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Source Profile of Volatile Organic Compounds(VOCs) of a Petrochemical Industry in the Yangtze River Delta,China

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The profiles of major volatile organic compound (VOC) sources in petrochemical industry of the Yangtze river delta, China, were experimentally determined. Source samples were taken using summa canister near the petrochemical units. The concentrations of 72 VOC species were quantified using canister sampling and a gas chromatography–mass spectrometry system, and VOC source profiles were developed for source apportionment of VOCs. Based on the measurement of source profiles, possible tracers for various emission sources were identified; The VOCs emitted from the whole refinery were characteristic by aromatic (43.2%), alkane (27.7%), halonhydrocarbon (21.2%) and oxygenated VOCs(7.3%). And the obvious differences in VOCs chemical profiles among four main sectors (Petroleum refining, Olefin refining, Aromatic refining and Wastewater treatment sectors). Petroleum refining with the higher proportions of C3-C10 alkanes, Olefin refining with the higher proportions of BTX(benzene, toluene, m,p-xylene). and C2-C4 alkenes. Aromatic refining with the higher proportions of BTX(benzene, toluene, m,p-xylene), wastewater treatment with the higher proportions of BTX (benzene, toluene, m,p-xylene), and part halonhydrocarbon and oxygenated VOCs were also its characteristic compounds .

1. Introduction

Volatile organic compounds(VOCs) play an important role in the atmospheric air, for the production of ozone and secondary organic aerosol, which influences the air quality and human health. Up to now, VOCs pollution has become a service air pollution problem in China.

In addition, VOCs emissions especial from anthropogenic sources have been an increasing concern. Some researches established the national and regional VOCs emission inventories with high sectoral, temporal, spatial and chemical-profile resolutions, and found road gasoline vehicles, biomass burning, paint coating, petroleum industry as the top 4 emission sources, with the national contribution of 23-30%, 18-20%, 8-10%, and 7-9%, respectively (Wei W et al., 2008; Bo Y et al., 2008). The studies on the source apportionment of shanghai VOCs identified road vehicles and industry as main contributors(Cai C J et al.,2010), however, as the lack of the source profile of local petrochemical industry, there can not be provide the source contribution of petrochemical industry more clearly(Liu Y et al., 2008; Pandya G H., 2006).

Therefore, source profiles of VOCs are the fundamental information regarding the chemical composition of emissions from ozone and particle, VOC emission inventories used in air quality models and identifying source contributions using receptor models.in this study, we focused on the four typical sectors of a petrochemical industry and collected source samples directly from inside manufacturing facilities in order to establish industrial sector-based VOC source profiles.

2. Experimental

2.1 Source sampling

For a Petroleum refinery, it need to processing through different units,such as petroleum refining(e.g.crude distillation unit(CDU)/vacuum distillation unit(VDU)),olefin refining, aromatic refining and wastewater treatment. Sampling times were carefully selected and the Standard Operating Procedures (SOPs) were followed to ensure consistent procedures throughout the field sampling part of the study. A total of valid 28 source samples were collected from the main units of the four petrochemical industrial sectors that were being

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operated under normal conditions. Table 1 summarizes the number of source samples for each sector or process, and the locations where samples were collected. The emissions samples were collected using a leak-free, evacuated 3-liter electro-polished stainless steel canister (UCI, USA) equipped with a restricted sampler operating at 38 mL min^{-1} (Entech Instruments Inc., California, USA).In order to assure the representativeness of samples, the sampling staff held the canister as near as possible the production unit. The system was purged with pure nitrogen gas before sampling. For each sample, a pressure gauge was used to insure completion of sample collection.

