement with the spiked amounts by GIG within 16% for all target OVOCs except for butyraldehyde. Amounts of butyraldehyde determined by HKUST were in agreement with the spiked amounts within 30%. The accuracy of butyraldehyde-DNPH was poorer due to interference of a coeluting peak from the cartridge blank. Results of field duplicate samples show that better than 25% precision was achieved for formaldehyde, acetaldehyde, and acetone and better than 30% precision for other target OVOCs.

### 3. Results and discussion

#### 3.1. VOC characteristics in PRD region

In the present study, a total of 645 field samples, excluding 58 samples which did not comply with the QA/QC requirements, were analysed for CO, CH<sub>4</sub>, 39 non-methane hydrocarbons (NMHCs), 4 halocarbons, 5 alkyl nitrates and DMS. The average mixing ratios of these 51 species are summarised in Fig. 2. Briefly, the average mixing ratio of CO was  $600 \pm 20$  ppbv (95% confidence interval) and CH<sub>4</sub> was  $2100 \pm 19$  ppbv. The top 5 non-methane VOCs, in terms of abundance, were toluene, ethane, ethyne, propane and ethene, and their average mixing ratios were  $4180 \pm 400$ ,  $3670 \pm 130$ ,  $3130 \pm 150$ ,  $2900 \pm 130$  and  $2490 \pm 140$  pptv, respectively. The most abundant VOCs observed in the study, accounted for more than 80% of the total VOC composition, comparable with results previously reported for other cities (Table 2). Among these species, good correlations were found between ethyne, ethene and benzene ( $R^2 > 0.70$ ) suggesting common sources, vehicle exhaust and combustion (Liu et al., 2008a). The three species made up about 23% of total VOCs. Secondly, species associated with LPG evaporation, including propane, n-butane and i-butane (Liu et al., 2008a), correlated quite well ( $R^2 > 0.75$ ) and added up to about 20% of the total VOCs. Toluene, ethylbenzene and the xylenes (TEXs),  $R^2 > 0.73$ , are known to be emitted from industrial solvent use and gasoline evaporation (Tang et al., 2008). They accounted for another 20% of the total VOCs. Lastly, no significant correlations were found between isoprene and those abundant VOC species ( $R^2 < 0.17$ ).

From the above analysis, the distinct correlations among the abundant VOC species suggested a significant contribution from vehicle related sources, including vehicle exhaust, LPG and gasoline

