

Seasonal Chemical Characteristics of PM_{2.5} in Zhuhai, China

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ABSTRACT: Fine particulate matter (PM_{2.5}) is associated with adverse health effects but exactly which characteristics of PM_{2.5} are responsible for this is still widely debated. We evaluated seasonal dynamics of the composition and chemical characteristics of PM_{2.5} in Zhuhai, China. PM_{2.5} characteristics at five selected sites within Zhuhai city were analyzed. Sampling began on January 10, 2015, and was conducted for 1 year. The ambient mass concentration, carbon content (organic and elemental carbon, OC and EC) and level of inorganic ions of PM_{2.5} were also determined. Study finds that average concentrations of PM_{2.5} ($36.43 \pm 22.56 \mu\text{g}/\text{m}^3$) in Zhuhai are lower than the National Ambient Air Quality Standard (NAAQS) 24 hour average of $65 \mu\text{g}/\text{m}^3$. Study also reveals that the daily PM_{2.5} concentration in Zhuhai city exhibits clear seasonal dynamics, with higher daily PM_{2.5} concentrations in autumn and winter than in spring and summer.

KEYWORDS: PM_{2.5}, Chemical composition, Seasonal characteristic, Zhuhai

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I. INTRODUCTION

Atmospheric particulate matter (PM) has been identified as one of the most serious air pollutants in urban areas (Chang et al., 2013). Numerous studies have demonstrated that airborne fine particulate matter (PM_{2.5}) has adverse effects on the environment, leading to reduced visibility and an increase in albedo, as well as on public health, causing chronic respiratory, cardiopathic, and carcinogenic diseases (Sena et al., 2013). In China, diesel vehicles have contributed significantly to urban PM_{2.5} air pollution. Besides vehicle emissions, coal combustion, biomass burning, and cooking activities are important PM_{2.5} sources. In recent years, frequent severe haze episodes over a vast area of China have drawn public attention. These events disturb local and regional transport systems and interfere with urban activities (Wu et al., 2016).

PM_{2.5} is a complex mixture of primary and secondary particles that consists of water-soluble ions, carbonaceous species (organic and elemental carbon, OC and EC), and other elements (Kulshrestha et al., 2009; Lonati et al., 2005; Xu et al., 2012). Therefore, understanding the chemical composition of PM_{2.5} and assessing its impact on air quality and human health are essential (Liu et al., 2016). Many studies of atmospheric pollution sources have been conducted in coastal regions and islands (Ikeda et al., 2014; Manousakas et al., 2017; Yin et al., 2014) because characterizing coastal or island aerosols can provide information about atmospheric inputs to the adjacent land and ocean ecosystems (Liu et al., 2016). To date, numerous scientific studies have addressed PM_{2.5} levels, chemical composition, and sources in Chinese coastal regions, including studies in Qingdao (Guo et al., 2004), Tianjin (Li et al., 2009), Xiamen (Viana et al., 2007) and Fuzhou (Xu et al., 2012).

Being one of the most developed regions in China, the Pearl River Delta in southern China is highly polluted. With recent increases in economic activity and the number of vehicles in the region, high PM_{2.5} levels and poor visibility have become serious problems. Zhuhai is a city in southern Guangdong Province, China, located on the western Pearl River estuary at the southern edge of the Pearl River delta, and is one of the four initial Chinese Special Economic Zones (SEZs) chosen in 1980 for economic reform experiments. Today, Zhuhai is an exemplary city, suppressing industrialization to preserve high environmental quality for sustainable development, which led to its recognition by the United Nations as a Best Model of International Residential Environment Improvement in 1998, making it the third Chinese city to earn that distinction. Therefore, control of the PM_{2.5} level in Zhuhai is essential to improve visibility and protect human health. At present, insufficient studies of the detailed chemical composition and source apportionment of aerosols have been conducted, and there is a lack of long-term data. In this study, we determined PM_{2.5} pollution levels, as well as its chemical properties. This information will help determine the effectiveness of pollution-control strategies and provide useful data for regulatory agencies to create strategies to control PM_{2.5} in the atmosphere.

