

Pollution data analysis and characteristics of volatile organic compounds in the environment

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Abstract. Volatile organic compounds (VOCs) have a wide range of sources and have a significant impact on the ecological environment and human health, which have attracted wide attention of many researchers. In this paper, the pollution characteristics of VOCs, the role of VOCs in atmospheric chemistry including OH reaction reactivity (L_{OH}), Ozone Formation Potential (OFP) and SOA generation potential (SOAP), VOCs source apportionment were discussed and reviewed.

1 Introduction

As an important precursor of ozone and two organic particulate matter, Volatile Organic Compounds (VOCs) play an important role in the atmospheric chemical reaction process, and have attracted more and more attention. VOCs generally refer to volatile organic compounds with higher saturated vapor pressure (greater than or equal to 0.01 kPa at 20 °C), low boiling point, small molecular weight and at room temperature[1]. Usually, VOCs are divided into non methane hydrocarbons including alkanes, alkenes, alkynes and aromatic hydrocarbons (NMHCs), oxygen containing organic compounds including aldehydes, ketones, alcohols, ethers and halogenated hydrocarbons (OVOCs), nitrogenous compounds, sulfur compounds and other categories[2].

As a kind of important gaseous pollutants in the atmosphere, VOCs not only have a direct impact on human health and ecological environment, but also can participate in photochemical reactions generated two pollutants such as ozone (O_3), peroxyacetyl nitrate and organic aerosol, so VOCs are one of the important precursors of O_3 and $PM_{2.5}$ [3]. Hydrocarbons in volatile organic compounds react with nitrogen oxides to produce ozone, which can cause atmospheric photochemical smog and cause harm to human health and plant growth. Ozone is a typical pollutant of photochemical smog. VOCs are one of the most important reasons for the increase of atmospheric ozone concentration and the formation of regional photochemical smog, acid rain and haze.

At present, the natural and anthropogenic sources of VOCs are widely studied at home and abroad. As far as the global scale is concerned, the contribution of natural sources to the VOCs is more than the human source.

Transportation is the world's largest VOCs anthropogenic sources, using solvent is the second largest emitter.

2 Study on the pollution characteristics of VOCs

It is very important to study the distribution of ambient VOCs to take effective air pollution control measures.

2.1 Ambient concentration

From the level of pollution, the VOCs ambient concentration in different areas has a certain difference. Wang[4] measured the concentration of VOCs in Beijing road site at a high level, and road air pollution is more serious than the air pollution in the region. Pankow[5] measured the concentration of benzenes at 13 sampling points in the United States (including the suburbs and cities) and find that lower than that in other countries. Thus, the emission of motor vehicles has become a major factor in the quality of the road air and the main source of volatile organic compounds in urban areas is motor vehicle exhaust. Table 1 presents a comparison between VOCs compounds in different cities. It can be seen from the table that in the seven cities, the concentrations of alkanes and aromatics in Beijing and Guangzhou are higher in domestic cities, which are related to the large emission of motor vehicles and more manufacturing industry in Beijing and Guangzhou areas. Compared with foreign cities, the concentration of isoprene and toluene in Singapore were higher than those in foreign cities. North and American were the next, Charleston and Los Angeles were the minimum while the mixing ratio of propane were higher than those in foreign cities. The VOCs emission characteristics between different cities were significantly different. This difference is related to

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the change of the source of each city, the observation period and the method of observation and experiment.

Table 1 Comparison of the concentration of VOCs in different cities (ppbv)

Region	Propane	n-Butane	i-Butane	Ethene	Isoprene	Benzene	Toluene
Beijing 2014[6]	10.8	3.27	2.32	7.18	0.11	1.98	3.31
Guangzhou 2011-2012[7]	3.66	3.07	2.67	2.99	1.14	0.62	4.59
Hongkong 2010.09-10[8]	2.34	4.37	2.60	1.85	0.12	0.73	2.55
North American 2016.5[9]	-	0.86	-	-	-	2.2	1.1
Singapore 2011[10]	-	-	-	-	3.56 ± 1.42	1.06 ± 0.18	6.39 ± 2.11
Charleston 2008[11]	3.54 ± 1.02	1.01 ± 0.35	0.44 ± 0.17	0.3 ± 0.15	1.82 ± 0.85	0.084 ± 0.033	0.12 ± 0.055
Los Angeles 2007[12]	6.05 ± 3.58	2.34 ± 1.31	1.24 ± 0.6	2.4 ± 1.36	0.27 ± 0.13	0.48 ± 0.24	1.38 ± 0.72

2.2 Time distribution characteristics

In terms of time distribution, the peak value varies from daily and season. The time distribution of VOCs in the atmosphere changed significantly, with obvious seasonal and diurnal variations. The strong emission source and meteorological conditions are the most important factors that affect the time distribution of VOCs in the atmosphere. Guo[13] investigated spatial variations of volatile organic compounds (VOCs) in the atmosphere and found that the concentration of VOCs in the atmosphere of Hongkong has significant seasonal difference and composition, which control the seasonal variation of VOCs concentration in urban atmosphere by a source of emissions, dichloromethane, xylene and trimethyl benzene concentration in summer was slightly higher than in winter, and methyl chloride, benzene and four vinyl chloride concentration peak appeared in the winter atmosphere. Shao[14] studied the daily variation of total volatile organic compounds (TVOC) in summer in Guangzhou. The results showed that the early and late peak concentrations of alkanes and olefin species appeared at 8:00 to 10:00 and 18:00 to 22:00 respectively, which were in accordance with the peak traffic time. The estimate is mainly related to the emission of motor vehicles. Moreover, the peak level of TVOC in the evening is higher than that in the morning because of the decrease in the height of the boundary layer at night.

