A comprehensive classification method for VOC emission sources to tackle air pollution based on VOC species reactivity and emission amounts

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ABSTRACT

In China, volatile organic compound (VOC) control directives have been continuously released and implemented for important sources and regions to tackle air pollution. The corresponding control requirements were based on VOC emission amounts (EA), but never considered the significant differentiation of VOC species in terms of atmospheric chemical reactivity. This will adversely influence the effect of VOC reduction on air quality improvement. Therefore, this study attempted to develop a comprehensive classification method for typical VOC sources in the Beijing–Tianjin–Hebei region (BTH), by combining the VOC emission amounts with the chemical reactivities of VOC species. Firstly, we obtained the VOC chemical profiles by measuring 5 key sources in the BTH region and referencing another 10 key sources, and estimated the ozone formation potential (OFP) per ton VOC emission for these sources by using the maximum incremental reactivity (MIR) index as the characteristic of source reactivity (SR). Then, we applied the data normalization method to respectively convert EA and SR to normalized EA (NEA) and normalized SR (NSR) for various sources in the BTH region. Finally, the control index (CI) was calculated, and these sources were further classified into four grades based on the normalized CI (NCI). The study results showed that in the BTH region, furniture coating, automobile coating, and road vehicles are characterized by high NCI and need to be given more attention; however, the petro-chemical industry, which was designated as an important control source by air quality managers, has a lower NCI.

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Introduction

The Beijing–Tianjin–Hebei (BTH) region is situated at 36°05′–42°40′N north latitude and 113°27′–119°50′E longitude, and includes the two municipalities of Beijing and Tianjin as well as 11 prefecture-level cities in Hebei province (Fig. 1). Over the past decades, the BTH region has become one of the most severely polluted regions in China, due to the dramatic increase in economic level, industrial production and vehicle population (Ma et al., 2012). In particular, ozone (O₃) pollution represents a significant environmental issue in this region, followed by PM₂.₅. High concentrations of ground-level O₃ occur frequently at many monitoring stations in the BTH region in summer (Liu et al., 2005). The hourly average O₃

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concentration has frequently exceeded the second grade of China's National Ambient Air Quality Standard (200 μg/m³), while an hourly O₃ concentration of 412 μg/m³ has been observed in Beijing (Ji et al., 2016). It is well known that sunlight-driven photochemical reactions result in high ground-level O₃ with the involvement of various precursors, including volatile organic compounds (VOCs) and nitrogen oxides (NOₓ) (Sillman, 1999; Carter, 1994). However, the formation mechanisms for the high O₃ vary greatly in different areas, mainly because the photochemical O₃ production rate responds nonlinearly to its VOC and NOₓ precursors. Recent studies have indicated that O₃ formation was controlled by ambient VOCs in urban areas of the BTH region, and the control of photochemical O₃ can be largely accomplished by a concerted reduction of VOC and NOₓ emissions (Shao et al., 2009).

In recent years, scientists have developed highly species-resolved VOC emission inventories in the BTH region. In terms of the VOC emission inventory, Wei et al. (2008, 2011) developed an emission inventory from anthropogenic sources in China for the year 2005, and obtained the VOC emission amounts in each province, including the BTH region. Li (2014) developed a VOC emission inventory in the BTH region for the year 2013, reporting anthropogenic VOC emission amounts of 285, 243, and 1520 kton/year respectively, in Beijing, Tianjin, and Hebei province. In terms of VOC source chemical profiles, local VOC profiles for major emission sources have been measured in the BTH region, such as vehicular exhaust, coal burning, biomass burning, petrochemical industry, and solvent use for coating and printing (Yuan et al., 2010; Wei et al., 2014; Yao et al., 2015a, 2015b). Yuan et al. (2010) reported on VOCs from solvent use in Beijing (e.g., auto painting, furniture painting, architectural painting, and printing), and observed that toluene and C8 aromatics were the most abundant species in emissions from paint applications, while high-carbon alkanes and some aromatics were the dominant species in emissions from printing. Yao et al. (2015a, 2015b) investigated VOC emissions from diesel vehicles and motor vehicles in Beijing, and found that aromatics and alkanes were the dominant VOC species in these emissions. Wei et al. (2014) observed that VOCs emitted from a refinery were characterized by C4–C6, propene, 1-butene, benzene, and toluene.

