Atmospheric Environment 115 (2015) 153-162

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Characteristics and reactivity of volatile organic compounds from non-coal emission sources in China



ATMOSPHERIC ENVIRONMENT

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HIGHLIGHTS

• Abundant VOCs species profiles for non-coal sources in China were presented.

• The source profiles developed in our study showed some differences with others reported.

• B/T is a good marker to distinguish some VOCs sources but not all.

Most of the VOCs emissions from non-coal sources have high air reactivity.

ARTICLE INFO

Article history: Received 22 August 2014 Received in revised form 26 May 2015 Accepted 28 May 2015 Available online 30 May 2015

Keywords: Volatile organic compounds (VOCs) Source profiles BTEX ratios Chemical reactivity

ABSTRACT

Volatile organic compounds (VOCs) were sampled from non-coal emission sources including fuel refueling, solvent use, industrial and commercial activities in China, and 62 target species were determined by gas chromatography-mass selective detector (GC-MSD). Based on the results, source profiles were developed and discussed from the aspects of composition characteristics, potential tracers, BTEX (benzene, toluene, ethylbenzene and xylene) diagnostic ratios and chemical reactivity. Compared with vehicle exhausts and liquid fuels, the major components in refueling emissions of liquefied petroleum gas (LPG), gasoline and diesel were alkenes and alkanes. Oppositely, aromatics were the most abundant group in emissions from auto-painting, book binding and plastic producing. Three groups contributed nearly equally in printing and commercial cooking emissions. Acetone in medical producing, chloroform and tetrachloroethylene in wet- and dry-cleaning, as well as TEX in plastic producing etc. were good tracers for the respective sources. BTEX ratios showed that some but not all VOCs sources could be distinguished by B/T, B/E and B/X ratios, while T/E, T/X and E/X ratios were not suitable as diagnostic indicators of different sources. The following reactivity analysis indicated that emissions from gasoline refueling, commercial cooking, auto painting and plastic producing had high atmospheric reactivity, and should be controlled emphatically to prevent ozone pollution, especially when there were large amounts of emissions for them.

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1. Introduction

As an important air pollutants in urban atmosphere, VOCs have being attracted more and more concerns in the world. They can chemically interact with oxides of nitrogen and sunlight to form ground-level ozone, and even take part in the formation of haze, which now is the most serious environmental problem in China with frequent and large-scale occurrences in recent years (Anand et al., 2014; Durkee, 2014). More importantly, they also have detrimental effects on human health by contributing to respiratory illnesses, even being mutagenic or toxic to reproduction and harmful to the unborn (Anand et al., 2014).

Many studies indicated that chemical composition of VOCs emissions varied with different fuels or solvents, regions or countries, and operating sectors or processes (Na et al., 2004; Liu et al., 2008; Zheng et al., 2013; Zhang et al., 2013). The diverse sources



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and complex compositions of VOCs make it difficult to identify major emission sources and estimate the relative importance of each source to ambient VOCs concentrations, consequently hinder us from understanding the formation mechanism of secondary pollutions and devising effective control policies in urban areas seriously. Source profiles are the composition pattern of species emitted from each source category, and so are the fundamental information for developing the speciated pollutants emission inventories used in air quality models, and identifying source contributions via receptor models (Zheng et al., 2009; Marmur et al., 2007). To make sure the accuracy of emission inventories and source contributions, a unique, comprehensive and real-time updated "profile" (composition) is required for each source.

In present China, high population density (19.3% of the world total in 2014, WPS, 2015) and fast growing economy beginning in 1980s, have being accompanied by more and more pollutants emission. For example, the total VOCs emission increased from 13.1 Tg in 1995 to 20.1 Tg in 2005, and possibly would be 25.9 Tg in 2020 as estimated by Wei et al. (2011). Scientists in China have begun in recent years to measure local VOCs profiles for major emission sources, such as vehicular exhaust, gasoline evaporation, coal burning, biomass burning, petrochemical industry and solvent use of painting and printing (Liu et al., 2008; Yuan et al., 2010; Guo et al., 2011; Zhang et al., 2013; Zheng et al., 2013; Wei et al., 2014; Wang et al., 2014). These studies have developed some domestic VOCs source profiles in China, but those profiles are far from enough in covering all the VOCs sources such as LPG refueling, cleaning, plastic producing and book binding etc, or need more supporting evidences, making it hard to establish accurate emission inventories or apportion sources using CMB model in China (Wang et al., 2014a).

