

INVESTIGATION OF OZONE GENERATION POTENTIAL, CHEMICAL REACTIVITY AND ACTIVE COMPONENTS OF VOLATILE ORGANIC COMPOUNDS IN WENZHOU 2019-2021, CHINA

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Abstract. From April to October 2019-2021, the concentrations of 70 volatile organic compounds (VOCs) were measured in the atmosphere of Wenzhou city. The Mann-Kendall test was employed to analyze trends in air pollution. The critical change period for concentrations of VOCs was identified using both the Mann-Kendall test and the cumulative anomaly method. Atmospheric hydroxyl radical consumption rate (L_{OH}) and ozone forming potential (OFP) were used to determine the chemical reactivity of VOCs and their main active components were explored. The results showed that, the average concentrations of VOCs in Wenzhou were 120.19, 58.40 and 59.27 $\mu\text{g}/\text{m}^3$, respectively. The change point of concentration occurred in April 2020. The VOCs predominantly consisted of alkanes, olefins, aromatic hydrocarbons, and oxygenated volatile organic compounds (OVOCs). Alkanes, olefins, and aromatic hydrocarbons were the most significant components. Among them, alkanes were the main components. L_{OH} and OFP were directly related to the concentration, and the values of L_{OH} and OFP were higher in summer than in other seasons. Aromatic hydrocarbons were key active components in atmospheric pollution. The toluene/benzene concentration ratio showed that the primary source of VOCs in the atmosphere of Wenzhou was vehicle exhaust. This study provided a reference for atmospheric environment management in Wenzhou.

Keywords: volatile organic compounds (VOCs), Wenzhou City, ozone formation potential (OFP), Mann-Kendall test, chemical reactivity

Introduction

Volatile organic compounds (VOCs) in the atmosphere pose a direct threat to human life and health due to their toxicity (Kumar et al., 2018). VOCs act as precursors to photochemical reactions with atmospheric nitrogen oxides, hydrocarbons and oxidants when exposed to sunlight. VOCs indirectly affect crop growth and lead to ground-level ozone (O_3) pollution, which in turn creates secondary aerosol pollution (Sun et al., 2016). O_3 reacts with human organs and causes permanent damage to human health (Li et al., 2019). Therefore, it is necessary to investigate the photochemical reactivity of

VOCs as ozone precursors and to alleviate air pollution problems in cities. However, the composition of air pollutants and the mixing of VOCs are complex. Due to the different chemical reactivity of different VOCs, they contribute differently to the formation of O₃, resulting in large differences in their ozone formation potentials (Wang et al., 2020; Ling et al., 2011), which in turn creates difficulties in pollution control and management of O₃. VOCs play a critical role in air quality management. They are important precursors and active participants in the formation of O₃. Considering that VOCs are emitted from a large number of sources with a complex composition, studies investigating the differences in the concentration and activity of individual VOCs are beneficial for further management. The ozone generation potential (OFP) and the loss rate to OH radicals (L_{OH}) have been widely used to assess the chemical reactivity of VOCs (Ye et al., 2023; Shaw et al., 2020). Due to the different industrial structures, different regions show obvious differences. A related study found that alkanes (45.6%) and aromatic hydrocarbons (45.2%) were the main contributors to OFP in Beijing (Liang et al., 2023). Olefins and aromatic hydrocarbons also dominated L_{OH} and OFP in Wuhan (Guo et al., 2022). Oxygenated VOCs (OVOCs) were not only the most abundant VOCs in Lasa, but also dominated in OFP and L_{OH} (Ye et al., 2023). The study of the trend of VOCs composition can help accurate prevention and control. Trend test is widely used in hydrological (Zhang et al., 2015), meteorology (Zang et al., 2023), economy (Reyes et al., 2020), agriculture and forestry (Liu et al., 2023) and water quality (Wang et al., 2023) etc. in time series analysis. Predicting future trends from past data can be specifically divided into parametric and non-parametric methods. Generally, parametric methods are more accurate than non-parametric methods, but they require the data to be independent or normal distribution. Non-parametric methods only require data to be independent and allow for the presence of outliers or missing data. Therefore, the non-parametric method is widely used in practical problems due to its advantages such as low requirements for data and easy realization. The Mann-Kendall test (M-K test) is derived from the rank correlation test between two sets of observations proposed by Kendall (Dong et al., 2016). In the M-K test, the correlation between the observations and the corresponding time is considered, and the original assumption is that the data are independent and random, i.e., there is no trend or serial correlation (Mishra et al., 2009). It has been suggested that the O₃ concentration in the Guanzhong urban agglomeration in Shaanxi Province has a significant upward trend in winter, with no significant trend in other seasons (Zhao et al., 2022); the average growth rate of O₃ concentration in the Pearl River Delta (PRD) region from 2006 to 2019 was 0.80 µg·(m³·a)⁻¹, and the concentration mutation point was in 2016, and there were obvious spatial and seasonal variability in the trend of concentration change in the region, mainly concentrated in the summer season (Zhao et al., 2021); between 2015 and 2020, near-surface O₃ concentrations in Henan Province showed a first increase and then a decrease, with the highest concentration in 2018, and most cities in the eastern part of Henan Province belong to the VOCs control area (Yan et al., 2022).