It is recognized that different emission sources are characterized by different VOC chemical compositions, which then take part in atmospheric chemical processes in different ways. It is essential to scientifically understand the chemical composition of VOC emissions, not only in terms of a VOC emission inventory but also in VOC control policy-making (Watson et al., 2001; Zhang et al., 2008; Zheng et al., 2009). However, research on the speciation of VOC emissions is limited in China, especially in the BTH region. The current VOC abatement policy is mainly based on the VOC emission amounts, never considering their chemical speciation. This will adversely influence the effect of VOC reductions on air quality improvement.

Therefore, the objective of this study was to develop a comprehensive classification method for VOC emission sources based on VOC species reactivity and emission amount, through a case study in the BTH region. In order to improve the knowledge of the VOC chemical composition of various sources, VOC measurements were additionally carried out for 5 key sources. Through application of this classification method in the BTH region, an integrative control index could be estimated for individual VOC sources, and the rank of VOC sources as control targets could be determined. We believe that this study can greatly help policy-makers to make effective decisions for VOC emission reductions, to tackle the regional air pollution in BTH.

1. Methods

1.1. Overview of VOC sources

In this study, 15 anthropogenic VOC sources were considered for classification in the BTH region, including power plant coal burning, industrial coal burning, residential coal burning, biomass burning, coking industry, petrochemical industry, iron and steel industry, diesel vehicles, gasoline vehicles, motorcycles, automobile coating, furniture coating, architectural coating, printing and fuel oil evaporation. The VOC emission amounts of these 15 anthropogenic VOC sources accounted for more than 90% of the total anthropogenic VOC emission amounts in the BTH region. Our comprehensive literature research found that the chemical profile of VOCs for most sources had been measured and obtained in previous studies, and the literature was listed in Table 1. For example, the VOC profiles from the emission sources of industrial coal burning, residential coal burning, biomass burning (wheat, corn, and wood), gasoline and diesel fuel evaporation, vehicle exhaust (gasoline vehicles, diesel vehicles, motorcycles), and the petrochemical industry were obtained from Liu et al. (2008). The VOC profile from the architectural painting source was obtained from Yuan et al. (2010), and the VOC profile from the iron and steel facility sources

Fig. 1 – Overview of study area.
The major VOC species reported in the literature are as follows. The VOC species from biomass burning and coal burning were mainly acetylene, C2-C3 alkenes such as ethylene and propylene, alkanes like ethane and propane, and aromatics like benzene and toluene. The major VOC species from gasoline and diesel fuel evaporation were C4-C7 alkanes and alkenes, and aromatics, namely isobutene, n-butane, trans-2-butene, n-pentane, benzene, and toluene. The chemical compositions of VOCs from gasoline-powered vehicles were very similar to those from diesel vehicles for compounds containing <10 carbon atoms; ethylene, isopentane, benzene, and toluene were the main species in exhaust emissions. Alkanes were the dominant VOC group from the petrochemical industry, and hexane was the most abundant species, followed sequentially by cyclohexane, pentane, butane, isopentane, n-heptane, methylcyclohexane, 2-methylpentane, and propane. The major VOC species in the emissions of water-based architectural paints were mainly C3-C6 alkanes and <C9 aromatics, namely toluene, benzene, n-butane, propane, and n-pentane; whereas the principal emission species in solvent-based architectural paints were C7-C8 aromatics, m/p-xylene, toluene, o-xylene, ethylbenzene, and styrene. The major VOC species in the exhaust from the sintering process included toluene, isopentane, benzene, 1-butene, m/p-xylene, ethylbenzene, n-pentane, 1,2,4-trimethylbenzene, n-butane, and 2-methylpentane; toluene, m/p-xylene, 1,2,4-trimethylbenzene, benzene, 1-butene, ethylbenzene, styrene, O-xylene, and octane were the major VOCs from the hot forming process; toluene, benzene, isopentane, o-xylene, m/p-xylene, ethylbenzene, styrene, 1-butene, and n-pentane were the major VOC species from the cold forming processes.