As a very large pollution source in China which is facing notorious air pollution, coal burning always attracts the most attention, but non-coal sources like fossil fuel evaporation (refueling, diurnal and hot-soak), solvent utilization and industrial processes cannot be ignored. After America, China is the second-biggest consumer of LPG and motor gasoline consuming 740.2 and 1615.9 thousand barrels per day respectively in 2010 with the consumption still increasing (EIA, 2015a). During their handling and usage, large amounts of VOCs are discharged. It was reported that approximately 185,000 tons vehicular evaporative emissions were emitted in 2010 in China, among which refueling contributed 67% (Yang et al., 2015). For both solvent utilization and industrial processes, Wei et al. (2011) predicted they would become the highest two VOCs contributors in 2020, emitting 37% (9.40 Tg) and 24% (5.92 Tg) of the total VOCs emissions, respectively, even if China's legislative standards for VOCs emissions would be implemented effectively in the future (Wei et al., 2011). To further enrich the database of VOCs source profiles in China, various non-coal emission sources including refueling of LPG and fossil oils, auto painting, printing, wet and dry cleaning, medicine and plastic producing, as well as commercial cooking in a coastal region of China were investigated, with their potential tracers and BTEX ratios being discussed in our study. Their atmospheric chemical reactivity was also evaluated to give more insights for targeted pollution control.

2. Methods

2.1. Sample collection

Different volumes of stainless steel canisters (Entech Instrument, Inc., Simi Valley, CA, USA) and Tedlar bags (Dalian Delin Gas Packing Co., Ltd, China) pre-cleaned with high purity nitrogen and evacuated to vacuum were used for sampling. Whole-process samplings were conducted for refueling, auto painting and printing emissions to explore the general features for them. For the emissions of medical producing, plastic processing and commercial cooking, instantaneous sampling above the exhaust ducts was conducted by the aid of a pump connected to the sampling bags. After sampling, all the samples were delivered to the laboratory for chemical analysis within a week. Detailed information is as follows:

2.1.1. Re-fueling of LPG

In China, a large proportion of residents living in rural places and city villages used the tanked-LPG for cooking instead of coal for convenience and light pollution. The tanks can be used repeatedly by re-inflating. For each sample, refueling emissions were collected from the launch to the stop of inflating operation to a civilian gas tank (capacity, 13.5 kg) using a 400-mL canister in an inflating workshop (n = 10; T, 24.5 °C). Before collecting, the connecting joint between gas inflating and releasing nozzle was wrapped to form a small enclosed space. One side of a tubule was also wrapped in it while the other side was connected to a sampling canister. The average sampling duration was 9.64 ± 0.64 s.

2.1.2. Re-fueling of gasoline and diesel

Oil refueling operations include transferring fuel from bulk storage tanks into transport vehicles like road tankers, road tankers into service station tanks and service station tanks into vehicle tanks. During filling of tanks, vapor evolves as a result of displacement of headspace vapor by the incoming oil, splashing and turbulence. In our study, vapors from storage tanks and vehicle tanks during refueling with gasoline and diesel were collected into 400-mL canisters through inserting sampling intake-tubules into the upper space of the tanks without touching the liquid surface. For gasoline, the vehicles investigated included cars and motorcycles. The sampling number for each refueling source was 10. Rush hours (9:00–10:00 a.m.) were chosen for sampling. The average sampling duration was 2.57 \pm 0.39 min for storage tanks, and 36 \pm 9.61 s for vehicle tanks. The ambient temperature during the sampling period was 28.3 °C with no strong wind.

2.1.3. Auto painting (automobile painting)

Painting is an important work in car-related industries. In an auto-painting workshop of a typical garage where gasoline-based paints were still the common used paints, 12 canister samples were collected in three different corners far from the door (4 samples for each corner) while 8 bag samples (2.5-L) were collected from the exhaust duct of the auto-painting workshop. There are three most important processes in painting, namely primer painting, finish coat painting and paint-drying with different paints being used (Yuan et al., 2010). With 1L paints for 5 m² car surface on average, sampling inside the workshop lasted 108 min covering all the 3 steps of painting with the indoor temperature being 24.9 °C. To avoid influences from other emission sources, all windows in the sampling room were closed and canisters were held near the VOCs sources.