At present, most of the studies on the chemical reactivity of VOCs in China were concentrated in mega-cities with high population density (urban resident population of 10 million or more), such as Beijing (Wang et al., 2017), Guangzhou (Yu et al., 2018), Shanghai (Jin, 2022) and Tianjin (Han et al., 2017). However, the spatial and temporal distribution of VOCs and the species composition of VOCs were quite different due to the different levels of urban development. Atmospheric chemical reactivity of VOCs in Beijing was dominated by olefins, followed by aromatic hydrocarbons and OVOCs, and

the key reactive components were ethylene, acetaldehyde, m/p-xylene, toluene, propylene, o-xylene, ethylbenzene, n-butane, 1-butene, and propanal, p-xylene, 1,3-butadiene, isoprene, etc.; summer was the O₃ high season in Shanghai, OVOCs were the main components of VOCs, of which formaldehyde and acetone had the highest volume fraction, and the chemical reaction activity of ambient air was the strongest in May, with the largest contribution of formaldehyde; the photochemically reactive species in Tianjin were dominated by low-carbon (C₂ to C₅) olefins and alkanes, and the reaction activity and contribution to O₃ generation. The more reactive species were mainly olefins such as 1,3-butadiene, propylene and ethylene. Few studies had focused on the characterization of VOCs pollution in medium-sized cities in China, which usually had different economic structures and development strategies from mega-cities, and thus may lead to different air pollution conditions. Wenzhou City is located in the southeastern coastal area of Zhejiang Province, China, bordering the East China Sea in the east, Ningde City, Fujian Province in the south, Lishui City in the west and northwest, and Taizhou City in the north and northeast, with a land area of 12,102.65 km², a sea area of 8649 km², and a land coastline of 514 km, with winding coasts and many good harbors. Wenzhou City is rich in natural resources such as water, plants, animals and minerals. As of 2018 the city's gross domestic product (GDP) was 600.62 billion RMB, the three-industry structure of the national economy was 2.4:39.6:58.0, the city's resident population was 9.522 million, and the per capita GDP was 65,055 RMB. According to the Wenzhou Environmental Condition Bulletin, Wenzhou's air pollution fluctuated in different time periods. The overall air quality rate was 95.1%, with 111 days of Class I (excellent), 236 days of Class II (good), and 18 days of Class III (mildly polluted), with exceedances of pollutants such as O₃, fine particulate matter (PM_{2.5}), nitrogen dioxide (NO₂), and respirable particulate matter (PM₁₀).

In this study, a continued monitoring on the pollution status of atmospheric VOCs was conducted in Wenzhou City from 2019 to 2022. The concentration characteristics of VOCs were analyzed. Change points of concentration were determined by Mann-Kendall test and cumulative anomaly method. Chemical reactivity was assessed by the depletion of the hydroxyl radical ($\cdot\text{OH}$) reaction (L_{OH}) and ozone production potential (OPP). Then, the key reactive components in the local atmosphere were identified.

Materials and methods

Sampling location

Wenzhou City is located in Zhejiang Province, eastern China, belonging to the central subtropical marine monsoon climate zone, with four distinct seasons and abundant rainfall. Lucheng District is the political, economic and cultural center of Wenzhou City, and the overall topography is high in the west and low in the east, with topographic features of plains, mountains, hills, beaches and islands. A sampling site (*Fig. 1*) was set up in Lucheng District (120.6748°E, 27.9939°N), which was on the roof of the Lucheng District Environmental Monitoring Station at a height of 20 m above the ground. It is adjacent to a major road in Wenzhou City. The sampling site is located in the center of a major commercial and residential area surrounded by high-rise buildings. There is heavy traffic in the sample area which is less affected by industrial areas. Therefore, the VOCs pollution status of this site could be representative of the city center area. From 2019 to 2021, data were collected every 6 days from April to October each year by using Suma canisters.



Figure 1. Sampling site

Sample collection and analysis

Fifty-seven VOCs were monitored using a gas chromatography mass spectrometry (GC-MS) analyzer (Agilent 7890BGC/5977BMS). The ambient air samples were collected in stainless steel canisters with inert inner walls, and then the samples were pre-concentrated in a cold trap to remove water and inert gases, and then separated by gas chromatography (GC), and the target compounds of C2~C3 were detected by a hydrogen flame ionization detector (FID, Agilent 5200-0176), and the rest of the target compounds were detected by a mass spectrometry (MS) detector. The C2~C3 target compounds were characterized by retention time and quantified by external standard method; the remaining target compounds were characterized by retention time and mass spectrometry in comparison with the standards, and quantified by internal standard method, and the parameters of the instrumentation and equipment are shown in *Table 1*. The monitoring methods for the remaining 13 VOCs were performed in accordance with the *Ambient air- Determination of volatile organic compounds-sorbent adsorption and thermal desorption/gas chromatography mass spectrometry method* (HJ 644-2013).

The data higher than the detection limit were defined as valid data, the species of VOCs with a significant data volume of less than 50% were excluded. Furthermore, the values below the detection limit in the remaining data were replaced by the lowest concentrations. The sampling and analysis period was 1 h. Online chromatography analyzer was calibrated internally with each use and externally once a month to ensure its reliability and validity (system accuracy > 90%; temporal resolution > 30 min). Benzene, n-butane and n-hexane were used as internal standards, and 69 VOCs were used as external standards. All standards were purchased from Air Liquide America, Specialty Gases LLC in United States.

Table 1. GC-MS instrument detection parameter settings

	C ₂ -C ₃ VOCs	Remaining VOCs
Column	PoralPLOT Q, 27.5 m×0.32 mm×10 μm	DB-1 ms: 60 m×0.32 mm×1.0 μm
Inlet temperature	150°C	
Column temperature	0°C for 10 min, increase to 140°C at 4°C/min, increase to 200°C at 6°C/min for 5 min	

Data analysis

Mann-Kendall test

Long-term trends in VOCs concentrations were analyzed by the Mann-Kendall test (MK test). A rank-based nonparametric test for detecting trends in time-series data that does not require the data to follow a normal distribution (Zhang et al., 2015).