Then, this study carried out a measurement campaign for the weak sources in the BTH region, including automobile coating, furniture coating, print, power plants, and coking plants. 1.2. Measurement campaign of VOC chemical profiles for weak sources 1.2.1. Schedule of field sampling

In this study, VOC samples were collected from a variety of emission sources, including automobile coating, furniture coating, printing, power plants, and coking plants. Table 2 lists the sampling information. The emissions from the painting, printing and coking were classified as “fugitive emission”, while the emission from the stacks of coal burning was considered as “stack emission”. Different methods were used for fugitive and stack emission sampling. In terms of fugitive emission, ambient air samples around the industrial units were directly collected into a 3.2 L stainless steel canister with a flow-controller (Silonite, Entech Instrument, USA) within 60 min (Tang et al., 2007). An ozone scrubber with anhydrous sodium sulfate in a glass tube was connected to the inlet of each sampling canister to remove high levels of ozone for fugitive emission sampling. In terms of stack emission sampling, a glass tube filled with anhydrous sodium sulfate and glass wool in series were used to remove the water vapor, ozone, and particulate matters, and a stainless-steel probe with a temperature-controlled thermocouple was linked to a condensate trap for stack gas cooling, and finally linked to a 3.2 L stainless steel canister with a flow-controller (Silonite, Entech Instrument, USA). The stack emission sampling generally lasted 10 min. In total, 45 VOC samples were collected and sent to the laboratory for analysis.

Before sampling, each canister was cleaned with high-purity nitrogen (99.999%) for three cycles of filling (~30 psia) and evacuating (~100 mTorr), and finally evacuated to a vacuum state (~30 mTorr).

1.2.1.1. Automobile coating and furniture coating. A typical automobile 4S (Sale-Sparepart-Service-Survey) shop and a typical furniture factory in Hebei province were selected for sampling the VOC emissions. Samples collected in the three different workshops corresponded to the three most important processes in coating, namely primer coating, finish-coat coating, and paint-drying. The paints used in the auto garage were all nitrocellulose-based resin paints, while the paints used in the factory were all nitrocellulose-based resin paints. The VOC samples for painting were collected in the spray booth during the primer paint-spraying period and the finish coat paint-spraying period. The samples for the paint-drying process were collected during the drying process after painting. Three samples were collected for each coating process, with a total of 9 samples collected in the automobile 4S shop, and 18 samples were collected in the furniture factory.

1.2.1.2. Print. A typical printing factory in Hebei province, which mainly prints books, magazines, newspapers, and packaging materials, was selected for sampling the VOC emissions. The VOC samples were collected around the operating offset lithographic printing press equipment. A total of 6 samples were collected in the printing factory.

1.2.1.3. Coking plant. Two coking plants in Hebei province were selected for sampling the VOC emissions, and two coke oven types (i.e., top charging coke oven and tamping coke oven) in each plant were investigated. The VOC samples were collected using a 6 L stainless steel canister with a flow-controller on the top of the two coke ovens, over a period of 6 hr for each sample. Three samples were collected for each coke oven, for a total of 6 samples collected in each of the two coking plants.

<table>
<thead>
<tr>
<th>No.</th>
<th>Emission sources</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Power plant coal burning</td>
<td>This study</td>
</tr>
<tr>
<td>2</td>
<td>Industrial coal burning</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>3</td>
<td>Residential coal burning</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>4</td>
<td>Biomass burning</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>5</td>
<td>Coking plant</td>
<td>This study</td>
</tr>
<tr>
<td>6</td>
<td>Petrochemical industry</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>7</td>
<td>Iron and steel facility</td>
<td>Tsai et al. (2008)</td>
</tr>
<tr>
<td>8</td>
<td>Diesel vehicles</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>9</td>
<td>Gasoline vehicles</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>10</td>
<td>Motorcycles</td>
<td>Liu et al. (2008)</td>
</tr>
<tr>
<td>11</td>
<td>Auto painting</td>
<td>This study</td>
</tr>
<tr>
<td>12</td>
<td>Furniture painting</td>
<td>This study</td>
</tr>
<tr>
<td>13</td>
<td>Architectural painting</td>
<td>Yuan et al. (2010)</td>
</tr>
<tr>
<td>14</td>
<td>Printing</td>
<td>This study</td>
</tr>
<tr>
<td>15</td>
<td>Fuel evaporation</td>
<td>Liu et al. (2008)</td>
</tr>
</tbody>
</table>

Table 1 – Volatile organic compound (VOC) emission sources for classification.
1.2.1.4 Power plant. Two power plants in Hebei province were selected for sampling the VOC emissions; two boiler types (i.e., circulating fluidized bed boiler and pulverized coal fired boiler) in each plant corresponding to different coal types were investigated. The VOC samples were collected in the stack after the desulfurization and dust removal device. Three samples were collected for each boiler, for a total of 6 samples collected in each of the two power plants.