II. MATERIALS AND METHODOLOGY

2.1 Study site and sample collection

Zhuhai city, located in the south of the Tropic of Cancer, has a subtropical monsoon climate with a mean annual temperature of 22.4°C, mean annual precipitation of 2011 mm, and potential evaporation of 1469 mm (Fu et al., 2012). Zhuhai is witnessed by four major seasons: spring (March, April, May), summer (June, July, August), autumn (September, October, November), and winter (December, January, February).

2.2 Chemical Analysis of PM_{2.5} Composition

The 24 hour PM_{2.5} samples were collected simultaneously at five sites in 1-day intervals between January 10, 2015, and November 10, 2015, in Zhuhai city (Fig 1). At each site, 10 medium-volume samplers (4 from Tianhong TH-16A, 6 from Zhongrui ZR-3930D, China) were deployed simultaneously to collect the desired samples. Two channels of the samplers were loaded with Teflon filters (Pall, 47 mm, USA) for mass measurement and ion and metal analysis, while another two were loaded with quartz filters to analyze carbon fractions (OC and EC). The samples were placed into plastic Petri dishes right after sampling and stored in a freezer at -18°C. All quartz filters were baked in advance (550°C for 5 h), and pre- and post-weighed with an analytical balance (reading precision 10 µg) after stabilization at a controlled temperature of 25 ± 1°C and humidity of 40 ± 3%. The PM_{2.5} concentration was obtained gravimetrically with an analytical balance (Sartorius 0.01 mg, Germany) as the difference in mass of filters before and after sampling.