For the time series data $Y = \{y_1, y_2, y_3, \dots, y_n\}$, define its statistical information as shown in Equation 1:

$$S = \sum_{i=1}^{n-1} \sum_{j=i+1}^n \text{sgn}(y_j - y_i), \text{sgn}(y_j - y_i) = \begin{cases} 1, y_j > y_i \\ 0, y_j = y_i \\ -1, y_j < y_i \end{cases} \quad (\text{Eq.1})$$

A sequence of random numbers $S_a = (a = 1, 2, 3, \dots, n)$ obeys a normal distribution and its variance $V_{(s)}$ is calculated from Equation 2:

$$V_{(s)} = \frac{n(n-1)(2n+5)}{18} \quad (\text{Eq.2})$$

Setting up an independent random sequence S and defining the M-K test Z_{M-K} value is calculated in Equation 3:

$$Z_{M-K} = \begin{cases} \frac{S-1}{\sqrt{V_{(s)}}}, S > 0 \\ 0, S = 0 \\ \frac{S+1}{\sqrt{V_{(s)}}}, S < 0 \end{cases} \quad (\text{Eq.3})$$

When the significance level $\alpha = 0.05$, the $\left|Z_{1-\frac{\alpha}{2}}\right| = 1.96$; when $\alpha = 0.01$, $\left|Z_{1-\frac{\alpha}{2}}\right| = 2.58$. First, assume that there is no change in the sequence of random numbers. When $|Z_{MK}| > 2.58$, it is considered that there is a significant trend of change.

A mutation is a rapid transition from one state to another. The basic principle of MK test for mutation point is as follows: construct a sequence based on the time series data; compute the statistics UF and UB; the intersection of the statistics UF and UB within the critical value after a given level of significance is the point of mutation of the sequence. If $UF > 0$, it indicates an upward trend in the development of the series over time, and if $UF < 0$, it indicates a downward trend. When they exceed the critical line, it indicates a significant trend of change.

Cumulative distance level method

Cumulative distance level method is a statistical tool for analyzing abrupt changes in hydrological, meteorological and water quality data (Wu et al., 2020). The steps for

calculating cumulative outliers are as follows: first, the difference between the long series of data and the mean is calculated. Then, the cumulative distance level value is accumulated year by year in the time series. For series x , the cumulative distance level is $\sum_{i=1}^t (x_i - \bar{x})$. It is calculated by *Equation 4*:

$$K = \frac{\sum_{i=1}^t (x_i - \bar{x})}{\bar{x}}, t = 1, 2, 3 \dots, n \quad (\text{Eq.4})$$

If the value of K gradually increases, it means that each point in the long series of data is larger than the average and is trending upward.

Chemical reactivity

The chemical reactivity of VOCs was evaluated by two parameters such as depletion (L_{OH}) for reaction with hydroxyl radicals ($\cdot OH$) and ozone production potential (OFP). The calculation process is shown in *Equations 5 and 6*:

$$L_{OH} = [VOC_i] \times k_{iOH} \quad (\text{Eq.5})$$

In *Equation 5*, L_{OH} represents the rate of $\cdot OH$ consumption of VOC species i (s^{-1}), and $[VOC_i]$ is the concentration of species i ($\mu g/m^3$), and k_{iOH} represents the reaction rate constant of species i with $\cdot OH$, and its value was obtained from Carter et al. (2015).

$$OFP = [VOC_i] \times MIR_i \quad (\text{Eq.6})$$

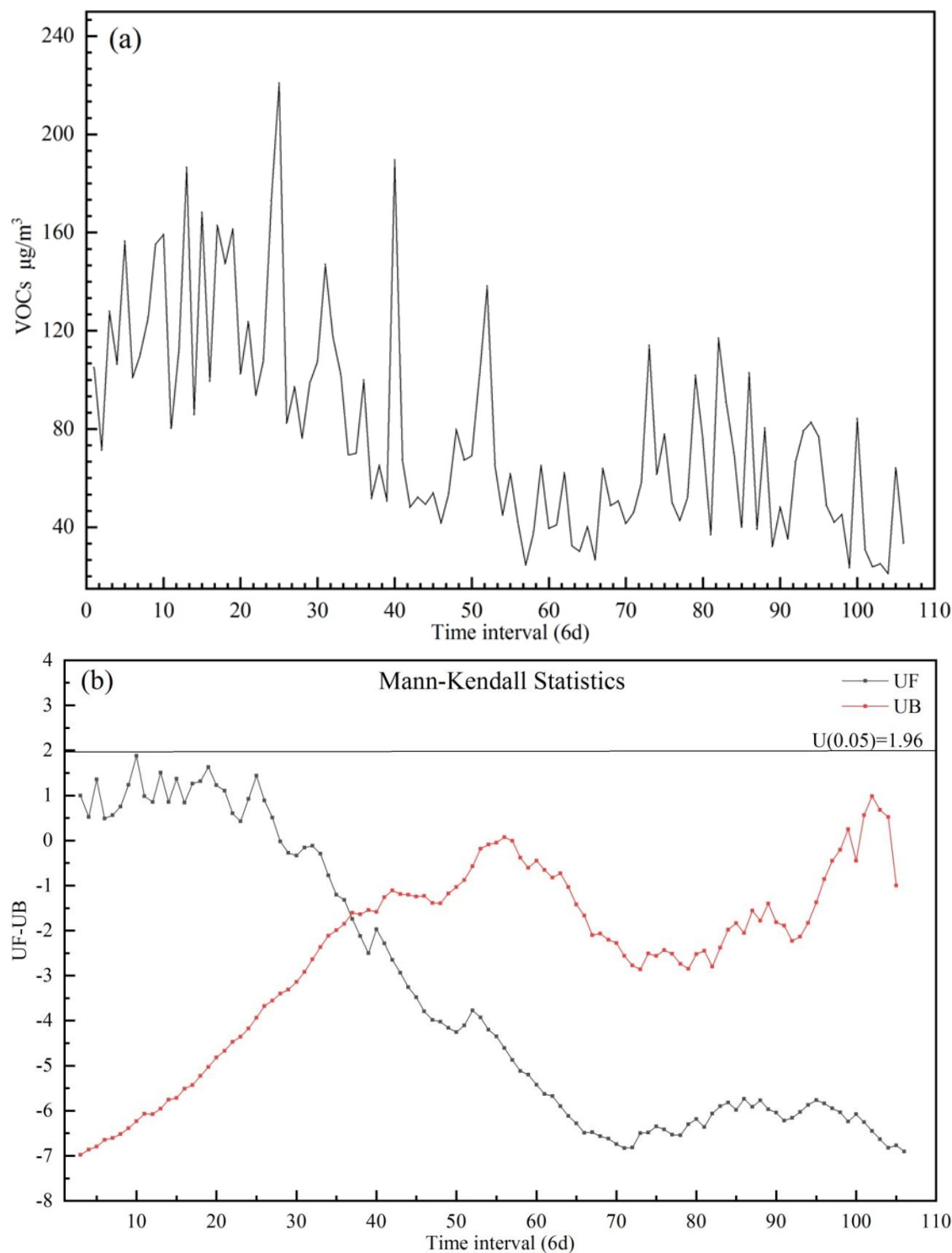
In *Equation 6*, the OFP represents the ozone production potential of species i ($\mu g/m^3$); $[VOC_i]$ represents the mass concentration of species i ($\mu g/m^3$); MIR_i represents the MIR coefficient of species i (Carter et al., 2015).