1.2.2. VOC analysis
The VOC samples were concentrated in a pre-concentrator (Model 7100, Entech Instrument, USA), and analyzed by a gas chromatography (GC) system (Model 7890A, Agilent, USA) equipped with a quadrupole mass spectrometer (MS) system (Model 5975C, Agilent, USA) and a flame ionization detector (FID). The C2–C3 hydrocarbons were separated on an Al2O3 porous layer open tubular (PLOT) column (30 m × 0.32 mm × 3.0 μm, J&W Scientific, USA) and quantified by FID. The C4–C12 hydrocarbons were separated on a DB-624 column (60 m × 0.32 mm × 1.8 μm, J&W Scientific, USA) and quantified by MS. The system is described elsewhere in detail (Liu et al., 2008). The pre-concentrator had a three-stage trapping system. In the first stage, the VOCs were adsorbed on glass beads at −150°C and desorbed at 15°C. In the second stage, they were trapped on Tenax at −30°C and desorbed at 180°C. Finally, in the third stage, the VOCs were condensed on a transfer line at −160°C and heated rapidly to 65°C. Then, the concentrated VOCs were injected into the gas chromatograph. Helium was used as the carrier gas for GC at a flow rate of 1.3 ml/min. The GC oven temperature was initially programmed at −50°C, holding for 2 min, and increasing to 220°C at 6°C/min. The mass spectrometer was operated in SCAN mode and scanned from 20 to 300. The ionization method was electron impact (EI, 70 eV), and the source temperature was 220°C.

The photochemical assessment monitoring system (PAMS) standard gas (57 species, Spectra Gases, USA) was used to confirm compounds’ retention times and identify compounds. In total, 55 species were identified and measured in this study. The target species were quantified by using the multipoint external calibration method. Calibration was performed at 5 different concentrations from 1 to 20 ppbv by the 55 PAMS gas standard. 1,4-Difluorobenzene and chlorobenzene-d5 were chosen as internal standards in the samples. The method detection limits (MDLs) of the various VOC species ranged from 0.009 to 0.035 ppbv (Liu et al., 2008).

1.3. VOC emission source classification
Fig. 2 presents an overview of the VOC emission source classification process. The VOC emission amount (EA) from a source was chosen as one important factor, and this information can be found from the emission inventory. In this study, the VOC emission inventory of the BTH region was obtained from Li (2014). The VOC emission source reactivity (SR) was chosen as another important factor for classification, it is defined as the ozone formation potential (OFP) of a unit VOC emission mass from a source, and is calculated using the following equation (Na and Kim, 2007):

\[
SR_j = \sum_{i} f_{ij} \times MIR_i
\]

where SR is the emission source reactivity of VOC source i (ton O3/ton VOCs), and is the estimated ozone formation amount when 1 ton of VOCs is emitted from source j; fi,j is the mass fraction of VOC species i in source j, and MIRi is the maximum incremental reactivity (MIR) value of species i (g O3/g VOCs) as proposed by Carter (2008).

After obtaining the EA and SR values for different emission sources, they were sorted from high to low. The range method was then applied to obtain the normalized emission amount index (NEA) and normalized source reactivity index (NSR) using the following equations:

\[
NEA_j = \frac{EA_j - EA_{Min}}{EA_{Max} - EA_{Min}}
\]

\[
NSR_j = \frac{SR_j - SR_{Min}}{SR_{Max} - SR_{Min}}
\]

where EAi is the VOC emission amount of source j (ton/year), EA_{Min} is the minimum EAi among VOC sources, EA_{Max} is the maximum EAi among VOC sources, NEA is the normalized VOC emission index of source j. SR_{Min} is the minimum SR among VOC sources, SR_{Max} is the maximum SR among VOC sources, NSR is the normalized index of source j.

After normalization, relative weights were arbitrarily assigned to NEA and NSR, and then a control index (CI) was calculated using the following equation:

\[
CI_j = k_1 \times NEA_j + k_2 \times NSR_j
\]

where k is the weight, k1 + k2 = 1.0; in this study, NEA and NSR have the same weight, so k1 = k2 = 0.5; CIj is the control index of source j.