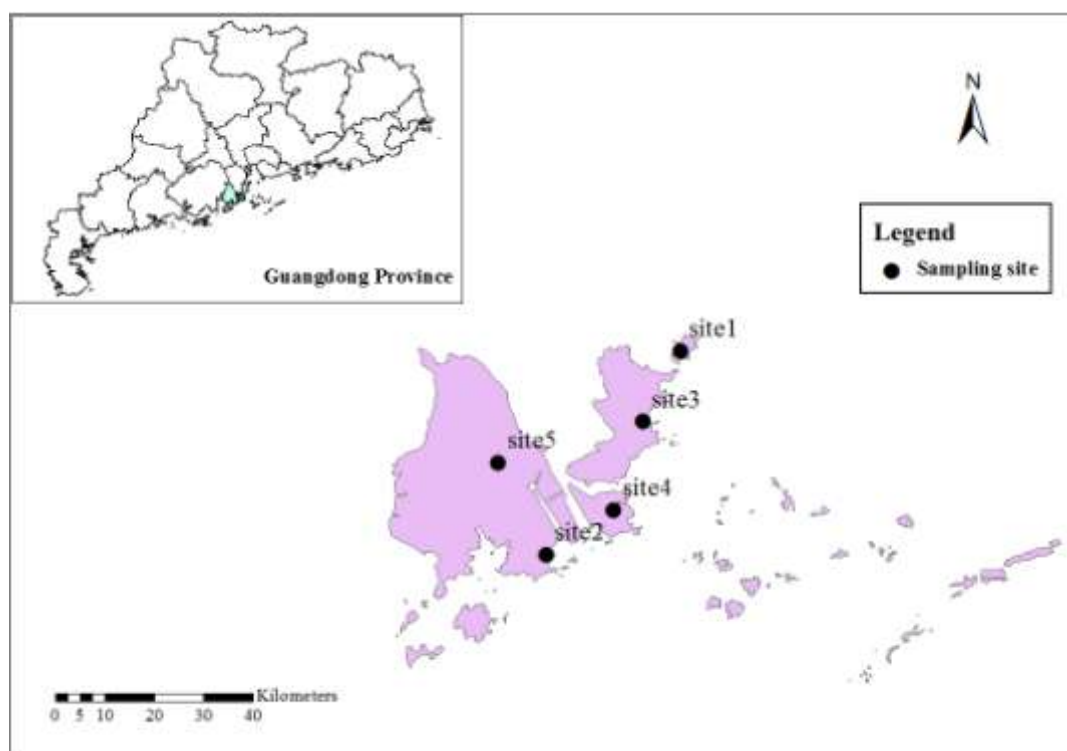


Fig. 1 Locations of five sampling sites in Zhuhai city, China

III. RESULTS: Chemical Components in PM_{2.5}

3.1 Seasonal characteristic of ambient PM_{2.5} concentration

The seasonal and annual average concentrations of PM_{2.5} observed in Zhuhai are summarized in Figure 2. Seasonal average PM_{2.5} mass concentrations ranged from 17.09±7.77 µg/m³ in summer to 62.22±21.35 µg/m³ in winter, with an annual average level of 36.43±22.56 µg/m³. According to Chinese ambient air quality standards (GB 3096-2012), the recommended limits of annual PM_{2.5} concentration for Class 2 and Class 1 ambient air quality zones are 35 µg/m³ and 15 µg/m³, respectively. The daily PM_{2.5} concentration in Zhuhai was 36.43±22.56 µg/m³, about 2.4 times greater than that required by the ambient air quality standards for class one. Furthermore, the daily concentration in Zhuhai exhibited clear seasonal dynamics, with values of 26.93±9.11, 17.09±7.77, 36.99±16.14, and 62.22±21.35 µg/m³ in spring, summer, autumn, and winter, respectively. The daily concentrations in autumn and winter were higher than those in spring and summer, with seasonal averages in winter 2.2 times greater than those in summer. Values in autumn and winter were greater than 35 µg/m³, similar to observations in other cities in China, such as Lanzhou (Hang and Oanh,

2014),Guangzhou(Tao et al., 2014) and Shanghai(Wang et al., 2013). Researcher reported that this typical seasonal pattern was not only related to meteorological conditions, but also was attributed to various contributions from local and regional emission sources between seasons(Li et al., 2009).

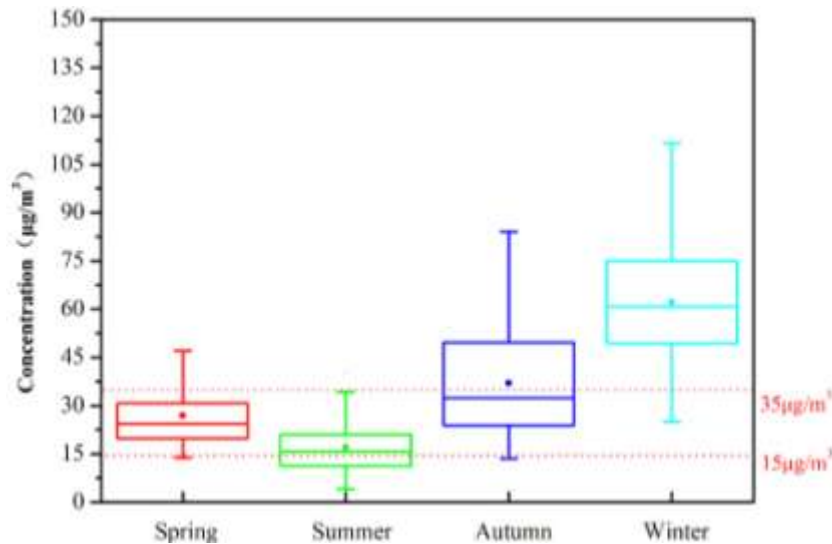


Fig 2. Seasonal variation in PM2.5. The dots represent average PM2.5 concentrations, the upper bars represent maximum values, and the lower bars represent the minimum values of observed PM2.5 concentrations

It was found that PM2.5 concentration is not only often associated with wind speed and wind direction, but also affected by other meteorological parameters, including temperature, relative humidity(Zhou et al., 2015). The meteorological parameters such as temperature, relative humidity (RH), wind speed and wind direction were recorded in site 1. Sampling site was selected in order to evaluate the effects of meteorological conditions on PM2.5 concentrations, and correlations between PM2.5 concentrations and ambient temperature (T), relative humidity (RH), atmospheric pressure, wind direction and wind speed were also determined. The results of correlation analyses are listed in Table 1.

Table1 Correlation analysis among hourly PM2.5 concentration and major meteorological factors (n=8760)

	PM2.5(µg/m³)	WS (m/s)	WD (°)	T (°C)	RH (%)	AP (hPa)
PM2.5(µg/m³)	1					
WS (m/s)	-.331**	1				
WD (°)	.013	.460**	1			
T (°C)	.029	-.304**	-.423**	1		
RH (%)	-.094**	-.079**	.104**	.317**	1	
AP (hPa)	.187**	.113**	.120**	-.587**	-.550**	1

** Correlation is significant at the 0.001 level (two-tailed);WS: wind speed; WD: wind direction; T: ambienttemperature; RH: relative humidity; AP: atmospheric pressure; n=number of samples.