Results and discussion

Characterization of VOCs concentrations

In *Figure 2a*, total concentration of VOCs in Wenzhou City in 2019 ranged from 69.44 to 220.90 $\mu g/m^3$. In 2020, the concentration was from 24.53 to 189.56 $\mu g/m^3$. In 2021, the concentration was 21.02 - 116.91 $\mu g/m^3$. The average concentrations for three years were 120.19, 58.40, and 59.27 $\mu g/m^3$, respectively, showing an overall decreasing trend. The trend of VOCs' concentration in Wenzhou City was analyzed by MK test, and the change points of concentration were explored by MK test and cumulative distance level method respectively. *Figure 2b* showed that the value of $|Z|$ in the MK test = 6.905 > 1.96, which was a significant trend. UF is the trend curve obtained from a positive time series. When $UF > 0$, it is an upward trend, if not, it is a downward trend. Results demonstrated that the concentration of VOCs in Wenzhou City showed a significant trend of decline, further indicating that the concentration was higher in the pre-monitoring period and then decreasing year by year. The moment corresponding to the intersection point of the MK test species UF and UB curves is the change point of concentration, indicating that the change of concentration occurred around the 35th

monitoring time (end of October 2019). In *Figure 2c*, the value of $|T|$ in the cumulative anomaly method = $9.05 > 1.96$, the point of change was around the 40th monitoring time (end of April 2020). Therefore, the significant time point for VOCs concentration was 2020.