Table 2 – Sampling information of VOC emission sources.

<table>
<thead>
<tr>
<th>No.</th>
<th>Emission Sources</th>
<th>Description</th>
<th>Number of samples</th>
<th>Emission type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Auto coating</td>
<td>Samples collected in the spray booth of a garage when workers were painting auto parts</td>
<td>9</td>
<td>Fugitive emission</td>
</tr>
<tr>
<td>2</td>
<td>Furniture coating</td>
<td>Samples collected in the spray booth of a furniture factory when workers were painting wood pieces</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Print</td>
<td>Samples collected in the workshop of a typical printing factory when the press equipment was operational</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Coking plant</td>
<td>Samples collected on the top of the coke oven</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Power plant boilers</td>
<td>Samples collected in the stack after desulfurization and dust removal device</td>
<td>6</td>
<td>Stack emission</td>
</tr>
</tbody>
</table>
The obtained CI value was then normalized as follows:

$$\text{NCI}_j = \frac{\text{CI}_j - \text{CI}_{\text{Min}}}{\text{CI}_{\text{Max}} - \text{CI}_{\text{Min}}}$$  \hspace{1cm} (5)

where CI_{Min} is the minimum of CI_j, CI_{Max} is the maximum of CI_j, NCI_j is the normalized control index (NCI) of source j.

The obtained NCI value was then used for VOC emission source classification. In this study four levels were identified for VOC emission sources, in order to distinguish the VOC emission sources needing priority control by environmental protection departments. Levels I, II, III and IV VOC emission sources had NCI between 0.75–1.00, 0.50–0.75, 0.25–0.50, and 0–0.25, respectively. Level I represents the most important VOC emission sources, which should require priority control.

2. Results and discussion

2.1. VOC characteristics of emission sources

In this study, 55 VOC species (C2–C12) were detected in the collected samples, including 29 alkanes, 10 alkenes, and 16 aromatic hydrocarbons. Naphthalenes, oxygenated hydrocarbons and halogenated hydrocarbons were not detected.

2.1.1. Furniture coating

Nearly all of the paints used in the furniture manufacturing industry (>96%) were solvent-based. Table 3 lists the 10 most abundant species and their percentages in the VOCs from two different furniture coating emissions (PU and NC paints). The number listed in this table represents the average VOC profile for the three different painting processes, as mentioned above. The polyurethane paints and NC paints are associated with different top 10 VOC species due to different paint formulations. For example, styrene was included in the top 10 species from PU paints but not from NC paints. In general, the top 10 species were mainly <C9 aromatics.

2.1.2. Power plant

The VOC species emitted from the power plant coal burning process depend largely on the coal type. Table 4 lists the 10 most abundant species and their percentages in VOCs from the emissions of the two boiler types. It was found that benzene had a higher percentage in VOCs from the circulating...
2.1.3. Coking plant
Coking plant emissions are an important anthropogenic VOC source in the BTH region. Table 5 lists the 5 most abundant species and their percentages in VOCs from the emissions of the two coke oven types. It can be found that five hydrocarbons, namely acetylene, benzene, ethane, toluene, and propene, accounted for >86% of VOCs from the coking process emission. The content of benzene in VOCs was higher from the top charging coke oven than from the tamping coke oven, but the acetylene content showed opposite variation. This difference was due to the different coal types used for coking, with high-quality coal (e.g., coking coal) being used as material by the top charging coke oven, and low-quality coal (e.g., coking coal mixed with gas coal and lean coal) by the tamping coke oven.

2.1.4. Overview of the source chemical profiles
Table 6 lists the detailed VOC profiles measured for different emission sources, while the profile from furniture and auto painting was obtained by averaging the measured VOC profiles from the three different painting processes, and the VOC profile for furniture painting was calculated by averaging from two different solvents. The VOC profile for printing was obtained by averaging the measured VOC profiles from the printing process. The VOC profile for power plant coal burning emission was obtained using the average value measured from the two different boiler types, and the profile for the coking process was calculated by averaging the measured values from the two different coke ovens.

As shown in Table 6, o-xylene was the most abundant VOC species from furniture painting emissions, accounting for 11.6% of its total VOCs. Other major species from furniture painting emissions were 1,2,4-trimethylbenzene, ethylbenzene, m-ethyltoluene, toluene, m/p-xylene, p-ethyltoluene, and 1,3,5-trimethylbenzene, accounting for 11.5%, 11.4%, 8.5%, 8.1%, 11.4%, 7.6%, 6.5%, and 6.3% of its total VOCs, respectively. In total, aromatic species accounted for 93.9% of the furniture painting VOC emissions.