Table 1: Sampling units and Industry sectors

Industry sectors	Sampling Units
petroleum refining	crude distillation unit(CDU)/vacuum distillation unit(VDU) Kerosene hydrotreater High-pressure hydrocracking delayed coking
Olefin refining	olefin tank olefin compression Olefin cracking
Aromatic refining	Aromatic tank Aromatics extraction Aromatics adsorption and separation Aromatics waste water
Wastewater treatment	Denitrifying pool aeration tank Oxidation ditch

Table 2: VOC species detected in the study

VOC species	VOC species	VOC species	VOC species
m-ethyl toluene	1,2,4-trimethylbenzene	o-Xylene	2,2-dimethylbutane
n-butane	vinyl chloride	n-propenylbenzene	cyclopentane
1,3-butaene	n-decane	isopropenylbenzene	Methyl ethyl ketone
1-butene	1,3,5-trimethylbenzene	Styrene	Ethyl acetate
isobutane	o-Ethyltoluene	m/p-Xylene	chloroform
Propane	p-Ethyltoluene	2-methylhexane	1,2-dichloroethane
Propene	3-Methylheptane	Benzene	3-methylpentane
n-pentane	n-octane	cyclohexane	2-methylpentane
Isoprene	1,2-dichlorobenzene	trichloroethylene	n-hexane
isopentane	1,4-dichlorobenzene	bromodichloromethane	1-hexene
1-pentene	chlorobenzene	1,1,2-trichloroethane	2,4-dimethylpentane
Freon-12	1,1,1,2-tetrachloroethane	tetrachloroethylene	Methylcyclopentane
n-dodecane	bromomethane	n-heptane	m-diethylbenzene
trans-2-butene	chloroethane	2,2,4-trimethyl pentane	
chloromethane	acetone	3-methylhexane	
cis-2-butene	ethylbenzene	2,3-dimethylpentane	
p-diethylbenzene	dichloromethane	2-methylheptane	
N-undecane	n-nonane	toluene	
1,2,3-trimethylbenzene		2,3,4-trimethyl pentane	
		methyl cyclohexane	
		trans-2-Pentene	
		cis-2-Pentene	

2.2 Analysis of VOC species

The samples collected in summa canister were analysed by Gas Chromatograph-Mass Spectrometer (GC-MS, Model 7890A/5975A, Agilent Inc.) in our laboratory to determine VOCs concentrations, according to EPA TO-15 Method (US EPA, 1999). Before the 400 ml sample was injected into GC-MS, a pre-process was needed to remove N2, O2, CO2, CO and H20 in sample and to further concentrate sample in volume by cryogenic preconcentrator (Model 7100, Entech Inc.). The VOC species quantified by the GC-MS system are listed in Table 2. For each target compound, a calibration curve was drawn based on the relationship between the integrated peak area and the corresponding concentration (5 levels: 0, 2, 5, 10 and 20 ppbv); the resulting calibration curves generally yielded good correlation coefficient values of above 0.99. For QA/QC, the cryogenic preconcentrator was baked after each analysis, and the GC column was also baked after analysis of every 20 samples.

3. Results and discussion

3.1 Overall source profile patterns

Source profiles were obtained by averaging the results of measured samples from different petrochemical industrial sectors or processes. The source profiles of each sector were developed to illustrate the potential differences in the compositions in the different emissions. A total of 73 VOC species were detected in this study and divided into six groups; namely, alkenes, alkanes, aromatics, halohydrocarbons and OVOCs.

Fig. 1 illustrates the overall VOC composition patterns of the four petrochemical industrial sectors. As shown in Fig. 1, alkanes were the most significant VOC groups in petroleum refining sectors, accounting for about 70% of the VOCs observed. The aromatics were the largest VOC group for the aromatics refining manufacturing sectors, accounting for about 80% of the VOCs observed. While the aromatics were also the largest VOC group for the olefin refining manufacturing sectors, the alkenes contributed most in olefin refining than other sectors, accounting for about 27% of the VOCs in olefin refining. At last, alkanes, aromatics and Halonhydrocarbon were three main groups in wastewater treatment, respectively accounted for about 28%, 43% and 21%.It was noted that complex source profile patterns were found for wastewater treatment. This phenomenon is understandable since the factories of wastewater treatment mainly disposed various kinds of wastewater in the petrochemical industry.