2.3 Spatial distribution characteristics

In terms of spatial distribution, the concentration of VOCs varies with the change of height and distance. The total energy consumption in urban areas is higher, fuel volatilization, incomplete combustion and industrial activities will discharge a large amount of VOCs, which is closely related to human activities. For example, the high concentration of VOCs in large urban areas is alkane with a carbon number less than 4 ppbv, followed by alkenes and aromatics. The composition and concentration of VOCs in the atmosphere of remote areas are mainly influenced by the emission of natural sources and the long distance transmission of the atmosphere.

Wei[15] has calculated unsaturated hydrocarbons and benzene in the atmosphere of Guizhou, Guangxi, Sichuan and other places in China and the results showed that the proportion is higher than that of the eastern developed cities (Beijing, Tianjin, Shanghai, Zhejiang, etc), which is related to the distribution difference between the fixed burning source and the road vehicle emission source in the provinces.

3 The role of VOCs in atmospheric chemistry

3.1 Reactive activity of VOCs

Volatile organic compounds (VOCs) are important precursors of ozone products in the atmosphere, and their concentrations in the atmosphere usually directly affect the level of ozone pollution. Owing to the great variety of VOCs and the great difference in the chemical structure of the different VOCs, the contribution of different VOCs in ambient air to atmospheric oxidation capacity is very different[16]. At present, there are two ways to calculate the chemical activity of VOCs in ambient air. One is the reactivity of VOCs to OH radical (L_{OH}), the other is the increment reaction activity of VOCs (MIR) to calculate Ozone Formation Potential (OFP).

3.1.1 OH reaction reactivity

The method of measuring the reactive activity of VOCs in the photochemical reaction process of the atmosphere mainly includes the activity of OH radical reaction. The OH reaction activity analysis method considered the reaction rate constant of the concentration of each VOCs species and the OH radical, which is usually a OH consumption rate method. The reaction rate of the VOCs species and the OH free radical reaction L_{OH} reflects the speed of the chemical reaction of the VOCs species in the atmosphere. The concentration of the species and the rate constant of its reaction with the OH radical determine L_{OH} and the calculation formula of L_{OH} is as follows:

$$L_{OH} = [VOC]_i \times K_{iOH} \quad (1)$$

In the formula, $[VOC]_i$ is the concentration of i in the species in VOCs, K_{iOH} is a constant of the rate of the reaction between the species i and the OH radical, L_{OH} is the rate of OH consumption of the species i . Shao[17] used the reaction rate of VOCs species in the atmosphere and OH free radical to analyze the chemical activity of all kinds of VOCs species in Beijing. The results show that the atmospheric VOCs mixture ratio of 15% olefin provides about 75% of the atmospheric chemical activity in the atmospheric VOCs. The contribution of the olefin components of C_4 and C_5 is the greatest

3.1.2 Ozone Formation Potential (OFP)

L_{OH} neglects the production of O_3 , which is consumed by the oxidation of other pollutants. In order to be able to synthetically measure the effects of the chemical reaction activity of the VOCs species on the formation of ozone. Carter[18] proposed VOCs incremental reactivity (IR), that is, a change in the O_3 concentration produced by adding or removing a unit specific VOCs in a mixture of a given gas mass VOCs. In general, the greater the IR is, the faster the VOCs species reacts. The maximum value of IR is achieved by changing the ratio of VOCs / NO_x , which is called the maximum incremental reactivity (MIR)[18]. In the study, the ozone generation potential (OFP) is usually used to indicate the maximum contribution of the VOCs species to the ozone generation under the optimal conditions. Its calculation formula is as follows:

$$OFP = [VOC]_i \times MIR \quad (2)$$

Among them, $[VOC]_i$ is the concentration of i in the VOCs species, and OFP is the ozone generation potential of i of the VOCs species. Czader[19] uses the maximum increment reactivity (MIR) and the concentration of VOCs to study the ozone formation potential (OFP) in the Houston region. The results show that propylene, ethylene and formaldehyde are the larger species of OFP.