2.1.4. Printing

Sampling was conducted in a comparatively large printing factory that mainly printed books, magazines, newspapers, and packaging materials. The press equipments in the factory were all offset lithographic printing machines. 10 canister samples (2-L) were collected at different sites of the printing room (total area was 4000 square feet), and another 10 were collected in binding room (total area was 5000 square feet) when all the press equipments were operating. The sampling duration was 1 h, during which 20 thousand papers were printed. As the sampling for auto-painting, windows in the sampling rooms were also closed. The average temperature in the printing factory was 23.2 °C.

2.1.5. Commercial cleaning

VOCs emission from commercial cleaning is due to the use of detergents. The major components in the wet-cleaning detergents were the mix of chloroform and tetrachloroethylene, while in the dry-cleaning detergents tetrachloroethylene was the unique component. To explore the VOCs emission profiles of wet- and dry-cleaning, the valves of sampling canisters (400-mL) were opened and put into washing machines promptly just after they stopped working, and then the lids were immediately closed until the sampling finished. The samplings were conducted during work hours, and lasted 15 min for wet cleaning and 10 min for dry cleaning. The average environment temperature during sampling was 25 °C.

2.1.6. Medicine producing

The pharmaceutical factory investigated in this study mainly produced western medicine including oral drugs, parenteral drugs, inhalant and topical drugs, etc. 8, 10 and 10 samples of 500 ml bags were collected above the exhaust ducts of manufacturing workshops, wastewater treatment workshops and centrifugal workshops respectively during several intermittent exhaust stages with one sample covering one exhaust stage. The average temperature near exhaust ducts was 25.0 °C.

2.1.7. Plastic processing

Plastics processing, is also commonly referred to as polymer processing, involves molding, forming, shaping, or altering plastic resins or plastic materials. All of the operations could give rise to VOCs emissions, resulting mainly from the volatilization of free monomer or solvent in the primary polymer blend during processing, secondary process materials, such as blowing agents, additives, and lubricants (mold release compounds) and byproducts formed by chemical reactions or formed during heating of resins. 15 bag samples (500-mL) were collected above the exhaust ducts during the melting processes of propene polymer (PP) and poly ethylene (PE) respectively in a plastic processing factory. The average temperature near exhaust ducts was 34.7 °C.

2.1.8. Commercial cooking

8 and 7 bag samples (500-mL) were collected above the exhaust ducts of a Chinese restaurant and a barbecue restaurant respectively during peak-hour business (at noon), and the average temperatures near their exhaust ducts were 35.6 and 37.3 °C respectively. The major cooking styles in Chinese restaurant were deep-fry, stir-fry, steam and boil, all of which were done in a unique kitchen with LPG being used as the major cooking fuel, while the styles in barbecue restaurant were roast and fumigate on electric oven with one exhaust pipe hanging above each dinner table and the emissions converging finally in the ducts.

2.2. Chemical analysis and quality assurance

VOCs samples were concentrated in the Model 7100 preconcentrator (Entech Instruments Inc., USA), and then transferred into a gas chromatography-mass selective detector (GC-MSD/FID, Agilent 7890A/5975C, USA). A HP-1 capillary column (60 m \times 0.32 mm \times 1.0 μ m, Agilent Technologies, USA) was first used in this system to separate the mixture, which was then split into two ways: one is to а PLOT-Q column $(30\,m \times 0.32\,mm \times 2.0\,mm$, Agilent Technologies, USA) followed by FID for detecting C_2-C_3 hydrocarbons; another is to a $80 \text{ cm} \times 0.10 \text{ mm}$ I.D stainless steel line followed by MSD for C₄-C₁₂ hydrocarbons. The MSD was used in selected ion monitoring (SIM) mode and the ionization method was electron impacting (EI). Target compounds were identified based on their retention times and mass spectra, and quantified by multi-point external calibration method with TO-14 (39 compounds) and TO-15 (25 compounds) standard mixtures from Spectra Gases Inc., USA. To avoid misjudgment, the retention times of VOCs species were determined also by MSD with SCAN mode for qualitative accuracy. The detailed description can be found elsewhere (Zhang et al., 2012). The method detection limits of target compounds in present study were all below 0.1 μ g/m³.

2.3. Data analysis

In each sample, 62 VOCs species were measured as shown in Table S1. VOCs source profiles were developed by using average percentage of mass known as weight fraction. For each source, the average constant OH loss rate (K^{OH}) and the maximum incremental reactivity (MIR) (sign as k-avg and MIR-avg) of VOCs, and the relative contribution from each species to the total VOCs reactivity (OH loss rate (L^{OH}) and the ozone formation potential (OFP)) were estimated according to the methods reported by Wang et al. (2014).