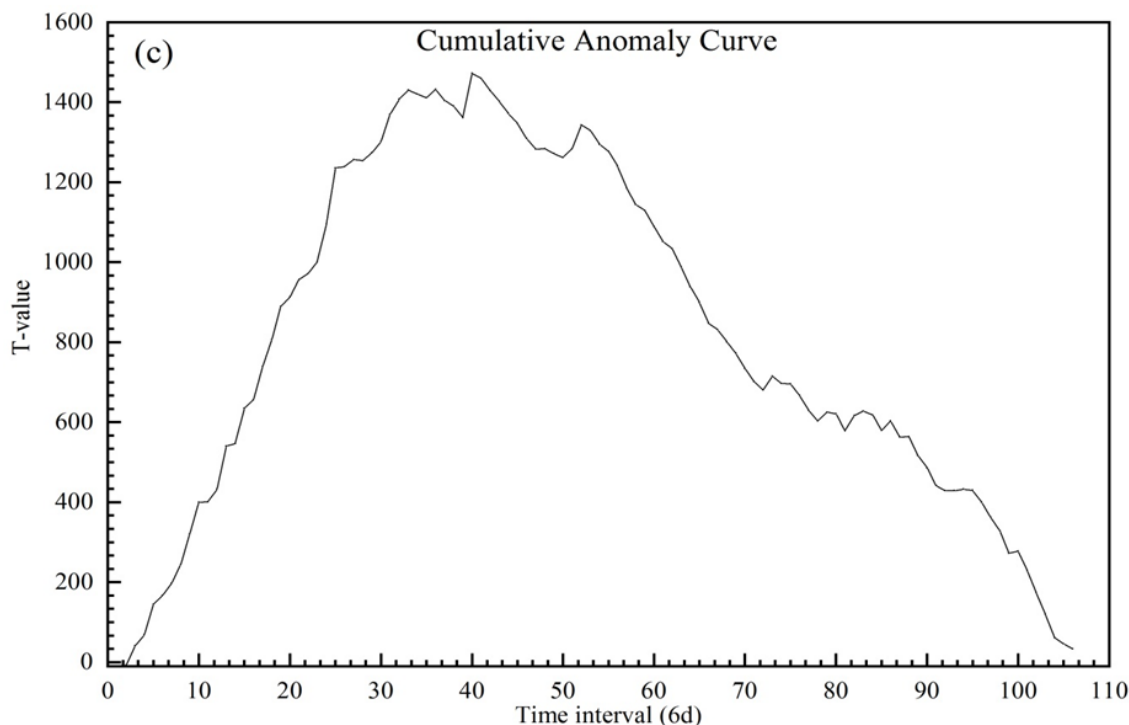


Figure 2. Characteristics of VOCs concentration in Wenzhou City, 2019-2021

As shown in *Figure 3a-c*, VOCs in Wenzhou City were mainly composed of alkanes, olefins, aromatic hydrocarbons and OVOCs, in which alkanes accounted for a relatively high concentration. The average concentrations of alkanes, olefins, aromatic hydrocarbons and OVOCs in 2019 were 56.28, 5.58, 34.49 and 22.74 $\mu\text{g}/\text{m}^3$, and in 2020 the average concentrations of the four were 24.26, 2.67, 6.95 and 24.76 $\mu\text{g}/\text{m}^3$, and 26.22, 3.02, 10.94 and 17.39 $\mu\text{g}/\text{m}^3$ in 2021. After 2019, the concentration of VOCs decreased significantly, which was consistent with the conclusions of trend analysis from a numerical perspective. The concentration of VOCs decreased significantly after 2019, and numerically this result was consistent with the conclusions of the trend analysis. In 2019, the concentration ranked alkanes > aromatic hydrocarbons > OVOCs > olefins, whereas since 2020, OVOCs concentrations increased, second to alkanes. The concentration of aromatic hydrocarbons decreased and then increased, but the values were significantly lower than those in 2019. And the average concentrations in 2020 and 2021 were 20.16% and 31.73% of those in 2019. As showing in *Figure 3a-c*, October 2019, September 2020 and October 2021 were the months with the lowest concentrations in the year, which were 85.40, 38.66 and 33.50 $\mu\text{g}/\text{m}^3$, respectively. And June 2019, June 2020 and May 2021 were the months with the highest concentrations in the year, which were 1.65, 2.36 and 2.36 times higher than the lowest values of the concentrations in the same years. In addition, the concentrations in April-June were higher than those in other periods of the same year. The reason for the high concentration in April might be due to an increasing in VOCs emissions from natural sources. In spring, plants were in their growth period and respiration was strengthened. These lead to an increasing in VOCs emissions from forests, grasslands, oceans, and other plants, then impact of biomass on VOCs increased (Liu et al., 2018). The higher concentration in May and June was due to the fact that

Wenzhou was in the rainy season in that month, with high precipitation and high humidity, and the humidity had a direct effect on the emission of VOCs, which had a greater effect on OVOCs.