The details of the source profiles in each industrial sector or process and possible differences are discussed in the following subsections.

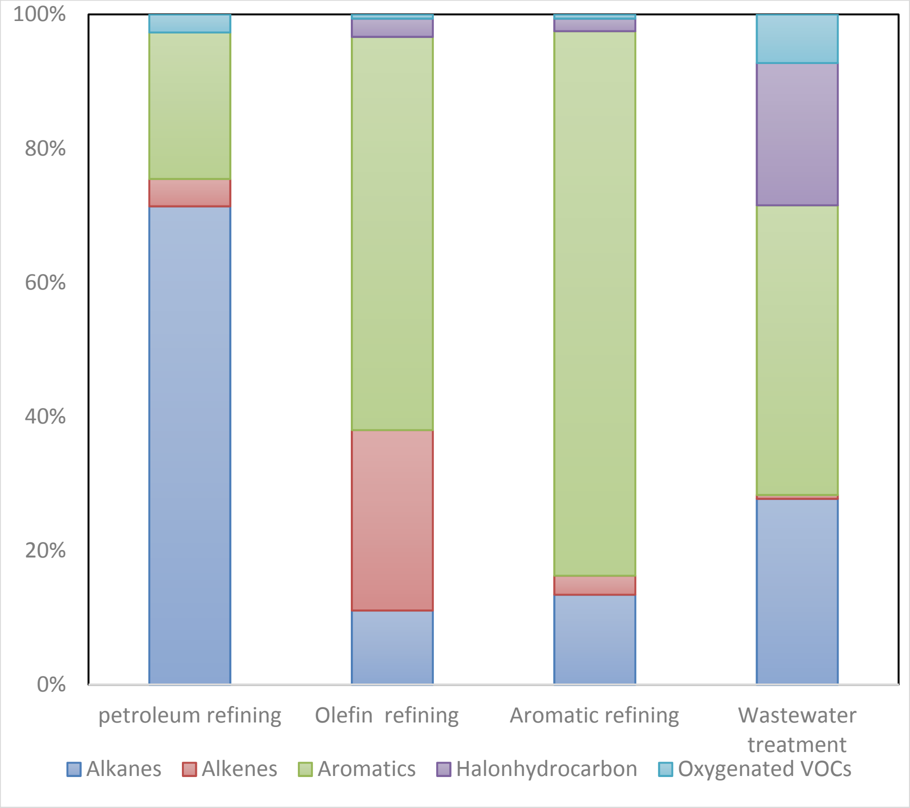

Figure 1: Overall VOC composition patterns of four petrochemical industry sectors.