**Table 2**  
VOCs mixing ratio comparison with previous studies.

Study area	28 US cities		UK cities		PRD – China		Guangzhou – China		Dongguan – China		43 Chinese cities		Hong Kong – China		PRD – China	
	Urban	Urban	Urban and Rural	Urban	Industrial	Industrial, urban	Industrial, Sub-urban	Urban	Urban	Urban	Urban	Urban	Rural, urban	Industrial, urban, rural	Industrial, urban, rural	Avg.
CO (ppmv)	0.15–0.64	–	–	1.4	0.7	0.5	0.5	0.47–2.63	0.29–3.71	–	–	–	0.31–0.51	0.15–1.73	0.60	
CH <sub>4</sub> (ppmv)	1.76–2.25	–	–	2.1	2	2	2	1.93–4.85	1.87–2.73	–	–	–	1.89–2.02	1.72–3.59	2.10	
Ethane	0.56–8.74	4.2	4.2	2.3	1.8	1.4	1.4	0.81–3.47	0.64–2.32	–	1.89–2.36	–	3.7–17.0	1.12–13.42	3.67	
Propane	0.29–6.05	2.0	2.0	3.7	2.5	2.1	2.1	1.30–19.80	0.48–8.13	–	1.5–20.8	–	0.86–2.55	0.34–14.75	2.90	
n-Butane	0.16–2.34	3.2	3.2	2.6	1.5	1.3	1.3	0.76–9.77	0.37–6.50	–	0.6–14.5	–	0.59–2.63	0.05–8.87	1.78	
i-Butane	0.08–1.26	–	–	1.6	1	0.8	0.8	0.47–6.14	0.19–3.36	–	0.4–4.6	–	0.34–1.46	BDL–6.65	1.45	
n-Pentane	0.11–1.20	0.6	0.6	1.3	0.5	0.4	0.4	0.22–3.83	0.12–4.95	–	0.2–7.7	–	0.17–0.54	0.04–8.04	0.77	
i-Pentane	0.28–2.79	–	–	2.2	1.3	0.9	0.9	0.54–8.57	0.32–4.66	–	0.3–18.8	–	0.37–1.14	0.06–9.73	1.29	
Ethene	0.26–2.43	3.4	3.4	5.1	2.6	2	2	0.78–11.10	0.65–10.70	–	2.1–34.8	–	0.86–2.67	0.22–11.88	2.49	
Ethyne	0.26–2.38	4.6	4.6	6	4	3.1	3.1	1.71–13.40	1.02–16.70	–	2.9–58.3	–	1.37–2.87	0.13–14.64	3.13	
Benzene	0.06–0.48	1.1	1.1	2.8	2	1.3	1.3	0.65–6.80	0.27–6.45	–	0.7–10.4	–	0.40–0.73	0.05–12.74	1.52	
Toluene	0.12–1.43	2.2	2.2	13.5	11.5	7.3	7.3	0.72–19.60	0.53–25.30	–	0.4–11.2	–	1.03–4.34	0.06–45.17	4.18	
Ethylbenzene	0.01–0.26	–	–	2	0.9	0.8	0.8	0.14–1.24	0.07–7.45	–	0.1–2.7	–	0.12–0.55	0.01–9.50	0.80	
m-Xylene	0.04–0.82	0.4	0.4	4.9	2.5	1.7	1.7	0.25–4.98	0.11–5.95	–	0.4–15.3	–	0.16–0.93	0.00–7.02	0.63	
o-Xylene	0.02–0.37	0.4	0.4	1.2	0.7	0.5	0.5	0.10–1.77	0.05–2.11	–	0.1–6.9	–	0.06–0.31	0.00–3.76	0.37	
Isoprene	0.05–2.59	0.1	0.1	0.6	0.4	0.5	0.5	0.18–4.46	0.11–4.74	–	0.04–1.7	–	0.19–0.33	BDL–3.204	0.21	

Notes: All units are in ppbv unless otherwise stated.

evaporation. Industrial solvent emissions were also an important VOC source in the PRD region.

### 3.1.1. Spatial VOCs variations in the PRD region

The spatial characteristics of the PRD region were further analysed by dividing the entire gridded area into three sub-regions, namely the Eastern PRD (EPRD), the Pearl River Estuary (PRE) and the Western PRD (WPRD), based on their geographic locations (Fig. 1). The mixing ratios of CO, CH<sub>4</sub>, isoprene and the remaining VOCs, grouped in five classes, were determined for these sub-regions (Fig. 3). The total non-methane alkanes were found to be the highest at the PRE (18.3 ± 1.4 ppbv), followed by the WPRD (13.9 ± 1.0) and the EPRD (11.7 ± 0.6). Aromatics, the second highest abundant class, showed similar patterns with 12.8 ± 1.6 at PRE, 8.2 ± 1.2 at WPRD, and 5.4 ± 0.8 at EPRD. Consistent trend in the spatial variation of the five VOCs classes indicated that PRE was the most polluted area, while EPRD was the cleanest area.

Further, the ethyne to CO (E/C) ratio was analysed to evaluate the air mass age as ethyne and CO share a common source, i.e. combustion. They have different lifetimes (approximately 2 months for CO, and 2 weeks for ethyne) because of different removal rates in the troposphere by their common sink, OH. E/C ratios ranging from 2.2 to 6.1 pptv ppbv<sup>-1</sup> were reported in US cities (Baker et al., 2008), while in Hong Kong, E/C ratios for fresh combustion sources ranged from 5.6 to 7.5 pptv ppbv<sup>-1</sup> (Guo et al., 2007). In the present study, E/C ratios for the EPRD, PRE and WPRD were 5.0 ± 0.24, 5.6 ± 0.32 and 4.9 ± 0.21 pptv ppbv<sup>-1</sup>, respectively, which indicated the three sub-regions were generally associated with freshly emitted pollutants. Relatively lower values at the EPRD and WPRD suggested that the air masses in these two sub-regions have undergone a small degree of photochemical processing.