As shown in Table 1, it was revealed that the PM2.5 concentration was positively correlated with ambient pressure (p < 0.05), and negatively correlated with the wind speed and relative humidity during the sampling periods (p < 0.05). Therefore, PM2.5 concentration is closely related to the wind speed, relative humidity and atmospheric pressure.

In order to further study the influences of wind speed and wind direction on local ambient PM2.5 concentrations, PM2.5 concentrations against wind speed and wind direction was plotted(Fig 3). Very stable with abnormally high frequency of calm wind is one of the key reasons for heavy air pollutions, while higher wind speed (>4.4m/s) could move out of the air mass and lead to low PM2.5 levels(He et al., 2017). The dominant wind directions in Site 1 during the sampling period were south (22%), south-south-west (11.9%),

south-south-east (11.9%) and east-south-east (11.9%), and the wind directions with wind speed (1-2 m/s) (71.2%), 1-2 m/s(13.6%), 0-1 m/s(11.9%), respectively. And when the wind directions were south, south-south-west, south-south-east, ratio of PM_{2.5} concentrations of more than ($>20\mu\text{g}/\text{m}^3$) were 15.3%, 10.2% and 10.2%, respectively. So, it can conclude that wind speed and wind direction had a great influence on the spread of ambient of PM_{2.5} in Zhuhai city.