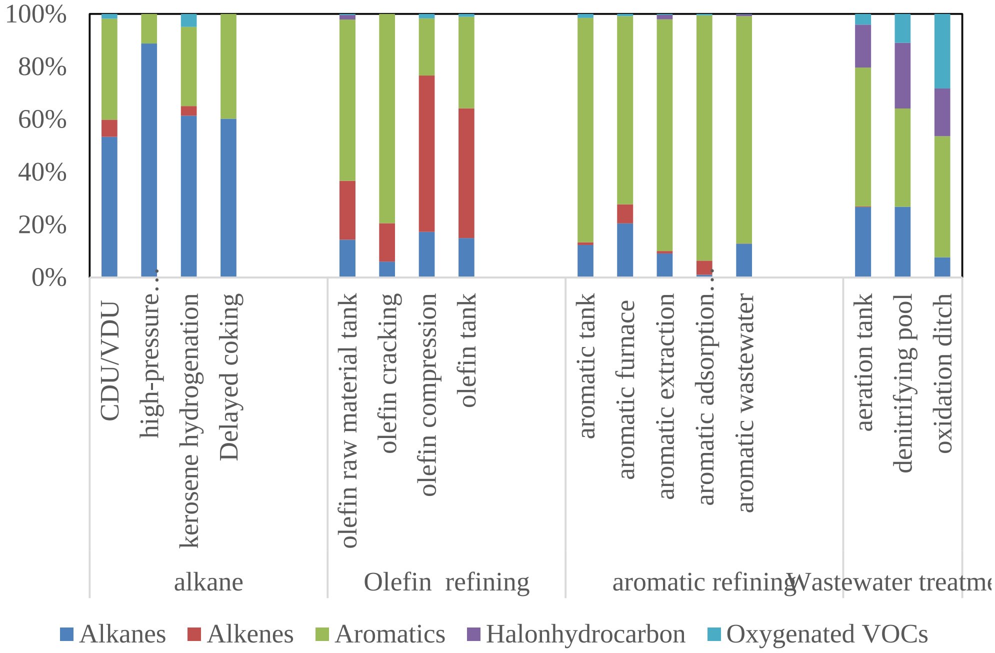

Figure 2: Overall VOC composition patterns of four petrochemical industry sectors for all units.

3.2 Petroleum Refining

Petroleum refining were the first step and main sectors in a petrochemical factory. In this study, inner 4 units, including crude distillation unit(CDU)/vacuum distillation unit(VDU), kerosene hydrogenation unit, high-pressure hydrotreating unit and delayed coking unit, were measurement. As illustrated in Fig.2, alkanes are the major components of all four units, accounted for 50%-90% of total VOCs.

For crude distillation unit(CDU)/vacuum distillation unit(VDU), alkanes compounds accounted for over 50%of the total VOCs, of which C3-C10 linear alkanes (32%) are main compounds, of which n-pentane,propane,n-decane,n-butane, n-nonane,n-hexane, n- n-octane and n-heptane were the most abundant speicies, contribution 6.3%, 5.9%, 5.0%, 4.1%,3.7%,3.2%,2.3% and 1.9% of the total VOC emissions, respectively. Aromatic compounds were the second main compounds, contributing 38%of the total VOC. Alkenes and OVOCs contributed much less to the profile, contributing less than 10%.the high weight percentage of alkane compounds was probably a result of the constituent of crude oil. These results suggest that unorganized emission are also one of the main VOC sources.

Kerosene hydrogenation unit and high-pressure hydrotreating unit are also two common units in the petrochemical industry. alkanes compounds accounted for 60% of the total VOCs in kerosene hydrogenation unit, of which C3-C10 linear alkanes (32%) are main compounds, contribution 38.4% of the total VOC emissions.in addition aromatics contributed almost 30% of total VOCs in kerosene hydrogenation unit , mainly benzene, m,p-xylene and toluene. In contrast, alkanes compounds accounted for 85%of the total VOCs in high-pressure hydrotreating unit, of which isopentane, propane and n-pentane were the most abundant speicies, contribution 21.9%, 16.2% and 14.8% of the total VOC emissions, respectively.

Delayed coking unit is the last main unit of dealing with residual oil. Alkanes and aromatics compounds are the main VOCs, contributing 56.7% and 37.5%.propane, benzene, toluene, n-butane and m,p-xylene respectively accounted for 23.4%,18.5%, 10.2%,7.8% and 5.9%. These data probably reflect the fact that alkanes and aromatics are the main components if crude oil, and along with the different unit, the proportion of alkane and aromatic exist certain variance.

As noted above, alkane and aromatic are two main groups in the petroleum, however, there is a variety of the proportion of alkane and aromatic in the different units. Due to the limited number of samples collected for other units in petroleum, the profiles developed in this study might not adequately represent VOC emission characteristics for whole petroleum refining.

3.3 Olefin Refining

Olefin refining mainly produce ethylene and propene, which are in large demand in other region. four regions were sampling and analysed, including olefin material tank, olefin cracking, olefin compression and olefin product tank. As showed in Fig 2, alkenes accounts for less than 20% in olefin material tank and olefin cracking, however alkenes accounts for more than 40% in olefin compression and olefin product tank along with the processing of olefin refining.