Moreover, as benzene is mainly emitted from vehicular combustion and toluene is released from industrial applications, the benzene to toluene (B/T) ratio was used to evaluate the relative importance of these two sources over the three sub-regions. In addition, a B/T ratio higher than emission sources could also result from older air masses due to their differences in lifetime (approximately a factor of 5 (Guo et al., 2007)). In the UK and US, B/T ratios were ranged from 0.2 to 0.7 (Derwent et al., 2000; Baker et al., 2008). A high B/T ratio (0.7) was found for vehicular sources by Tang et al. (2008) in the PRD region. In the present study, a B/T ratio of 0.4 ± 0.04, lower than that of vehicular sources (B/T = 0.7), was obtained at the PRE, suggesting this sub-region exhibited the

characteristics of having both vehicular and industrial sources. In the EPRD and WPRD, B/T ratios were 0.8 ± 0.08 and 0.8 ± 0.07 respectively, which were slightly larger than 0.7 indicating a strong contribution from vehicular emissions with a certain degree of photochemical process. From the E/C and B/T ratios as well as the VOCs mixing ratios results, it can be concluded that the PRE area generally experienced higher VOCs levels, possibly due to the intense local sources from the condensed urban and industrial developments. In the four sampling campaigns, the prevailing winds originated from the Northeast quadrant. Therefore, the WPRD was the next most polluted area as it is situated downwind of major emission sources. The EPRD was the cleanest. Although the studied area was expected to be influenced by the sources outside the PRD region, this analysis demonstrated that spatial VOCs variation was significantly affected by the freshly emitted pollutants from local sources in the PRD region during days of elevated pollutant concentrations under poor atmospheric dispersion conditions.

Since the sampling design of the present study focused on the spatial VOC characteristics in the PRD region, the temporal resolution (i.e. number of samples in each day) and sampling duration (i.e. number of days) in each campaign were limited. These data were not sufficient to determine the trend of temporal and seasonal variations, which deserves further investigations.

### 3.1.2. Alkyl nitrate evolution

Alkyl nitrates (RONO<sub>2</sub>) evolution traces air mass age by evaluating its photochemical reaction processes. This information is particularly useful to determine whether the pollutants originated from local sources or from long-distance transport. The evolution time (*t*) for the air mass can be determined by assuming an initial ambient alkyl nitrates mixing ratio of zero (Bertman et al., 1995; Simpson et al., 2003; Worton et al., 2010).

The alkyl nitrate evolution time depends on the concentration of OH, [OH]. Recently, Hofzumahaus et al. (2009) found that the [OH] in PRD region was unexpectedly high and could reach on the order of 1 × 10<sup>7</sup> molecule cm<sup>-3</sup>, about one order of magnitude higher than that adopted in previous studies (Simpson et al., 2003; Worton et al., 2010). It should be noted that [OH] on the order of 1 × 10<sup>5</sup>–1 × 10<sup>6</sup> molecule cm<sup>-3</sup> is generally found in clean air, while [OH] on the order of 1 × 10<sup>7</sup> molecule cm<sup>-3</sup> characterises a highly polluted atmospheric environment. To investigate the effects of this local characteristic, sensitivity of evolution time (*t*)

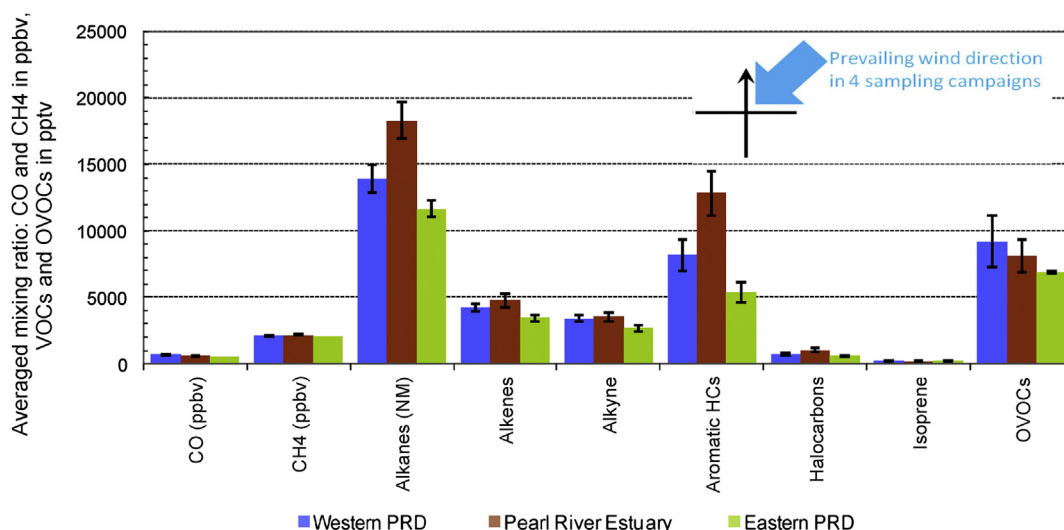


Fig. 3. Averaged Mixing ratios of CO, CH<sub>4</sub>, VOC groups and OVOCs with respect to three sub-regions (Error bars showing ±95% confidence interval).