3. Results and discussion

3.1. Refueling emissions

Vehicle refueling, emitting 124,000 tons VOCs in 2010, has become an important source of VOCs related with fossil fuel usage except for vehicle emissions (Yang et al., 2015). VOCs source profiles for LPG, gasoline and diesel refueling investigated in the current study were shown in Fig. 1. Alkanes and alkenes were in high proportion (>86%) in all of the refueling emissions, with higher hydrocarbons based in gasoline (>C4) and diesel (>C4), while light alkanes (<C5) based in LPG. Some C4 compounds like isobutane, cis-2-butene and isopentane could be emitted from any of them (Table S2). Aromatics, the main components in fuel (Zhang et al., 2013), took up high proportions in gasoline and diesel vehicle exhausts (Liu et al., 2008; Guo et al., 2011; Schauer et al., 1999) but little in headspace vapors (Zhang et al., 2013) and refueling emissions (Our study and Zhang et al., 2013) for their relative low vapor pressure. In gasoline refueling emissions, the percentage of alkanes (29.6-35.56%) from our study were lower than that of 55.33-65.8% reported by Zhang et al. (2013), which was opposite for alkenes and aromatics

Different filling rates and different ways of splashing and turbulence might lead to the small variations about the VOCs composition among the refueling emissions of gasoline from storage tanks, as well as car and motorcycle tanks with different inner structures (Fig. 1B), while different oil composition was the major reason for the differences among the emissions from industrial, low-sulfur and vehicle-used diesels (Fig. 1C). Except for mutable composition of the oils in the market of China, different sampling methods also contributed to the difference. Our data gave the average situation during the whole refueling process, compared with the special situation when the vacuum assisted recovery systems were turned on and turned off. We inserted sampling intake-tubules connected with canisters into the upper space of the tank, but Zhang et al. (2013) just collected the vapors about 2 cm above the car tank vents.

Propane and butanes were widely used as tracers of LPG leakage in some countries like USA and Korea etc., where only propane or nbutane or they both dominated the total emission (Ayoko et al., 2014; Na et al., 2004), while our study found that the composition of LPG refueling emissions in China was more complex. It included 6 major species: n-butane, isobutane, acetylene, ethane, propane and propylene (Table S2). Among them acetylene, ethane and propylene were characteristic compounds of LPG which could



Fig. 1. VOCs source profiles of the emissions from refueling of LPG (A), gasoline (B), and diesel (C). The ID number of each species was the same as that of Table S1 (No. 1–59). Hollow pillars represented the data from our study, while colorized dots showed the data from other reported studies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

distinguish it from the refueling vapors of gasoline and diesel (compared Fig. 1A with others). Combination of abundant butenes, isopentane, 2-methylpentane and MTBE could be used to differentiate gasoline and diesel refueling emissions from other sources, while combination of high percentages of isopentane, toluene and MTBE could be used to distinguish gasoline vehicle exhausts from other sources concerned in our study (compared Fig. 1B with others). Some heavier alkanes, such as n-heptane, n-undecane and methylcyclohexane, which were relatively abundant in diesel, especially in vehicle-used diesel but low in gasoline, might be taken as indicators for distinguishing the diesel refueling emissions from gasoline (Table S2). Although MTBE was often used as a tracer of the sources relative to gasoline, its role in diesel refueling emissions could not be ignored (Fig. 1C).

3.2. Solvent use emissions

Common activities involving solvent use in urban cities mainly include paint application, printing processes, wet and dry cleaning, etc. In China, small-sized workshops offering the above services are not only widespread but popular among people for their convenience and low expense in many neighborhoods. They always directly discharge their organic exhausts into the air, without exhaust collection and treatment systems. In our study, representative individual workshops were investigated as shown in Fig. 2 to provide more knowledge about them. Those samples collected inside the manufacturing workshops were classified as "fugitive emission" samples, while those collected from the chimneys were classified as "stack emission" samples.

3.2.1. Auto painting

In fugitive emissions, BTEX were found to be the main trace species, with m/p-xylene accounting for the largest percentage, followed by ethyl-benzene, o-xylene, toluene (Fig. 2A; Table S3). The results were consistent with other reported analyses (Yuan et al., 2010; Wang et al., 2014), which also found the same aromatic tracers in paint application emissions (Fig. 2A).