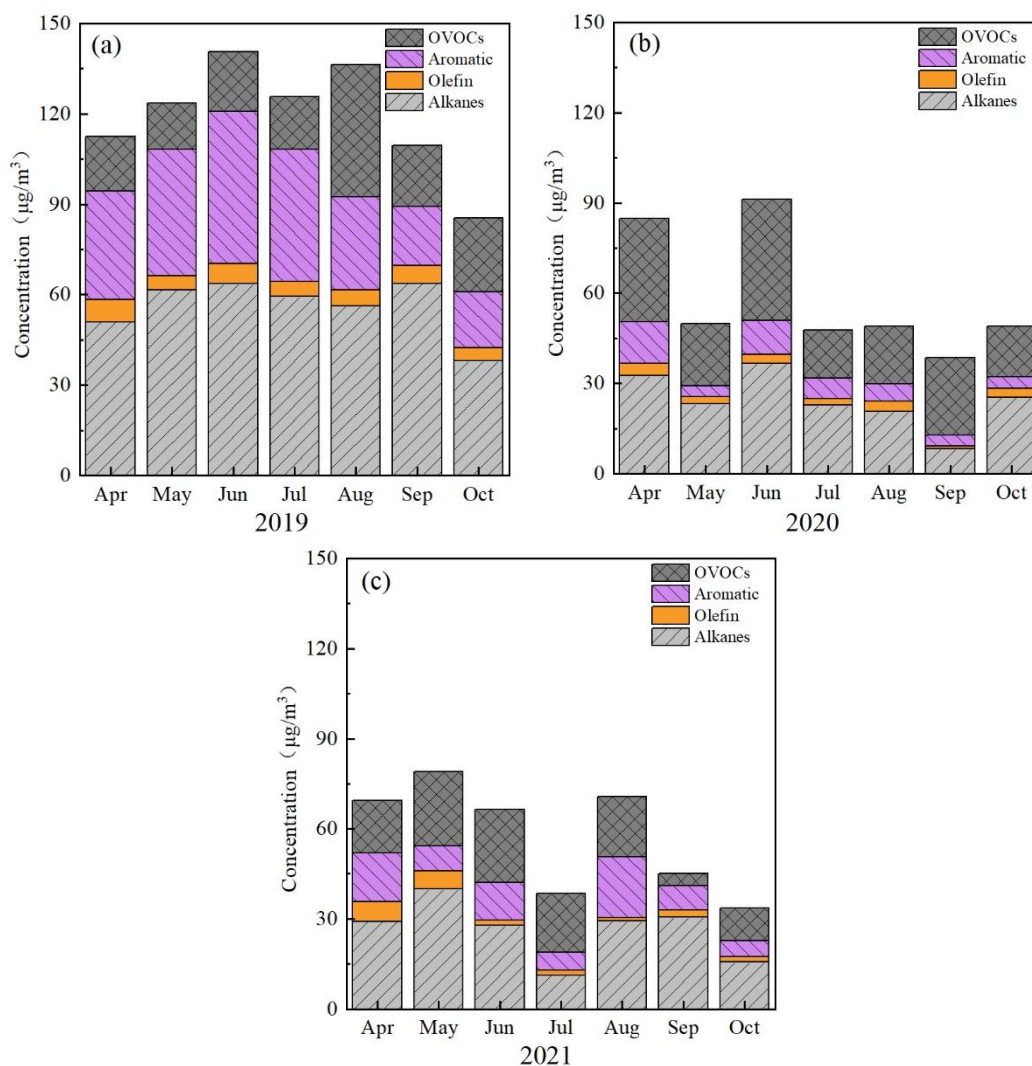


Figure 3. Change in monthly concentration of VOCs in Wenzhou City, 2019-2021

Chemical reactivity

L_{OH} and OFP were the sum of all individual VOC values, and the assessed chemical reactivity was slightly lower than the actual values due to the unknown values of K_{OH} and MIR for some VOCs species. Combined with the analysis in Figure 4a, b, the L_{OH} and OFP values in Wenzhou City were 854.84 and 325.66 $\mu\text{g}/\text{m}^3$ in 2019, 162.70 and 91.23 $\mu\text{g}/\text{m}^3$ in 2020, and 362.45 and 129.41 $\mu\text{g}/\text{m}^3$ in 2021. The VOCs contribute to the atmospheric pollution were different due to their unique chemical structure and properties. Based on their chemical properties and molecular structures, VOCs were specifically divided into four groups (alkanes, olefins, aromatic hydrocarbons, and OVOCs). In 2019, the mixing ratio of alkanes in VOCs was 47.26%, with 18.19% and 17.53% contributions to L_{OH} and OFP, respectively, while olefins accounted for 4.69%

of VOCs and contributed 12.69% and 12.04%, the share of aromatic hydrocarbons, the contribution of L_{OH} and OFP were 28.96%, 65.66% and 58.70% respectively, and the rest consisted of OVOCs. The large contribution of aromatic hydrocarbons to the chemical reactivity of total VOCs in 2019 suggested that aromatic hydrocarbons may be the key reactive components of VOCs in the urban environment of Wenzhou City. It showed that in Xi'an (Song et al., 2021) and Shanghai (Zhang et al., 2015) aromatic hydrocarbons are the main reactive components of VOCs, which was consistent with the phenomenon of this study. In 2020, the contribution of aromatic hydrocarbons to L_{OH} and OFP decreased to 24.60% and 28.33%, but the contribution of OVOCs to both increased to 7.5 times and 2.8 times of that in 2019.