It can be found from Table 6 that o-xylene was the most abundant VOC species from auto painting emission, accounting for 21.3% of its total VOCs, followed by ethylbenzene, toluene, mp-xylene, and 1,2,4-trimethylbenzene, accounting for 12.6%, 10.4%, 8.2%, and 7.1%, respectively. In total, aromatic species accounted for 83.2% of VOCs from auto factory painting emissions.

VOC emissions from printing factories are mainly from ink evaporation and detergents used to clean press machinery. The VOCs from printing factory emissions mainly comprised C10-C12 alkanes and aromatics, and n-undecane, n-decane, n-nonane

### Table 3 – The 10 most abundant species and their percentages in VOCs from furniture painting emission (unit: wt.%).

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>From PU paint</th>
<th>Species</th>
<th>From NC paint</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ethylbenzene</td>
<td>13.4</td>
<td>o-Xylene</td>
<td>13.1</td>
</tr>
<tr>
<td>2</td>
<td>1,2,4-Trimethylbenzene</td>
<td>10.9</td>
<td>1,2,4-Trimethylbenzene</td>
<td>12.1</td>
</tr>
<tr>
<td>3</td>
<td>o-Xylene</td>
<td>10.4</td>
<td>Toluene</td>
<td>9.4</td>
</tr>
<tr>
<td>4</td>
<td>m-Ethyltoluene</td>
<td>8.5</td>
<td>Ethylbenzene</td>
<td>9.4</td>
</tr>
<tr>
<td>5</td>
<td>Styrene</td>
<td>8.4</td>
<td>m/p-Xylene</td>
<td>8.9</td>
</tr>
<tr>
<td>6</td>
<td>Toluene</td>
<td>6.7</td>
<td>m-Ethyltoluene</td>
<td>8.5</td>
</tr>
<tr>
<td>7</td>
<td>p-Ethyltoluene</td>
<td>6.3</td>
<td>1,3,5-Trimethylbenzene</td>
<td>6.7</td>
</tr>
<tr>
<td>8</td>
<td>m/p-Xylene</td>
<td>6.2</td>
<td>p-Ethyltoluene</td>
<td>6.6</td>
</tr>
<tr>
<td>9</td>
<td>1,3,5-Trimethylbenzene</td>
<td>5.8</td>
<td>o-Ethyltoluene</td>
<td>6.6</td>
</tr>
<tr>
<td>10</td>
<td>n-Propylbenzene</td>
<td>5.3</td>
<td>n-Propylbenzene</td>
<td>6.5</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>81.5</td>
<td></td>
<td>87.8</td>
</tr>
</tbody>
</table>

PU paint: polyurethane-based resin paints; NC paint: nitrocellulose-based resin paints.

### Table 4 – The 10 most abundant species and their percentages in VOCs from power plant coal burning emission (unit: wt.%).

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>Circulating fluidized bed boiler</th>
<th>Species</th>
<th>Pulverized coal fired boiler</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Benzene</td>
<td>22.9</td>
<td>n-Decane</td>
<td>22.2</td>
</tr>
<tr>
<td>2</td>
<td>Acetylene</td>
<td>18.2</td>
<td>Acetylene</td>
<td>13.6</td>
</tr>
<tr>
<td>3</td>
<td>n-Decane</td>
<td>14.4</td>
<td>Benzene</td>
<td>10.2</td>
</tr>
<tr>
<td>4</td>
<td>Ethane</td>
<td>13.6</td>
<td>Ethane</td>
<td>9.0</td>
</tr>
<tr>
<td>5</td>
<td>Toluene</td>
<td>6.3</td>
<td>Ethylbenzene</td>
<td>6.1</td>
</tr>
<tr>
<td>6</td>
<td>Propene</td>
<td>5.1</td>
<td>m/p-Xylene</td>
<td>6.1</td>
</tr>
<tr>
<td>7</td>
<td>3-Methylpentane</td>
<td>3.6</td>
<td>Toluene</td>
<td>5.3</td>
</tr>
<tr>
<td>8</td>
<td>Propane</td>
<td>2.7</td>
<td>Propane</td>
<td>4.1</td>
</tr>
<tr>
<td>9</td>
<td>n-Undecane</td>
<td>2.4</td>
<td>o-Xylene</td>
<td>2.9</td>
</tr>
<tr>
<td>10</td>
<td>n-Dodecane</td>
<td>1.7</td>
<td>Propane</td>
<td>2.6</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>90.9</td>
<td></td>
<td>82.1</td>
</tr>
</tbody>
</table>