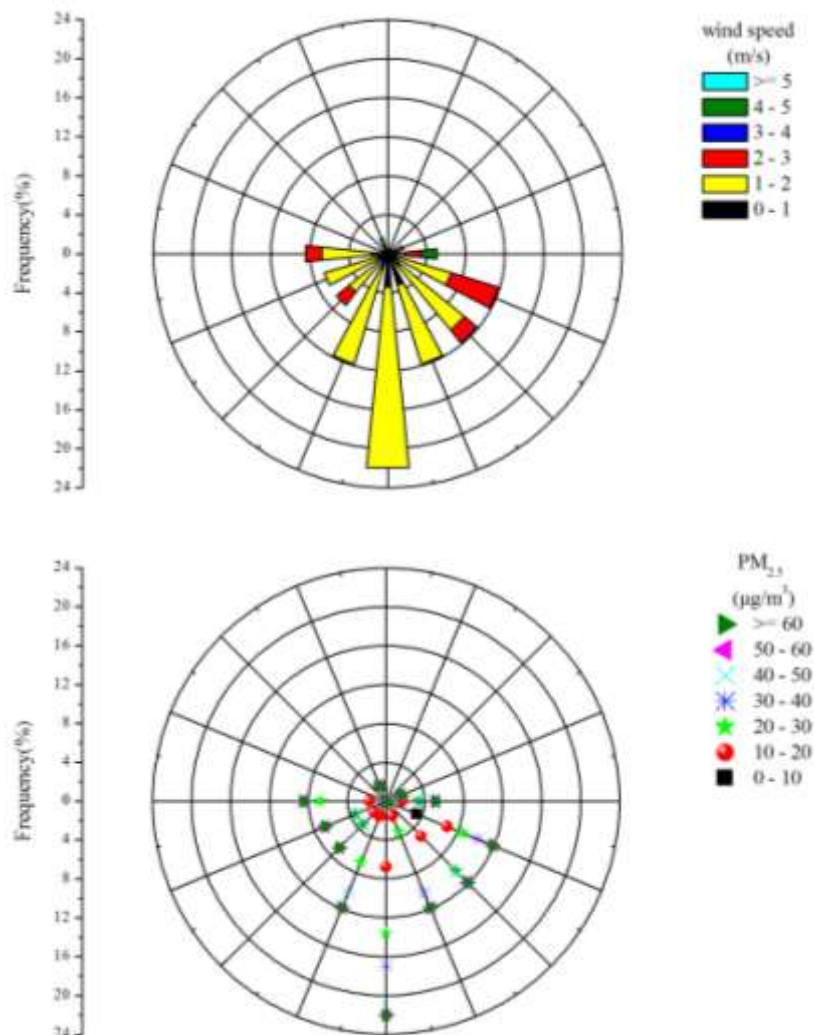


Fig 3. Polar plotting of PM_{2.5} against wind speed and wind direction

3.2 OC and EC

Concentrations of both OC and EC (Fig. 4) exhibited obvious seasonal variation, with average concentrations that were generally highest in winter and lowest in summer, similar to previous observations (Lv et al., 2016). The average concentrations of OC and EC in summer were $3.42\pm 1.66\ \mu\text{g}/\text{m}^3$ and $0.89\pm 0.60\ \mu\text{g}/\text{m}^3$, respectively, and their levels were roughly 3.4 and 4.0 times higher in winter than in summer. Although OC and EC exhibited the same seasonal pattern, with the highest concentrations in winter and lowest in summer, OC exhibited greater seasonal variability than EC.

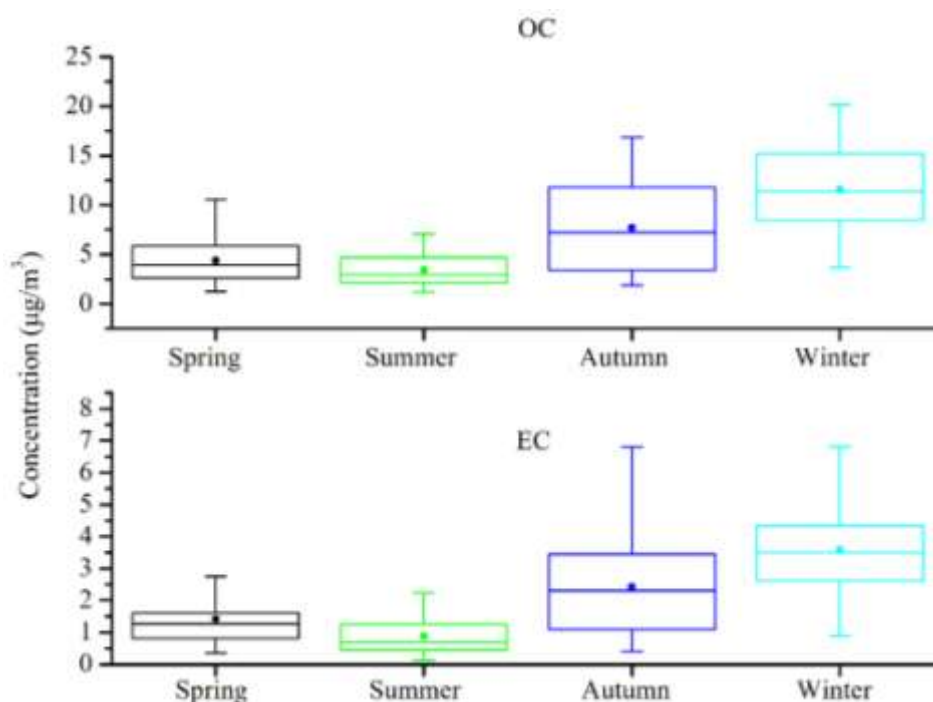


Fig 4. Seasonal variation in OC and EC concentrations

Carbonaceous aerosols, comprising primary species and secondary organic compounds, are composed of EC and OC, and are emitted from sources such as coal combustion, vehicles, and biomass burning (He et al., 2009), OC can also come from secondary reactions (Lv et al., 2016).

OC and EC concentrations in winter are higher than those in summer, but the OC/EC ratio is higher in summer than in winter, with means of 4.53 ± 1.56 and 3.29 ± 0.50 , respectively (Table 2). The OC/EC ratio has been used to distinguish among sources of carbonaceous aerosols (Viana et al., 2007). The average daily OC/EC ratio in Zhuhai in all seasons was 3.56, while a ratio greater than 2 indicates that the main carbon component is secondary organic carbon (SOC). Previous studies have found that the average OC/EC ratios in Xi'an are 3.0 for coal combustion and 1.6 for vehicle exhaust (Cao et al., 2005; Gray et al., 1986). The ratios in Colorado are 2.7 for coal combustion and 1.1 for motor vehicle exhaust (Watson et al., 2001). Thus, the ratios in Zhuhai indicate direct emissions from combustion sources.