with respect to [OH] on the photochemical process was determined, as shown in Fig. 4a. The corresponding laboratory kinetic data are listed in Table 3. Modelled ratios of n-propyl nitrate to propane were plotted against 2-butyl nitrate to n-butane. The increases in [OH] showed a significant effect on evolution time ( $t$ ), i.e.  $t = 5$  h for [OH] at  $1 \times 10^7$  molecule  $\text{cm}^{-3}$  compare to  $t = 2$  days for [OH] at  $1 \times 10^6$  molecule  $\text{cm}^{-3}$ . That is, high [OH] enhanced the reaction process tremendously in the PRD region. This important local characteristic warrants further investigations to improve the analytical and modelling approach for the photochemical transformation in the PRD region.

The measured and modelled data for the PRD, i.e. [OH] at  $1 \times 10^7$  molecule  $\text{cm}^{-3}$ , are plotted in Fig. 4b–d. Although the initial alkyl nitrate concentration is likely not zero, there would only be an over-estimation of air mass age due to this deficiency. In other words, the upper limit of the sampled air mass age can be adequately defined. From the figures, the estimated air mass ages among most of the samples were within one day. This indicated the pollutants affecting the PRD region during the four sampling campaigns were mainly from sources within the region. This finding is consistent with the meteorological conditions observed. Briefly, the two summer campaigns were conducted before the arrival of typhoons which induced stagnant conditions over the region, while one winter campaign was carried out before the arrival of a cold front and the second winter campaign took place during the passage of a weak cold front. The wind speeds during all these campaigns were generally calm which favoured pollutant accumulation. These are typical meteorological conditions where elevated ozone level occurs in summer and winter. From this semi-quantitative analysis of air mass age, the prominent effects of short-distance travelled pollutants suggests local emission control of ozone precursors is critical and could be effective to address the elevated ozone problem.

### 3.1.3. OVOCs characteristics in PRD region

OVOCs are an important fraction of the VOCs which significantly influence atmospheric photochemistry, including ozone formation, even at very low concentrations. OVOC samples were taken in the four sampling campaigns, as shown in Table 1. The average mixing ratios of the OVOCs are summarized in Fig. 2. The top five most abundant OVOCs are formaldehyde (average  $\pm 95\%$  confidence interval:  $2530 \pm 370$  pptv), acetone ( $2470 \pm 370$  pptv), acetaldehyde ( $1110 \pm 140$  pptv), methylglyoxal ( $890 \pm 160$  pptv), and glyoxal ( $440 \pm 70$  pptv), accounting for 87% of the total OVOC mixing ratio. In total, higher mixing ratios of OVOCs were observed during daytime (average  $\pm 95\%$  confidence interval:  $26.6 \pm 3.2 \mu\text{g m}^{-3}$ ) than at night ( $19.0 \pm 2.9 \mu\text{g m}^{-3}$ ). Meanwhile, summer ( $25.5 \pm 3.3 \mu\text{g m}^{-3}$ ) had a larger value than winter ( $20.2 \pm 3.0 \mu\text{g m}^{-3}$ ). These inter-comparisons among different times and seasons showed that a higher OVOCs mixing ratio was usually associated with a higher temperature and stronger sunlight. This infers the secondary formation of OVOCs in the PRD region plays an important role. The finding was further supported by the spatial analysis of OVOCs in the three sub-regions adopted in the VOCs analysis (Fig. 3). In contrast to the VOCs, the highest OVOCs mixing ratio was observed in WPRD ( $26 \pm 5.3 \mu\text{g m}^{-3}$ ), followed by PRE ( $23 \pm 3.4 \mu\text{g m}^{-3}$ ) and the EPRD ( $20 \pm 2.8 \mu\text{g m}^{-3}$ ). With the prevailing winds from the Northeast quadrant, the WPRD, which was downwind of the high VOC emitting areas in PRE, experienced higher OVOC levels in the ambient air. This consistently reflects the importance and the time delayed process of photochemical formation of OVOCs. However, the relative contribution of primary and secondary sources of OVOCs could not be identified and suggested for further studies.