3.2.2. Printing

Studies in VOCs profiles of printing source from this study and other reported data (Yuan et al., 2010; Wang et al., 2014) all indicated that alkanes were the most important species in the emissions followed by aromatics, but different composition characteristics were observed (Fig. 2B). In our study, vinyl acetate was only detected in printing emissions, so it should be an important tracer for this source. And toluene was found to be the most abundant species in the printing emissions contributing 12.74% of the TVOCs, MTBE, m,p-xylene and isopentane, followed it and contributed 6–8% respectively (Table S3), while the contribution of each of the rest 80% compounds was only 0.1–3% by mass (data not shown). However, n-decane (16.86%), n-nonane (14.84%) and n-undecane (12.96%) were found to be the abundant species in a printing factory by Yuan et al. (2010), while ethane (17.4), n-

pentane (13.1%), m,p-xylene (10.8%) and ethylbenzene (10.1%) etc. were found by Wang et al. (2014a,b) in mixed printing exhausts. It was learned that printing machines were often cleaned using gasoline, which could explain the high levels of isopentane and MTBE. The binding of printed materials using adhesives also emitted VOCs (Fig. 2B), but the average concentration of fugitive emissions in the binding room (1.41 mg/m³) was significantly lower than that in the printing room (23.04 mg/m³), and m,p-xylene and ethyl-benzene were the major species accounting for 46.72% and 14.52% of the total VOCs (Table S3).

3.2.3. Commercial wet- and dry-cleaning

Chloroform and tetrachloroethylene were found only in the emissions of dry- and wet-cleaning, and were good tracers for these activities. Chloroform and tetrachloroethylene accounted for 78% and 22% respectively by mass in wet-cleaning. Also, tetrachloroethylene was virtually the only component (\approx 100% of the total) emitted from dry cleaning process. The results were consistent with those conducted in drying cleaning buildings or facilities (McDermott et al., 2005; Chiappini et al., 2009), residential homes (Kinney et al., 2002) and buildings near drying-cleaning facilities (McWon et al., 2006).

3.3. Industrial and commercial emissions

3.3.1. Pharmaceutical industry

14 VOCs species were detected in the samples from the medicine producing industry. Acetone, a commonly used solvent in pharmaceutical industry, not only accounted for high percentage (>50%) in various pharmaceutical processes (our study and He et al., 2012) including production, wastewater treatment and centrifugation, but also was unique compared with other emission sources involved in our study. In emissions from production lines



Fig. 2. VOCs source profiles of the emissions from auto painting (A) and printing (B). The ID number of each species was the same as that of Table S1 (No. 1–59). Hollow pillars represented the data from this study, while colorized dots showed the data from other reported studies. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

and centrifugation, the second abundant individual species was npentane, accounting for 16.04% and 12.90% respectively, while in emissions from wastewater treatment, the second was toluene accounting for up to 43.66%. The rest VOCs species from the three sampling sites were n-heptane and other 11 benzene homologues (m, p-xylene, ethyl-benzene, o-xylene, benzene, 1, 2, 4trimethylbenzene, o-ethyltoluene, m-ethyltoluene, 1, 3, 5trimethyl-benzene, p-ethyltoluene and n-propylbenzene) (Table S4).

3.3.2. Plastic processing

The previous studies on the PE/PP plastic waste recycling found that four toxic monocyclic aromatic hydrocarbons (MAHs) (m,pxylene, ethyl-benzene, o-Xylene and toluene) had the highest overall concentrations in the volatile compounds emitted from the melting and powdering processes (Tsai et al., 2009; Huang et al., 2013). Also, our study found that the four species were also the main components of the VOCs exhausted by plastic processing, accounting for more than 98% of the total either for PP producing or for PE producing. However, the composition characteristics of the emissions from plastic recycling and producing were entirely different. Toluene only contributed 5.66% and 2.11% to the total VOCs emissions from PP and PE producing (our study), but accounted for about 40% of the total hydrocarbons emitting from melting and powering process (Tsai et al., 2009; Huang et al., 2013). And it was just opposite for m, p-xylene, ethyl-benzene and o-Xylene (Table S4).