3.2 SOA generation potential (SOAP)

Many studies have shown that VOCs is an important precursor for the formation of Secondary Organic Aerosol (SOA)[20, 21]. The SOAP can be used to estimate the concentration of SOA generated by VOCs in the atmosphere. There are two common ways to estimate SOA generation at present: One is to calculate the rate of consumption in the atmosphere according to the measured VOCs concentration, and then to estimate the generation rate of SOA (formula 3). In the formula, t ($\mu g \cdot m^{-3}$) and t ($molecule \cdot cm^{-3}$) are the concentrations of oxidants ($\cdot OH$, O_3 or NO_3) in t at the t time, respectively. The reaction rate constant ($cm^3 \cdot molecule^{-1} \cdot s^{-1}$); The other way is to deduce the initial emission concentration according to the measured VOCs concentration in the environment, assuming that all the VOCs emissions of these emissions are all consumed, and the potential of SOA is calculated by yield (formula 4).

$$\frac{\Delta SOA}{\Delta t} = \frac{\Delta VOC}{\Delta t} \times Y = k_{OX}[VOC]_t[OX]_t Y \quad (3)$$

$$SOA_{potential} = [VOC]_{initial} \times Y \quad (4)$$

In the global scale, the natural source VOCs is the main contributor to the SOA generated by the VOCs transformation. Lane[22] uses a model based on the VOC source list in the United States to estimate SOA. The results showed that the contribution of human source VOCs to SOA was higher in urban areas than in the suburbs, but it is still lower than the contribution of natural sources. In human precursors, the contribution of aromatic hydrocarbons, alkenes and alkanes to SOA is 36%, 32%, 32%, respectively.

4 VOCs source apportionment

Because of the variety of VOCs sources and the complexity of their emissions, it is of great importance to understand the proportion of main VOCs emissions and the proportion of each source of pollutants in the ambient air.

4.1 Benzene series ratio method

The ratio of benzene to toluene (B/T) is often used as a basis for judging the main sources of VOCs in the atmosphere[23]. When the B/T value is close to 0.5, the VOCs in the atmosphere mainly comes from the emission of vehicle exhaust[24, 25]. When the B/T value is more than 0.5, the VOCs in the atmosphere may come from biofuel or charcoal[26, 27]. It may also come from the use of petrochemical or paint. When the B/T value is more than 1, the VOCs in the atmosphere mainly come from coal combustion[28]. When the B/T value is less than 0.5, there may be other sources of VOCs in the atmosphere in addition to the motor vehicle[29]. Barletta[30] studied 27 road air samples in 25 cities in China and concluded that B/T was $(0.58 + 0.21)$. Therefore, when the B/T value is close to 0.6, the vehicle exhaust emission is the main source of VOCs pollution in the atmosphere, which is more in line with the actual situation in China. The results of Song's[31] study also demonstrate this view.

4.2 Source apportionment

Currently, the commonly used receptor models include CMB, PCA/APCS and PMF models[32]. CMB and PMF models are the source apportionment technology recommended by the United States Environmental Protection Agency. Common sources of pollution have characteristics of tracer, such as ethylene and acetylene as combustion source tracer; gasoline volatile source often tracer compounds to isopentane, n-butane and isobutene; high content of industrial emission sources in halogenated toluene, ethylbenzene and xylene; aromatic hydrocarbons are often from solvent use.

The analysis of VOCs sources in foreign countries began in 1970s. At that time, the American EPA used a model of the CMB1.0 version. By using the CMB receptor model, Vaga[33] found that the air VOCs from Mexico accounted for 58.7% of vehicle exhaust and

24.2% of LPG, which accounted for 81.9% of the total VOCs. Mahmoud[34] found that the sources of VOCs were mainly from the mobile source, the smelting of lead and the use of LPG.

Cai[35] used PCA/APCS (principal component analysis/absolute principal component scores) receptor model to analyze the source of air VOC in summer in Shanghai. The results show that there are five main sources of VOCs in the atmosphere of the central city. They are mainly vehicle emissions, fuel volatilization (liquefied petroleum gas / natural gas leakage and gasoline evaporation), solvent use, industrial production and biomass / biofuel combustion and marine sources. Their contribution rates are 34%, 24%, 16%, 14%, 12%, respectively.

In 1994, Paatero and Tapper[36] proposed the application of PMF model to solve source resolution problems for the first time. The PMF model is a matrix decomposition method that combines the error estimation in the data to solve a restricted weighted least square linear model. Maryam Sarkhosh[37] use PMF model to analyze the source of urban atmosphere in Tehran, Iran. The result showed that there were five sources of VOCs in Tehran, which accounted for 61% of vehicle emissions, 12% of fuel evaporation, 17% of urban natural gas, 8% of bio resources and 2% of industrial solvent sources.

5 Conclusion

In this paper, the research status of VOCs pollution at home and abroad is reviewed, and the following conclusions can be drawn: the main components of VOCs in the atmosphere are aromatic hydrocarbons, alkanes and alkenes; the concentration of volatile organic compounds in summer and winter in urban atmosphere is higher than that in spring and autumn; the diurnal variation of VOCs in urban air was in bimodal characteristic, which appeared at the peak of traffic in the morning and evening; natural sources are mainly from plant emissions and the main sources of human sources are automobile exhaust, fuel volatilization, and coating use.

It is of great significance to accelerate the study of the pollution characteristics of VOCs, and VOCs reactive activity which is to identify VOCs optimal control species and VOCs source apportionment. It is also of great significance to the protection of atmospheric environment and the prevention and control of VOCs pollution.

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