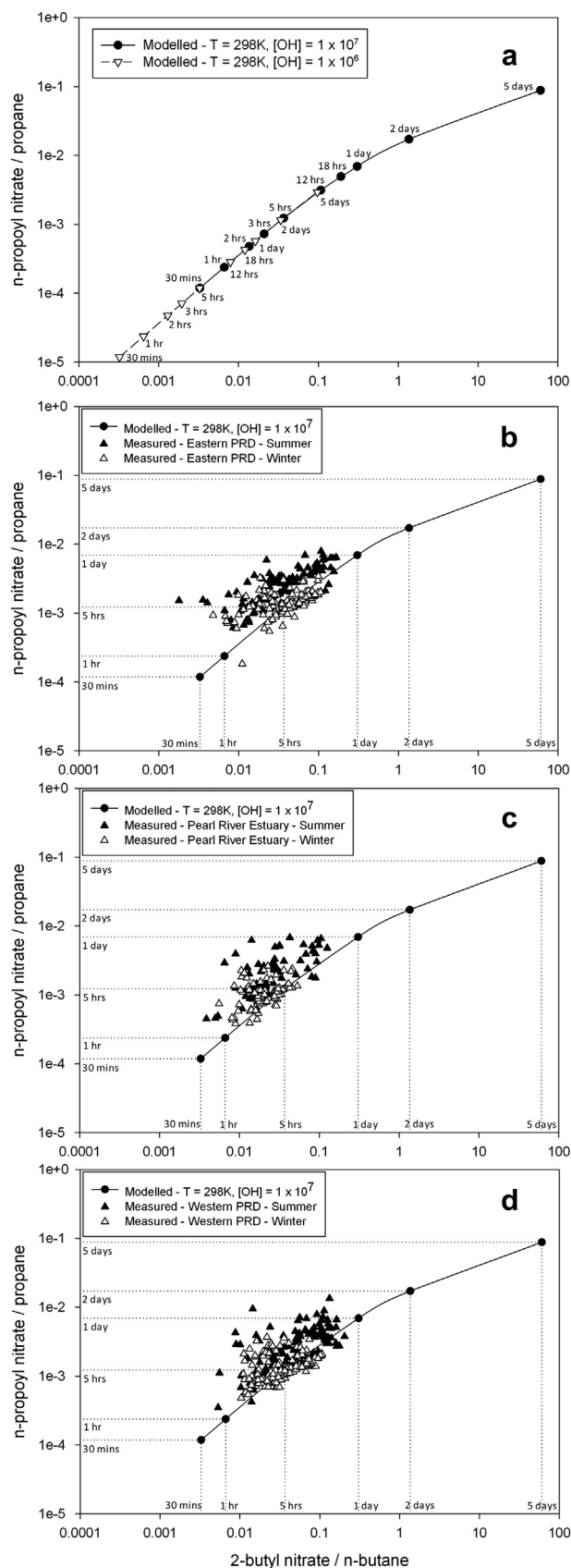


Fig. 4. (a) Modelled time evolution of n-propyl nitrate/propane versus 2-butyl nitrate/n-butane in different orders of [OH], (b)–(d) measured and modelled time evolution of n-propyl nitrate/propane versus 2-butyl nitrate/n-butane in different sub-regions and seasons.