Olefin material tank and olefin cracking were in the upstream of olefin and the raw material were atmospheric gas oil (AGO) and vacuum gas oil(VGO) et al. the main VOCs group were aromatic and alkenes. Benzene, toluene, m,p-xylene and styrene are four main aromatic compounds, accounted for 48%—55%. Propene and 1,3-butene are two main olefin compounds, contributed for 13%-16% of all VOCs. In addition, ethylene must also be one main compounds of alkenes, however ethylene are not measured in this study. This result may reflect the fact that aromatic compounds may also be main group in olefin material tank and olefin cracking.

Along with getting into the downstream of olefin refining, alkenes gradually became more and more in olefin compression and olefin product tank. As showed in Fig 2, alkenes contributed to above 40% of total VOCs, Propene and 1,3-butene are also two main olefin compounds, contributed for 41%-48% of all VOCs. This result was completely in accordance with the product of olefin refining.

3.4 Aromatic Refining

Aromatic refining sector mainly refined aromatic compounds. Five units were sampling and analysed, including aromatic material tank, aromatic furnace, aromatic extraction, aromatic adsorption and separation and aromatic wastewater. As showed in Fig 2, aromatic compounds accounts for almost 80% for the five units above mentioned and the representative components of above five units is similar. The most abundant species in the aromatic refining emissions were toluene (33%), m,p-xylene(16%), and benzene(7%).As expected, the compositions of these major VOC species were quite similar to those of the raw materials used for aromatic refining.

3.5 Wastewater Treatment

Wastewater treatment have always been one of the main concerns associated to VOCs and odour emissions(Kim K H et al.,.2013 and Capelli L et al., 2014). For this reason, several key units, including aeration tank, denitrifying pool and oxidation ditch were collected and analysed in this study. In these units, aromatics still were the main groups, accounted for 52.7%,37.8%,47.4% respectively, mainly included toluene (19%), benzene(11%) and m,p-xylene(9%). Compared with other sectors, halonhydrocarbon and oxygenated VOCs contributed more in wastewater treatment than in other sectors(Zarra T etal., 2014). Halonhydrocarbon compounds accounted for 16%, 25% and 17.6% in three units above respectively, namely 1,2-dichloroethane, chlorobenzene, dichloromethane, of which contributed 15.4%,23.2% and 11% in three units above respectively. Oxygenated VOCs accounted for 4%, 10% and 28% in three units above respectively, mainly Ethyl acetate and acetone. Ethyl acetate and acetone contributed to about 25% in oxidation ditch. This result may reflect the fact that wastewater treatment was the last and complex sector and can produced much more other compounds that were not emission directly, halonhydrocarbon and oxygenated VOCs were its specific feature.

4. Conclusions

A field VOCs measurement for a petroleum refinery in the Yangtze river delta was conducted in this study, and the characteristics of VOCs emitted from its inner four main sectors(16 units) were obtained. The results showed that the VOCs emission of the refinery was greatly important. The VOCs emitted from the whole refinery were characteristic by aromatic (43.2%), alkane (27.7%), halonhydrocarbon (21.2%) and oxygenated VOCs(7.3%). Four main sectors (Petroleum refining, Olefin refining, Aromatic refining and wastewater treatment) related to VOCs emissions were mainly analyzed in this study. VOCs of Sixteen units of these sectors were measured. And the obvious differences in VOCs chemical profiles among these sectors were found, Petroleum refining with the higher proportions of C3-C10 alkanes, Olefin refining with the higher proportions of BTX(benzene, toluene, m,p-xylene). and C2-C4 alkenes Aromatic refining with the higher proportions of BTX(benzene, toluene, m,p-xylene), wastewater treatment with the higher proportions of BTX (benzene, toluene, m,p-xylene), and part halonhydrocarbon and oxygenated VOCs were also its characteristic compounds .

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