3.3.3. Commercial cooking

Emission of VOCs in cooking events have drawn considerable concerns in recent years (Huang et al., 2011; Mugica et al., 2001) in China because of the characteristic stir-frying cooking process (stove and food) with oil being heated to a very high temperature. In our Chinese restaurant samples, alkanes and aromatics accounted for 50.85% and 35.39% of the TVOCs respectively, while alkenes accounted for 12.51%. Among the species, n-pentane (21.69%) was the most abundant component in Chinese restaurant exhaust, followed by styrene (11.98%) and m, p-xylene (11.10%) (Table S4). In our barbecue restaurant samples, the contribution of alkanes, aromatics and alkenes were 41.75%, 28.35% and 27.23% separately, while contributions from n-pentane, ethylene and styrene were 21.97%, 15.61% and 9.87% respectively (Table S4). Direct evaporation losses of cooking fuels, incomplete combustion of meat and grease, cooking methods and charcoal used etc. all could influence the VOCs composition of cooking emissions and make it relatively mutable in different studies (Huang et al., 2011; Mugica et al., 2001).

3.4. BTEX ratios

According to the analysis of VOCs composition characteristics of each source emissions in our study, the species that were unique or present in high concentrations in a certain emission source were selected as possible tracers for it (Table 1). Because the chemical composition of printing and cooking emissions was variable, the tracers given in our study need to be confirmed by more studies. Some sources emitting similar VOCs species led to the inevitable overlap, which can complicate the application of CMB models. The diagnostic ratios of paired VOCs species well correlated in ambient measurements have been demonstrated to be a good way to differentiate the overlapped sources, such as benzene to toluene ratio (B/T), around 0.5 (wt/wt) being reported to be a characteristic of vehicular emissions, while >1 the characteristic of biomass burning (Barletta et al., 2005; Tan et al., 2012). As common species in the real environment and always being discharged from the same source, the paired ratios of BTEX received more attention, and therefore were analyzed for each source using the data from our study and previous works (Zhang et al., 2013; Wang et al., 2014; Yuan et al., 2010).

As shown in Table 2, B/T ratios ranged 0.3–1.11 in refueling of gasoline and diesel emissions. 0.01–0.3 in solvent use emissions. and 0.005–0.016 in industrial activity emissions, while >1 was reported to be the characteristic of biomass burning (Barletta et al., 2005; Tan et al., 2012). Little overlap among these sources indicated that B/T ratio could be a good marker to distinguish them when conducting source apportionment of atmospheric VOCs using receptor models. Some challenges were also found for the application of B/T ratio. The LPG refueling emission had a B/T ratio of 1.7 as the biomass burning (>1). B/T ratios in refueling emissions of gasoline and diesel (Table 2) were similar with the ratios found in vehicle emissions (0.33–0.67 was proposed to be the typical range of B/T ratios for traffic dominated source of emission, Shi et al. (2015)). In addition, the average B/T ratios of 0.60 and 0.32 were also found in the emissions from coke production and thermal power plant respectively (Shi et al., 2015). Barletta et al. (2008) proposed specific B/T ratios of <0.20 as an indicator for air samples which were strongly affected by industrial emissions. Furthermore, autopainting, printing, medicine producing, plastic producing and commercial cooking all fit this characteristic at some extent and overlapped with each other (Table 2), making it hard to differentiate them well in detail.

Ratios of B/E (>2.38) and B/X (>0.35) for refueling emissions of gasoline and diesel were much higher than their counterparts in other emissions from painting, printing, medicine producing and commercial cooking, but overlapped with the ratios for that of coal burning (about 3 for B/X), coke production (about 3 for both B/E and B/X) and vehicle exhausts (about 2.5 for B/E and 0.4 for B/X) etc. when calculated using the average data reported by other researchers (Shi et al., 2015; Liu et al., 2008; Na et al., 2004) (Table 2). Therefore, it will be better to have a general knowledge before using them to explore the sources. There were more overlaps for T/E, T/X and E/X ratios, so they are not suitable as indicators of different sources.

3.5. Reactivity characteristics

VOCs could influence the ozone formation and the atmospheric oxidizing capacity after being emitted into the atmosphere (Lelieveld et al., 2008), so the sources or the compounds in a certain source having high atmospheric chemical reactivity should be given priority when devising control programs. In our study, the kavg and MIR-avg values representing the average VOCs reactivity of each source were given in Table 3. It can be seen that the k-avg of VOCs from gasoline refueling were the largest, which were followed by that from commercial cooking, auto painting and plastic producing. The k-avg for VOCs from gasoline refueling sampled in this study was similar to that of m-ethyltoluene (Atkinson and Arey, 2003), while the k-avg from commercial cooking, auto painting and plastic producing was a little higher than that of p-xylene. Therefore, those sources will serve as important reactive sources in the regions unless their emission amounts are very low. VOCs exhaust from the medicine producing had the smallest k-avg value which was close to that of n-butane, indicating it might have low effect on the atmospheric chemical reactivity.