**Table 3**  
Laboratory kinetic data for alkyl nitrates.

Parent RH	Daughter RONO <sub>2</sub>	Branching Ratios <sup>a</sup>			RONO <sub>2</sub> production			RONO <sub>2</sub> loss				
		$\alpha_{(\text{RO}_2)}^d$	$\alpha_{(\text{RONO}_2)}^d$	$\beta^d$	$k_{(\text{RH}+\text{OH})}^{b,d}$	$k_A^d$		$k_{(\text{RONO}_2+\text{OH})}^{b,d}$	$J_{\text{RONO}_2}^{c,d}$	$k_B^d$		
					$T = 298 \text{ K}$	$[\text{OH}] = 1 \times 10^7$ molecule cm <sup>-3</sup>	$[\text{OH}] = 1 \times 10^6$ molecule cm <sup>-3</sup>	$T = 298 \text{ K}$			$[\text{OH}] = 1 \times 10^7$ molecule cm <sup>-3</sup>	$[\text{OH}] = 1 \times 10^6$ molecule cm <sup>-3</sup>
C <sub>3</sub> H <sub>8</sub>	n-C <sub>3</sub> H <sub>7</sub> ONO <sub>2</sub>	0.307	0.020	0.006	1.07	10.70	1.07	0.58	0.33	6.13	0.91	
n-C <sub>4</sub> H <sub>10</sub>	2-C <sub>4</sub> H <sub>9</sub> ONO <sub>2</sub>	0.853	0.090	0.077	2.34	23.40	2.34	0.86	0.47	9.07	1.33	

Units: 10<sup>-12</sup> cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> for  $k_{(\text{RH}+\text{OH})}$  and  $k_{(\text{RONO}_2+\text{OH})}$ ; 10<sup>-6</sup> s<sup>-1</sup> for  $k_A$ ,  $k_B$  and  $J_{\text{RONO}_2}$  from Simpsons et al. (2003).

<sup>a</sup> Branching Ratios are from Atkinson et al. (1987).

<sup>b</sup>  $k$  values are from Atkinson et al. (2006).

<sup>c</sup>  $J$  values are from Simpson et al. (2003).

<sup>d</sup> The RONO<sub>2</sub> formation and destruction can be represented by Equations (T1)–(T3) and Equations (T4) and (T5), respectively:



where  $k_{(\text{RH}+\text{OH})}$ ,  $k_{(\text{R}+\text{O}_2)}$ ,  $k_{(\text{RO}_2+\text{NO})a}$ ,  $k_{(\text{RO}_2+\text{NO})b}$  and  $k_{(\text{RONO}_2+\text{OH})}$  are reaction rate constants,  $J_{\text{RONO}_2}$  is photolysis rate constant and the branching ratio  $\alpha_{(\text{RO}_2)}$  indicates the yield fraction of specific RO<sub>2</sub>, while  $\alpha_{(\text{RONO}_2)}$  indicates the yield fraction of alkyl nitrates from the reaction between RO<sub>2</sub> and NO. Equations (T1)–(T5) can be simplified as (T6) and (T7), respectively.



where  $k_A = k_{(\text{RH}+\text{OH})} \times [\text{OH}]$  and  $k_B = J_{\text{RONO}_2} + k_{(\text{RONO}_2+\text{OH})} \times [\text{OH}]$  are pseudo first order rate constants, and  $\beta = \alpha_{(\text{RO}_2)} \alpha_{(\text{RONO}_2)}$  combines the branching ratios for alkyl nitrates formations. Assuming initial ambient alkyl nitrates mixing ratio to be zero, the evolution time ( $t$ ) for the air mass can be determined by Equation (T8) (Bertman et al., 1995):

$$\frac{[\text{RONO}_2]}{[\text{RH}]} = \frac{\beta k_A}{(k_B - k_A)} \left( 1 - e^{(k_A - k_B)t} \right) \quad (\text{T8})$$

### 3.2. Ozone formation potential (OFP)

Ozone is a secondary pollutant resulting from the photochemical reactions by precursors NO<sub>x</sub> and VOCs in the presence of sunlight. In the urban areas of the PRD, ozone formation is generally VOCs sensitive (Shao et al., 2009; Cheng et al., 2010a) which implies that emission controls on anthropogenic VOCs sources is critical for reducing ground level ozone pollution. Generally, mass-based and reactivity-based approaches form the basis for controlling VOC emissions. The mass-based approach is commonly adopted in the US, UK, Japan and Hong Kong, as the amount of VOCs emission is relatively easier to be quantified. However, the ozone reduction efficiency is limited as photochemical ozone formation is more directly linked to VOCs reactivity rather than the mass of VOCs emitted. For example, recent research has demonstrated that reactivity-based VOCs control could be more effective than the mass-based approach to abate the ozone problem (Derwent et al., 2007; Cheng et al., 2010b).