### Table 5 – The 5 most abundant species and their percentages in VOCs from coking process emission (unit: wt.%).

<table>
<thead>
<tr>
<th>No.</th>
<th>Species</th>
<th>Top charging coke oven</th>
<th>Species</th>
<th>Tamping coke oven</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Acetylene</td>
<td>29.9</td>
<td>Acetylene</td>
<td>42.8</td>
</tr>
<tr>
<td>2</td>
<td>Benzene</td>
<td>25.1</td>
<td>Ethane</td>
<td>20.5</td>
</tr>
<tr>
<td>3</td>
<td>Ethane</td>
<td>16.6</td>
<td>Benzene</td>
<td>16.0</td>
</tr>
<tr>
<td>4</td>
<td>Toluene</td>
<td>9.5</td>
<td>Propene</td>
<td>5.6</td>
</tr>
<tr>
<td>5</td>
<td>Propene</td>
<td>5.7</td>
<td>Toluene</td>
<td>4.0</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>86.8</td>
<td></td>
<td>88.9</td>
</tr>
</tbody>
</table>
accounted for 6.0%, 3.9%, and 2.7% of the total VOCs; 1,2,4-trimethylbenzene, ethylbenzene, m/p-xylene, o-xylene, and p-ethyltoluene accounted for 6.8%, 6.0%, 5.4%, 5.2%, 4.7%, and 4.2% of the total VOCs. In total, the alkanes and aromatic compounds accounted for 44.8% and 47.4% of the total VOCs from printing emissions.

It can be observed from Table 6 that n-decane was the most abundant VOC species from power plant coal burning emission, accounting for 18.3% of its total VOCs. Other major species were benzene, acetylene, and ethane, accounting for 16.5%, 15.9%, and 11.3%, respectively. In total, alkanes, alkenes and aromatic species accounted for 42.9%, 22.1% and
35.0% of VOCs from power plant coal burning emissions, respectively.

The major VOCs species from coking plants were acetylene, benzene, and ethane, accounting for 36.3%, 20.5%, and 18.5% of VOCs, respectively. The alkanes, alkenes and aromatics species accounted for 24.1%, 45.6% and 30.3% of the VOCs from the coking plants, respectively.

2.2. Classification of VOC emission sources in BTH region

2.2.1. VOC emission amounts in BTH region

The VOC emission amounts for the year 2013 were obtained from the inventory of the BTH region developed by Li (2014). Fig. 3 presents the VOC emission information from different sources and cities. It can be observed from Fig. 3 that the VOC emissions were 2047 kton in the entire BTH region, and the VOC emissions from Beijing, Tianjin, and Hebei province were 285, 242, and 1520 kton, respectively. It can be found that Beijing had the largest VOC emission (285 kton), followed by Tianjin (242 kton), Tangshan (213 kton), Shijiazhuang (205 kton) and Baoding (200 kton). Gasoline vehicles represent the largest emission source in Beijing, whose emission amount was 94 kton. Gasoline vehicles and the petrochemical industry represent the largest emission sources in Tianjin, whose emission amounts were 39 and 35 kton. However, in Tangshan, Shijiazhuang and Baoding, industrial coal burning, biomass burning, and motorcycles were the top three VOC emission sources.

Fig. 3 – VOC source emission in the Beijing–Tianjin–Hebei (BTH) region.