The sources with high k-avg also had high MIR-avg. In our study, the MIR-avg of VOCs from the plastic producing was the highest, followed by that of auto painting, book binding, gasoline refueling, printing, and commercial cooking in the decreasing order. Coinciding with the k-avg, VOCs from the medicine producing exhaust had the lowest MIR-avg. The MIR-avg of VOCs emitted from the

Table 1

The potential VOCs tracers for various emission sources in China.

Туре	Source	Potential tracers		
Fuel refueling	LPG	Butanes, propane, acetylene, ethane, propylene		
	Gasoline	MTBE, butenes, isopentane, 2-methypentane,		
	Diesel	MTBE, butenes, isopentane n-undecane, methylcyclohexane, n-heptane		
Solvent use	Auto painting	m,p-Xylene, ethyl-benzene, o-xylene, toluene		
	Printing	Vinyl acetate,		
	Wet cleaning	Chloroform, tetrachloroethylene,		
	Dry cleaning	Tetrachloroethylene		
Industrial activities	Medicine producing	Acetone		
	Plastic producing	Xylenes, ethyl-benzene, toluene		
	Commercial cooking	n-Pentane, styrene, m,p-xylene, ethylene		

Table 2

The value of BTEX ratios for different emission sources.

Туре	Source	B:T	B:E	B:X	T:E	T:X	E:X
Fuel refueling	LPG ^a	1.70	_	1.94	_	1.14	0.00
-	Gasoline to ST ^a	0.70	14.39	5.78	20.58	8.26	0.40
	Gasoline to motorcycles ^a	0.30	16.49	0.35	55.88	1.18	0.02
	Gasoline to cars ^a	0.35	3.51	1.11	9.99	3.15	0.32
	Gasoline to tank truck ^b	0.31	5.92	1.97	18.92	6.31	0.33
	Gasoline to cars ^b	0.50	4.74	3.03	9.57	6.11	0.64
	Industrial diesel to ST ^a	0.59	2.64	1.01	4.44	1.70	0.38
	Low-sulfur diesel to ST ^a	1.11	12.28	4.41	11.04	3.97	0.36
	Diesel to car to ST ^a	0.42	2.38	0.72	5.71	1.73	0.30
Solvent use	Auto painting (fugitive) ^a	0.02	0.01	0.00	0.23	0.12	0.53
	Auto-paint spraying (fugitive) ^c	0.27	0.027	0.01	0.08	0.03	0.36
	Auto-paint drying (fugitive) ^c	0.04	0.02	0.01	0.48	0.18	0.37
	Auto paints ^d	0.01	0.03	0.01	2.31	0.61	0.27
	Printing (fugitive) ^a	0.08	0.28	0.09	3.58	1.17	0.33
	Book binding (fugitive) ^a	0.18	0.04	0.01	0.21	0.06	0.27
	Print (stack) ^d	0.13	0.05	0.03	0.39	0.23	0.60
	Printing factory (fugitive) ^c	0.15	0.21	0.08	1.38	0.51	0.37
Industrial and commercial activities	Medicine producing lines	0.08	0.25	0.09	2.97	1.11	0.37
	Medical wastewater treatment	0.01	0.30	0.16	53.20	27.93	0.53
	Medicine centrifugation	0.08	0.34	0.24	4.04	2.91	0.72
	PP producing	0.01	0.00	0.00	0.25	0.08	0.33
	PE producing	0.02	0.00	0.00	0.09	0.03	0.30
	Chinese restaurant cooking	0.12	0.13	0.03	1.03	0.28	0.27
	Barbecue restaurant cooking	0.32	0.47	0.13	1.48	0.42	0.28

BTEX, benzene, toluene, ethylbenzene and xylene; LPG, liquefied petroleum gas; ST, storage tanks.

^a This study.
^b Zhang et al., 2013.
^c Wang et al., 2014.
^d Yuan et al., 2010.

Table 3

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Comparison of the k-avg and MIR-avg among different emission sources.