To assess the reactivity and subsequent ozone formation potential (OFP) of various VOCs, a recently updated maximum incremental reactivity (MIR) scale (Carter, 2008) was applied in the following equation:

$$\text{OFP}_i = \text{VOC}_i \times \text{MIR}_i \quad (1)$$

where OFP<sub>*i*</sub> and VOC<sub>*i*</sub> are the ozone formation potential and the mixing ratio of VOC species *i*, both in units of μg m<sup>-3</sup>. MIR is a dimensionless coefficient for individual VOC species to indicate its contribution to local ozone formation.

Although being an important species for climate change, methane has very low photochemical reactivity and, thus, was exempted from the OFP analysis. Besides, CO, alkyl nitrates and DMS were not included in the calculation as MIR values were not available (Carter, 2008).

Fig. 5 shows the results for OFP analysis with respect to the three sub-regions and two different seasons. In summer, the total OFP of VOCs for EPRD, PRE and WPRD were 160 ± 20 μg m<sup>-3</sup>, 280 ± 40 μg m<sup>-3</sup> and 190 ± 30 μg m<sup>-3</sup>, respectively. While, in winter, relatively higher OFP were observed for both sub-regions, i.e. 180 ± 30 μg m<sup>-3</sup> for EPRD, 400 ± 70 μg m<sup>-3</sup> for PRE and 270 ± 50 μg m<sup>-3</sup> for WPRD. This seasonal trend was a result of the higher VOC mixing ratios measured in winter. Similarly, the highest OFP at PRE, followed by the WPRD and then the EPRD were in line with the findings in the spatial VOC characteristic analysis. Moreover, the contributions (in percentage) of the groups of 5 VOCs to the total OFP are also illustrated in Fig. 5. The aromatic HCs and alkenes, followed by alkanes, were the dominant contributors to OFP. Aromatics and alkenes together consisted of around 80% of the total OFP of VOCs, while alkanes contributed another 12–14%.

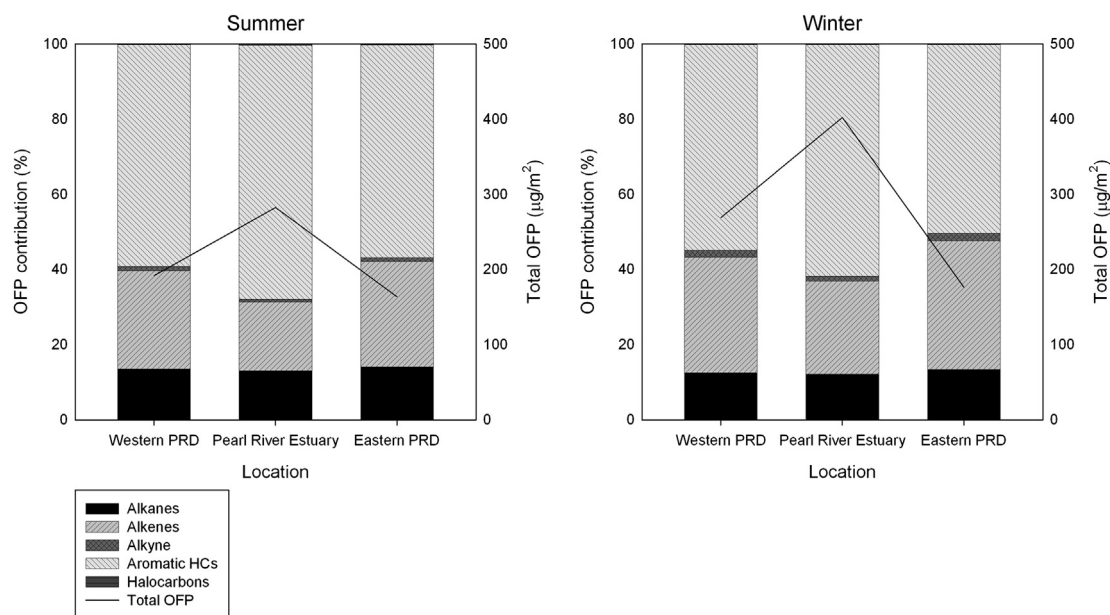


Fig. 5. OFP distributions (%) of 5 VOC groups and total OFP in summer and winter.