![VOC source emission in the Beijing–Tianjin–Hebei (BTH) region.](image)

![Comparison of VOC source reactivities among various anthropogenic sources. OFP: ozone formation potential.](image)
Fig. 5 – (a) Burning, (b) industry, (c) mobile and (d) solvent use emission source classification for various sources and cities of the BTH region. NCI: normalized control index.
2.2.2. VOC emission source reactivity

Fig. 4 presents the calculated VOCs emission source reactivities (SRs). SRs were calculated by using the VOC source profiles measured in Table 6 and other source profiles in the literature in Table 1. The SR of furniture painting emission was the highest (i.e., 5.89 ton O₃/ton VOCs) among all the VOC sources, followed by emissions from auto painting (5.59 ton O₃/ton VOCs), diesel vehicles (5.29 ton O₃/ton VOCs), fuel evaporation (4.67 ton O₃/ton VOCs), and gasoline vehicles (4.52 ton O₃/ton VOCs). However, the SR for power plant coal burning emissions was the lowest, because C₁₀–C₁₂ alkanes with low reactivities accounted for a major percentage in the total VOCs. As illustrated in Fig. 4, contributions to SRs from solvent-using emissions (i.e., furniture painting, auto painting, architectural painting, and printing) and iron and steel facility emissions were mainly from aromatic compounds. However, alkene compounds made a major contribution to the SRs of other anthropogenic sources. Given their higher SR values, controlling equal amounts of VOC emissions from furniture painting, auto painting, and diesel vehicle emissions would result in more reduction of ozone formation in the VOC-limited urban areas.

2.2.3. VOC emission source classification

Fig. 5 presents the VOC emission source classification results for various sources and cities of the BTH region. It was found that gasoline vehicle emission in Beijing had the highest NCI (1.00). Level I VOC emission sources include gasoline vehicles, auto painting, and furniture painting in Beijing, as well as furniture painting in Tianjin and Langfang. Level II VOC sources include gasoline vehicles in Tianjin, biomass burning in Baoding, Cangzhou, Xingtai, Handan, and Shijiazhuang, motorcycles in Tangshan, Baoding, Handan, and Shijiazhuang, industrial coal burning in Tangshan and Baoding, as well as the diesel vehicles, auto painting, and furniture painting in every city of BTH. Level III VOC sources mainly include industrial coal burning, biomass burning, iron and steel facilities, printing, and fuel evaporation in every city of BTH. Level IV VOC sources were mainly power plant coal burning, residential coal burning, coking, petrochemical industry and architectural painting.

In terms of emission source classification for the entire BTH region, it can be illustrated from Fig. 6 that furniture painting emission had the highest NCI. The painting applications (e.g., auto painting and furniture painting) and vehicles (especially diesel vehicles) had higher NCI than other VOC emission sources, and these sources should be controlled with priority in order to reduce ambient O₃ concentrations in the urban areas. In terms of emission source classification for every city in the BTH region, the NCI shows little variation between the cities in the BTH region.

2.3. Suggestions for VOC abatement policy based on the classification results

The National Action Plan on Air Pollution Control (2013–2017) that was released in 2012 explicitly required the reduction of anthropogenic VOCs, and focused on the sources of petrochemical industry, organic chemical industry, packaging printing and industrial coating. The requirements are as follows: implementation of leak detection and repair technology was required in the petrochemical industry; completion of oil and gas recovery and the control of gas stations, oil storage tanks and oil tankers within a limited time; improvement of the volatile organic limit standards for paint, adhesives and other products, and promotion of the use of water-based paint, to encourage the production, sale and use of low toxicity, low-VOC solvents. The national measures for pollution charges for VOCs were released in 2015, and pollution charges were levied for the petrochemical industry and packaging printing. However, the VOC emissions from industrial coating and vehicles have not received enough attention in the national policy. The corresponding control requirements were decided primarily based on VOC emission amounts (EA), but never considered the significant differentiation of VOC species in atmospheric chemical reactivity and significant differentiation.
of VOC sources in VOC species profiles. In this study, the VOC emission amount and source reactivity were used in the VOC source classification, and our classification results imply that the sources of furniture painting, auto painting and vehicles (especially diesel vehicles) have high NCI, and need priority control in the BTH region. The VOC source classification result has guiding significance for regional VOC priority emission abatement control.

3. Conclusions

In this study, the VOC source profiles were examined for furniture coating, auto coating, printing, power plants, and coking plants in the BTH region. Analysis of source reactivities indicated that the ozone formation potential is highest for furniture coating, followed by auto coating emissions, diesel vehicle emissions, fuel evaporation, and gasoline vehicles. The VOC NEA and the NSR were chosen to build the VOC source classification method, and this method was applied in the BTH region. The classification results showed that gasoline vehicle emission in Beijing was a Level I VOC source in the BTH region. Furniture coating, auto coating and vehicles (especially diesel vehicles) had high NCI, and need priority control in the BTH region.

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