Туре	Source	k-avg (10 ⁻¹² cm ³ /molecule/s)	MIR-avg (g O ₃ /g VOC)
Fuel refueling	LPG	7.42	2.03
	Gasoline to ST	21.23	5.14
	Gasoline to motorcycles	19.16	4.79
	Gasoline to cars	22.11	5.37
	Industrial diesel to ST	85.11	2.46
	Low-sulfur diesel to ST	14.44	3.70
	Diesel to cars	11.65	1.88
Solvent use	Auto painting (fugitive)	14.26	5.91
	Printing (fugitive)	10.65	3.45
	Book binding (fugitive)	13.75	5.35
Industrial activities	Medicine producing lines	2.37	1.34
	Medical wastewater treatment	2.85	2.21
	Medicine centrifugation	1.41	0.97
	PP producing	14.02	6.21
	PE producing	14.74	6.42
Commercial activities	Chinese restaurant cooking	16.51	3.34
	Barbecue restaurant cooking	15.12	2.93

ST, storage tanks.

plastic producing, auto paint and book binding in this study were higher than that from vehicle exhaust, biomass burning and coal combustion (Yuan et al., 2010). For painting and printing sources, the MIR-avgs of their emissions obtained in our study were close to the levels found in other studies (Wang et al., 2014; Yuan et al., 2010).

To provide more information to the targeted control of ambient ozone pollution and atmospheric oxidation, the top 10 VOCs species that contributed the most to the total L_{OH} and OFP of each source were listed in Table S5–10. For VOCs in emissions from refueling of LPG and gasoline, auto painting, book binding, medicine producing, plastic producing and commercial cooking, beyond 75% of their reactivity or L_{OH} and OFPs was explained by the top 10

species; On the contrary, the top 10 species just shared 60-70% of the total reactivity for emissions from diesel refueling and printing.

4. Summary

The composition characteristics and BTEX ratios of VOCs emissions from several major sources, including fuel refueling, auto painting, printing, medicine producing, plastic producing, commercial cooking, wet and dry cleaning in China were experimentally determined and compared with other studies. Because trichloroethylene, tetrachloroethylene and chloroform (No. 60–62 in Table S1) were only emitted from dry- and wet-cleaning, and were the unique species emitted from this source, they were



Fig. 3. VOCs source profiles from medicine producing (A), plastic producing (B) and commercial cooking (C). The ID number of each species was the same as that of Table S1 (No. 1–59).

excluded from the profiles shown in Figs. 1–3. Many factors could influence the chemical composition for one source, like different fuels and solvent composition, different technical processes and sampling methods etc. For some sources like gasoline refueling, auto painting, medicine producing, plastic producing, wet- and dry-cleaning, the species composition and tracers of their emissions were almost the same with other studies, so their profiles should be applicable in CMB model, and be taken as references to match with the results from PMF receptor model. For the printing and cooking emissions, their source profiles were variable and not fit to be used in receptor models for source apportionment.

B/T was a good marker to justify the pollution characteristics, and also to differentiate the traffic and combustion emission sources in a mixed environment polluted by local emissions. Our study further found that B/T ratio could be a good marker to distinguish the emissions from refueling of gasoline and diesel, solvent use and industrial activities. B/E and B/X ratios can also be used to differentiate some sources. Generally speaking, for a mixed environment, the more simplex the source composition was, the closer the ratio in that environment was to the ratio of the major source. On the other hand, our study also proposed some challenges about their application, which should be taken into consideration in actual use.

Ozone pollution has become a global problem, and VOCs are important precursors for the formation of ozone through reacting with hydroxyl radical \cdot OH. According to our study, the emissions of gasoline refueling, commercial cooking, auto painting, book binding and plastic producing were highly reactive, and could increase atmospheric loss of \cdot OH and O₃ formation. Therefore, they should be listed as precedence-controlled sources in solving O₃ pollution especially when there are large amounts of emissions.

China is the world's top coal producer, consumer and importer, and accounts for about half of the global coal consumption. According to the statistic data of EIA (2015b), coal supply constituted the vast majority (69%) of China's total energy consumption in 2011 (EIA, 2015b). In addition to industrial applications (mainly for industrial boilers and furnaces), coal is used throughout the country in power plant and household stoves for cooking and heating purposes. Coking plants are also very common around China (Barletta et al., 2005). Therefore, building up coal-related VOCs profiles should be our next goals.

Acknowledgments

This study was supported by the funding of the National Natural Science Foundation of China (No. 41172316), the Key Project of The National Ministry of Education of China (No. 211026), Shanxi Province Science Foundation for Youths (No. 2011021025-2, 2015021059), the Research Project Supported by Shanxi Scholarship Council of China (2011080) and Doctoral Scientific Research Foundation of TYUST (20132018).

Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2015.05.066.

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