Table 2 Average ratios and correlation between OC and EC

	Spring (n=69)	Summer (n=75)	Autumn (n=80)	Winter (n=80)
OC/EC	3.16 ± 0.78	4.53 ± 1.56	3.26 ± 0.58	3.29 ± 0.50
R ²	0.77**	0.86**	0.88**	0.83**

** Correlation is significant at the 0.001 level

The occurrence of the lowest OC/EC ratio in summer might also be attributable to lower emissions from coal combustion and more rainy days, which may effectively remove OC from the atmosphere but not EC, due to the lower washout efficiency of EC (Wang et al., 2015). OC/EC ratios can also be influenced by photochemical reactivity. The average ratio in summer was higher than in other seasons, perhaps because the greater rate of photosynthesis and higher humidity promote the formation of secondary aerosols in summer or because more precipitation falls in summer than in winter (Fig. 5). Thus, we concluded that higher OC/EC ratios in summer in Zhuhai might be the result of increased photosynthesis and higher humidity during this season.

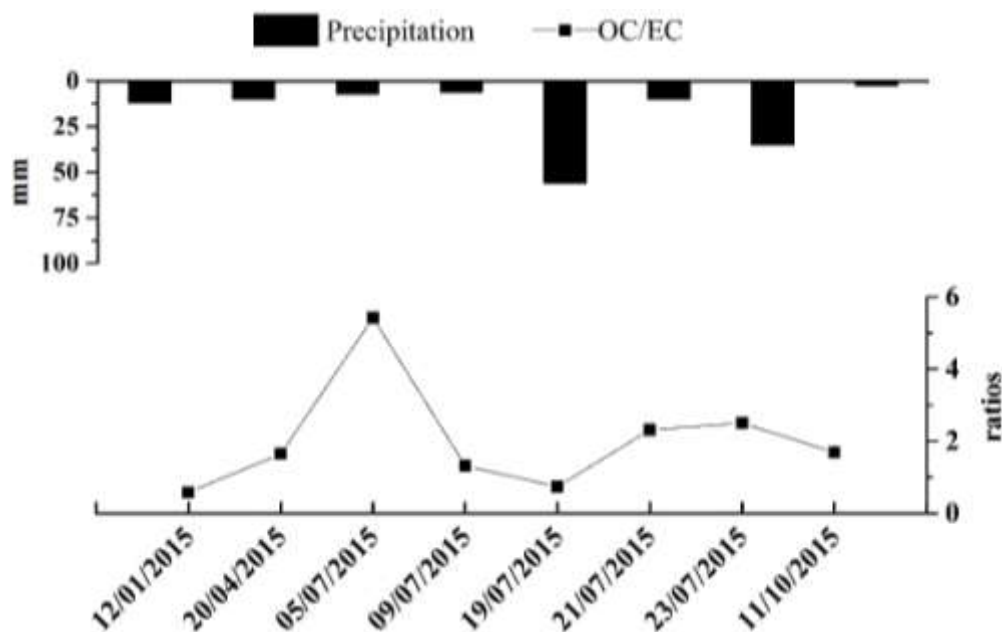


Fig 5. Selected ratios of OC/EC and daily precipitations during the observation period in sampling site 1

The correlation between OC and EC can reflect the source of inhalable particulate pollution to some extent, and the stability and consistency of OC and EC can be determined using correlation analysis. As shown in Table 2, OC and EC were significantly correlated (average $R^2=0.84$ and $P<0.001$) in all seasons. Strong correlations between OC and EC indicated a common source of these components (Wang et al., 2015), and coal combustion and vehicle exhaust were considered to be the dominant sources of carbonaceous aerosols in Zhuhai.

IV. CONCLUSION

Ambient PM_{2.5} and its major components were measured in all four seasons of 2015 in Zhuhai, and ambient PM_{2.5} pollution in Zhuhai was low during the study period. The seasonal averages of PM_{2.5} in winter were 2.2 times higher than those in summer. Meteorological conditions, local and regional contribution were closely correlated to the PM_{2.5} concentrations. NH_4^+ , SO_4^{2-} , NO_3^- and Na^+ were the major water-soluble ions in aerosols, and the highest and lowest concentrations of the dominant chemical components were also observed in winter and summer, respectively. Additional work is needed to discover the chemical species and source identification of PM_{2.5} in Zhuhai.

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