We note that the sample size, sampling time and the number of sampling locations between VOCs and OVOCs were not the same, nevertheless, the averaged OFP values from the two groups can be compared for evaluation of the relative importance of OVOCs. The OFPs from OVOCs, as shown in Fig. 6, were around 73% and 33% of that from VOCs in summer and winter, respectively. These results were comparable to the findings in the observation-based model (47–64%) by Cheng et al. (2010a) and consistent with the study by Lü et al. (2010), i.e. the OFPs in summer were 1–2 times higher than those in other seasons. The present study reveals a significant contribution from OVOCs in ozone formation in the PRD region. Among the 17 measured OVOCs, the leading four OFP contributors were formaldehyde, acetaldehyde, glyoxal and methylglyoxal, accounting for 80–85% of OFP by OVOCs. These four OVOCs had higher OFPs as a combined result of their relatively high mass concentrations and MIR values (>6). In comparison, acetone had the highest mass concentration among all measured OVOCs, but it made only a minor contribution to the overall OFP by OVOCs primarily because it has a low MIR value (0.35). The prominent contribution of a few reactive OVOCs has also been reported in other polluted environment (Grosjean et al., 2002; Lü et al., 2010). The OVOC data in this study strongly suggests further investigation of the OVOC sources and major precursors in this region are important in mitigating ozone pollution.

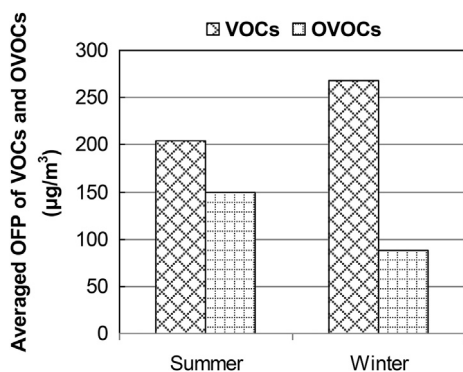


Fig. 6. Averaged OFP values from VOCs and OVOCs in summer and winter.

#### 4. Conclusions and implications for VOC control measures

Measurements of VOCs, OVOCs and CO were taken extensively in the PRD region, during summer and winter of 2008 and 2009. Elevated anthropogenic VOCs mixing ratios were found at the PRE which were associated with the characteristics of urban and industrial sources. Contributions from these local sources to the total ambient VOCs levels were significant especially during days under poor atmospheric dispersion condition. Fast photochemistry was observed in the PRD region due to its highly oxidising atmospheric environment. Besides, there were considerable contributions of OVOCs to ozone formation but its sources and characteristics were not well established. Better understanding on these observations is essential for fine-tuning the analytical and regional modelling approaches as well as implementing appropriate pollution control measures. These findings reinforced the current policies on controlling vehicular and industrial emissions and further supported the policy formulation for alleviating photochemical ozone problem in regional perspective.

Taking the science into consideration, the governments in the PRD region, including Guangdong, Hong Kong and Macao, could proactively collaborate and undertake enhanced air quality improvement and control measures. Firstly, the regional air quality monitoring network should be enhanced for analysing the characteristics and identifying emerging air pollution issues in the PRD region. Local features of the atmospheric environment, such as OVOC sources and characteristics, and the fast photochemistry in an elevated OH environment, deserve further scientific investigation.

Moreover, short-term elevated ozone concentrations are of more concern than the annual average. This problem could be effectively handled by controlling the emission intensity and distribution of ozone precursors, especially in upwind areas. Hence, a science-based land-use planning could play an important role, bearing in mind the easterly prevailing winds during elevated ozone conditions in the PRD region. In particular, the planning strategies could reprioritise the future development over the three sub-regions for the purpose of protecting the upwind area, i.e. Eastern PRD, limiting the growth of heavily polluted Pearl River Estuary and enhancing the development of the Western PRD.

For emission control, the dominant sources, i.e. vehicle-related and industrial emissions, are of major focus. For instance, both Guangdong and Hong Kong governments are striving to reduce vehicular emissions by progressively tightening fuel and emission standards. The promotion of green transportation could reduce vehicle-related emissions, while reduction of industrial emissions could be achieved by phasing out or upgrading outdated industrial processes, and implementing cleaner production requirements.

In the long run, a low-emission life style should be cultivated in our community. Both the Guangdong and Hong Kong governments could demonstrate their motivation by promoting energy conservation such as developing renewable energy and enhancing energy efficiency.

## Disclaimer

The content of this paper does not necessarily reflect the views and policies of the HKSAR Government, nor does mention of trade names or commercial products constitute an endorsement or recommendation of their use.

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