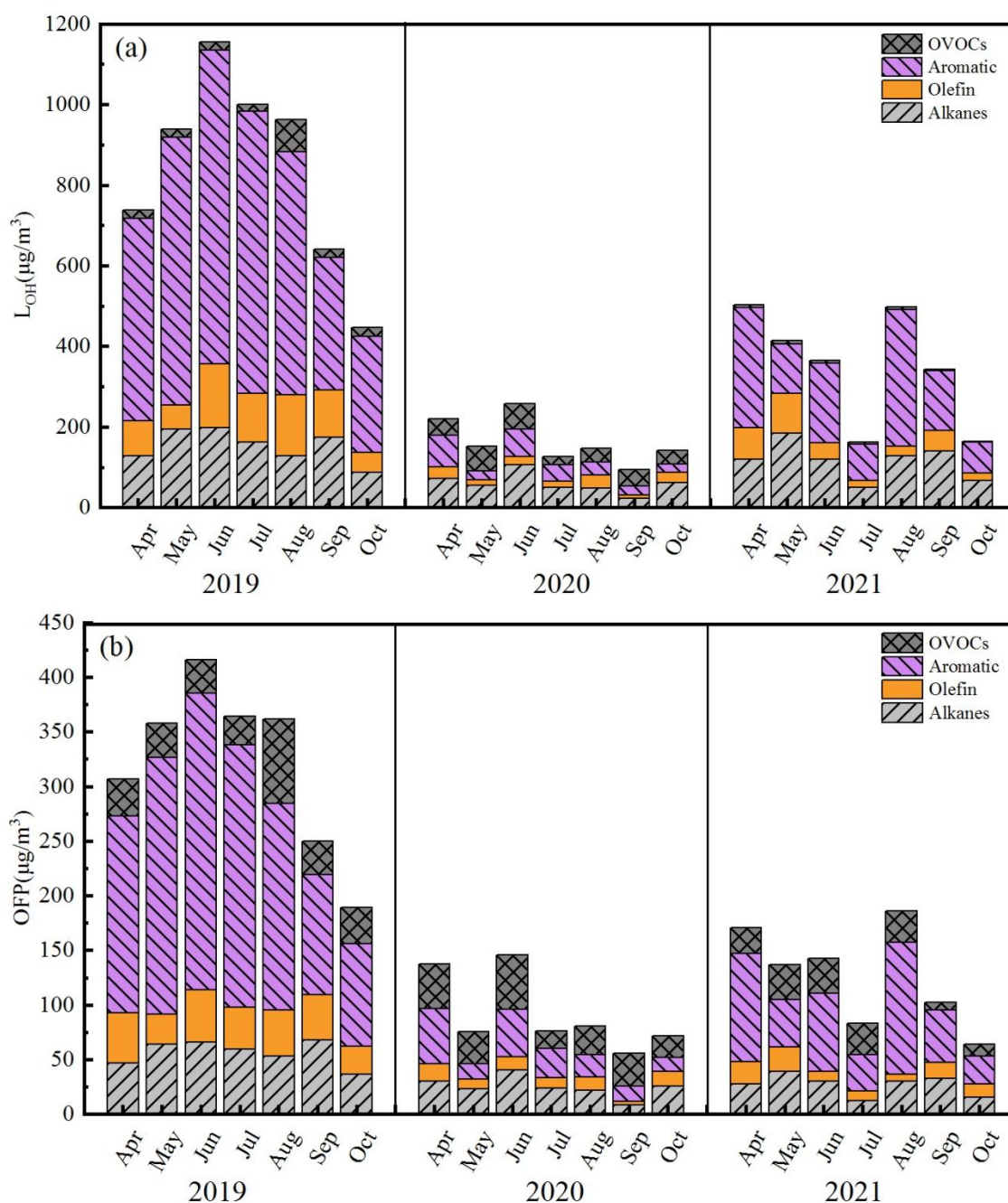


Figure 4. Chemical reactivity of VOCs in Wenzhou City, 2019-2021. (a) L_{OH} ; (b) OFP

The monthly L_{OH} and OFP of VOCs during the study were shown in *Figure 4*, and the distribution of L_{OH} and OFP was consistent with the concentration of VOCs, with an “inverted V” distribution. Concentrations and chemical reactivity were higher in summer and lowest in fall, and the highest concentrations of VOCs occurred at the turn of spring and summer, when the rate of $\bullet OH$ depletion and ozone generation potential were the highest, indicating that complex secondary air pollution (aerosols, ozone, etc.) was more likely to occur during this period. However, since the consumption rate of $\bullet OH$ was higher in summer, the concentration of VOCs should decrease after reacting with $\bullet OH$, but it contradicted to the results of this study, the cause of this phenomenon might be due to the higher temperature. The emission of VOCs sources was higher than the consumption. The chemical reactivity of VOCs was related to the temperature, and in 2019, 2020 and 2021, the average summer (mid-late May to mid-September) temperatures in Wenzhou City were 28.6, 29.5 and 27.3°C, which were higher than the average summer temperatures in previous years (22-28°C). In addition, more volatile organic compounds (VOCs) are emitted during the summer months due to the volatilization of organic solvents and the intense use of refrigerants (cyclopentane in refrigerators), as well as the strong metabolism of plants. Although spring temperatures were similar to those of fall, higher wind speeds, longer daylight hours and better dispersion conditions result in higher concentrations and reactivity of VOCs than in fall.

Main active components of VOCs

The top 10 of VOCs with the highest average concentrations, L_{OH} and OFP throughout the monitoring process were presented in *Figure 5*. In *Figure 5a*, formaldehyde had the highest average concentration of VOCs during the monitoring process in Wenzhou City, and other species with relatively high concentrations ($>3.0 \mu g/m^3$) were acetone, isobutane, toluene, propane, n-butane, 2-methylheptane, and iso-pentane. Olefin concentrations were low in this study, compared to Shanghai (Zhu et al., 2018) and Beijing (Zhang et al., 2020). And the characteristics of these cities where alkanes had the highest proportion of total VOCs were similar to Wenzhou, where isopentane, propane and toluene are included in the top 10 VOCs in these cities. In addition, the atmospheric reactive component VOCs in Wenzhou were mainly composed of light hydrocarbons (C3~C5) and low carbon OVOCs, which might be due to the high volatility of these VOCs relative to heavy chain VOCs.

The top 10 species in L_{OH} in *Figure 5b* differed significantly from OFP. Aromatic hydrocarbons had a high contribution in L_{OH} with a total contribution of $196.14 \mu g/m^3$ from m- xylene and p-xylene, toluene, styrene, 1,2,4-trimethylbenzene, 1,3,5-trimethylbenzene, and 1,2,3-trimethylbenzene, which accounted for 43% of all the VOCs, which was due to the larger L_{OH} of these substances. The high-contributing VOCs in L_{OH} were mainly olefins and benzene compounds, which derived from automobile exhaust, gasoline and other volatile solvents from evaporation processes. Benzene, toluene, m- xylene, p-xylene and o-xylene were typical substances emitted from gasoline vehicle exhaust. Due to the presence of other sources of toluene, the concentration ratio of toluene/benzene (T/B) could be used to assess the contribution of vehicle emissions. A value of 2.0 or lower for T/B indicated a significant contribution from vehicle emissions. In this study, the T/B values were 0.13 and 0.087 for 2019 and 2020, respectively. These provided that the main source of VOCs in urban air in Wenzhou was vehicle exhaust, which was also consistent with the fact that the sampling site was located in the city center with heavy traffic.

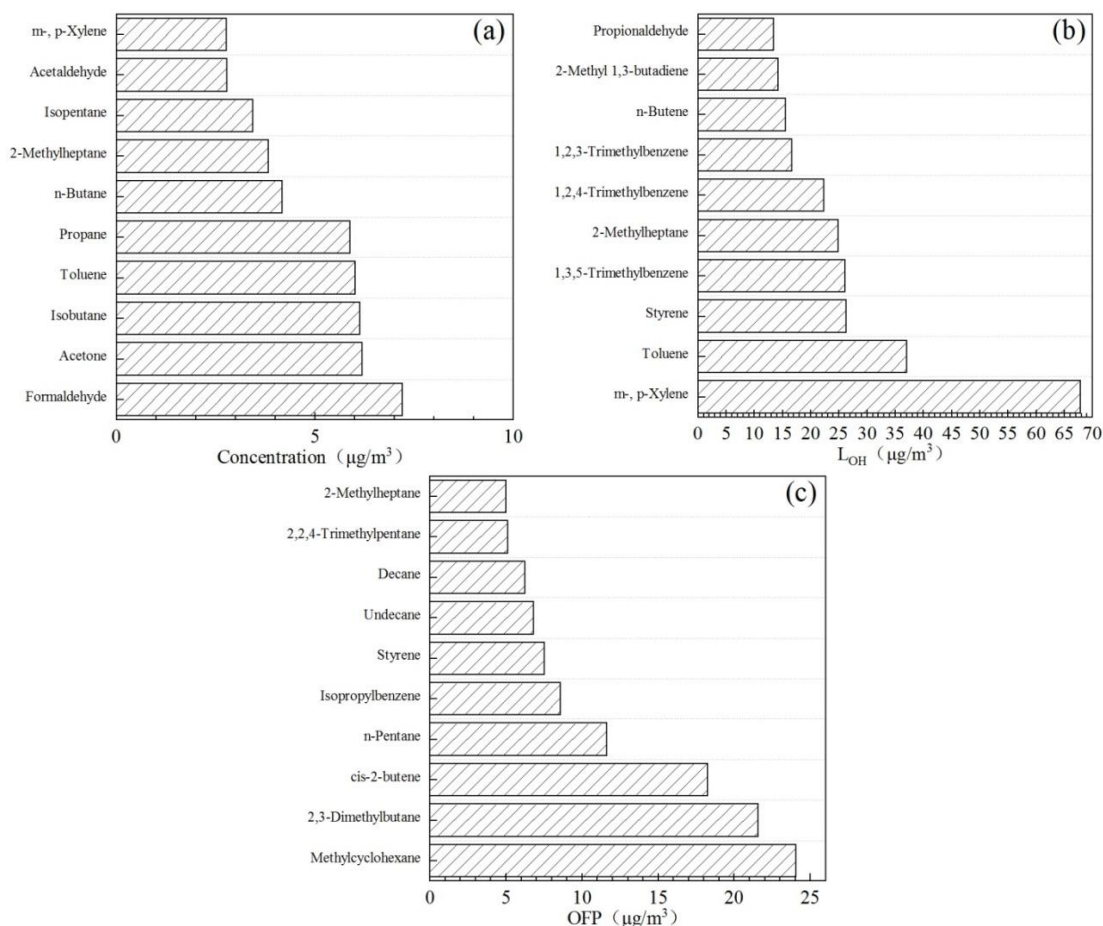


Figure 5. Top 10 species with average VOCs concentration (a), I_{OH} (b) and OFP (c) in Wenzhou, 2019-2021

The top 10 VOCs with the highest OFP in Wenzhou (Fig. 5c), accounted for 63.02% of the total VOCs. There were large differences in both substance and ordering compared to concentration. Methylcyclohexane, 2,3-dimethylbutane, cis-2-butene, n-pentane, isopropylbenzene, styrene, undecane, decane, 2,2,4-trimethylpentane, and 2-methylheptane had higher photochemical reactivity in VOCs. They were the main reasons for the higher ozone concentration and the key reactive substances in Wenzhou City. Although isobutane, propane, n-butane and formaldehyde had higher concentrations, their OFP values were smaller due to their lower chemical reactivity, however, heavy chain alkanes had larger OFP values. The species with significant differences from other regions were olefins, which were recognized as one of the major threats to human health due to their high reactivity, with the exception of cis-2-butene, the contribution of olefins in this study was low, which might be due to the low concentration of olefins and fewer detected species in this region. In addition, the contribution of aromatic hydrocarbons to OFP in Wenzhou City was low compared with other cities in China, and toluene ranked first in the contribution of OFP in Shanghai, Guangdong, and Kaohsiung, whereas isopropylbenzene and styrene were the aromatic hydrocarbons contributing to higher levels of OFP in the city. The reason for this difference is that the overall aromatic hydrocarbon concentrations in Wenzhou City in 2019-2021 ranged from 3.57 to 50.54 $\mu\text{g}/\text{m}^3$, which is lower than other cities.

Conclusion

From 2019 to 2021, the concentration of VOCs in Wenzhou City showed a significant decreasing trend, with three-year average concentrations were 120.19, 58.40 and 59.27 $\mu\text{g}/\text{m}^3$, respectively. And the main change point was in April 2020. VOCs in the city were mainly composed of alkanes, olefins, aromatic hydrocarbons and OVOCs, with alkanes being the main component. In 2019, the concentration of aromatic hydrocarbons was second only to alkanes, and since 2020, the concentration of OVOCs had increased more than aromatic hydrocarbons. In addition, May and June were the highest concentration months of the year. Due to the correlation between the concentration of VOCs and chemical reactivity, the change status of LOH and OFP in the city was similar to the concentration. In 2019, the LOH and OFP values in Wenzhou were 854.84 and 325.66 $\mu\text{g}/\text{m}^3$, and in 2020, the LOH and OFP values were 162.70 and 91.23 $\mu\text{g}/\text{m}^3$, and in 2021, their values were 362.45 and 129.41 $\mu\text{g}/\text{m}^3$, respectively. The highest period of chemical reactivity in the same year occurred at the turn of spring and summer. Aromatic hydrocarbons contributed most to the LOH and OFP values, and they were the key active components of VOCs in Wenzhou City. Vehicle exhaust was the main source of highly reactive VOCs in Wenzhou City, so the most effective way to avoid urban ozone pollution and improve air quality was to control vehicle exhaust emissions. The results of this study could provide a reference for the environmental problems of VOCs faced by Wenzhou City.

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