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Characteristics of Secondary $PM_{2.5}$ Under Different Photochemical Reactivity Backgrounds in the Pearl River Delta Region

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With the increasing control of air pollution, the levels of atmospheric particulates in the Pearl River Delta (PRD) region are gradually decreasing. However, ozone pollution has become more and more serious, and the problem of secondary aerosol pollution caused by photochemical reactions cannot be ignored. Based on the observation data of environmental and meteorological stations in the nine cities of the PRD during 2019, we investigated the variations of secondary $PM_{2.5}$ ($PM_{2.5\text{-sec}}$) in the PRD under different photochemical reactivity backgrounds. It was shown that the photochemical reactivities appeared more significant in the central and western areas than those in the eastern areas of the PRD and appeared more significant in inland areas than those in coastal areas. The days of moderate and high photochemical reactivities mainly appeared from August to November. $PM_{2.5\text{-sec}}$ concentrations were the highest in autumn, during which the regional discrepancies appeared most significantly with the highest levels in the southern areas. With the enhancement of the photochemical reactivity background, the $PM_{2.5\text{-sec}}$ level at each station increased significantly, which appeared significantly higher in coastal areas than in inland areas. Both $PM_{2.5\text{-sec}}$ and ozone concentrations showed single-peak variations, which appeared higher in the daytime than at night with the peak occurring at about 15:00. For each pollutant, the average maximum concentration appeared higher for polluted stations than for clean ones, indicating that the atmospheric oxidation background was conducive to the formation of $PM_{2.5\text{-sec}}$.

Keywords: secondary $PM_{2.5}$, ozone, photochemical reactivity, oxidation background, coordinated increase

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INTRODUCTION

With the strengthening of environmental governance, air pollution in some cities of China has been gradually transforming from single to complex pollution as a result of the increase in ozone and aerosol levels (Zhang et al., 2019; Wang et al., 2021a; Wang et al., 2021b; Wang et al., 2021c). Ozone and aerosols significantly influence human health, crop yield, and global climate change (Mills et al., 2009; Stoker et al., 2013; Zhang et al., 2017; Fleming et al., 2018), meaning that their coordinated control is very urgent. Therefore, many scholars have carried out relevant studies and found that their coordinated variations are fulfilled through the influence of aerosols on the levels of atmospheric radiation and hydroxyl radicals and

the influence of ozone on atmospheric photochemical reactivities (Yuan et al., 2012; Liu et al., 2021; Wang et al., 2021a; Wang et al., 2021b; Wang et al., 2021c). It is worth noting that the strengthening of atmospheric photochemical reactivities and the following significant growth of secondary aerosols resulting from ozone enhancement have become the common causes of complex pollution in China. However, because of the influence of weather background, emission source structure, and geographical factors, the characteristics of complex pollution are different (Liu et al., 2019; Zhao et al., 2021). Some scholars found that with the increase of $PM_{2.5}$ levels, the maximum values and change rates of ozone concentrations with different backgrounds in Guangzhou increase gradually, indicating the coordinated increase between $PM_{2.5}$ and ozone (Yao et al., 2021). Some scholars found that in Handan, the fourth largest city of Hebei Province, ozone increased with the enhancement of $PM_{2.5}$ during summer in the case of its concentration being below the standard values, whereas high-level $PM_{2.5}$ had an inhibitory effect on ozone formation in winter (Zhao et al., 2021).

The common precursors of aerosols and ozone (i.e., VOC_S and NO_x) can be transformed into secondary aerosols and inorganic salts through gas–particulate matter interactions (Xing et al., 2017), contributing to the formation of $PM_{2.5}$. Li (Li et al., 2020) evaluated the coordinated increase of ozone and secondary aerosols in Beijing, Shanghai, and Guangzhou and found that the formation of secondary aerosols in Shanghai and Guangzhou increased by multiples with the enhancement of photochemical reactivities, whereas that in Beijing was scarcely varied. Previous studies were mainly based on a single city or station and rarely focused on regional ozone and secondary aerosol variations (Wu et al., 2021).

The Pearl River Delta (PRD) region is located south of the Tropic of Cancer, bordering the South China Sea, with good thermal conditions. The regional economy is developed, the manufacturing industry is prosperous, and the population is dense. The precursors produced by a large number of industrial sources and man-made sources are conducive to the generation of ozone photochemical reactions. In recent years, the ozone levels in the PRD have gradually increased (Zhan, 2018; Yin and Wang, 2020), with complex pollution of ozone and secondary aerosols occurring frequently (Lai et al., 2018). In this article, we analyze the various characteristics of $PM_{2.5\text{-sec}}$ concentration in the PRD under different photochemical reactivity backgrounds, based on the observed data from environmental and meteorological stations in nine cities of the PRD in 2019; the correlation between ozone pollution and secondary $PM_{2.5}$ were revealed; and the possible mechanisms of formation of $PM_{2.5\text{-sec}}$ under different ozone levels were analyzed, which provide scientific support for the coordinated control of PM2.5 and ozone in the PRD.

DATA AND METHODS

Data Sources

This article selects the PRD as the research area including nine cities of Guangdong Province, i.e., Zhaoqing, Guangzhou, Foshan, Zhuhai, Jiangmen, Zhongshan, Huizhou, Shenzhen, and Dongguan. The data come from the national control station of the Department of Ecology and Environment of Guangdong Province (Station No. 1345A-1400A, **Figure 1**). Season classification criteria are as follows: spring (March, April, and May), summer (June, July, and August), autumn (September, October, and November), and winter (December, January, and February). The validities of atmospheric pollutant concentration data meet the requirements of the Environmental Air Quality Standard (GB3095-2012) and the Technical Specification for Environmental Air Quality Assessment (TRIAL) (HJ633-2013). The meteorological data come from the national basic meteorological observation stations of the respective cities, and the accuracy of all meteorological data was over 98% after quality control. Data on the 10 m mean wind and accumulated rainfall in the PRD in 2019 were obtained from the EC ERA5 monthly reanalysis data.

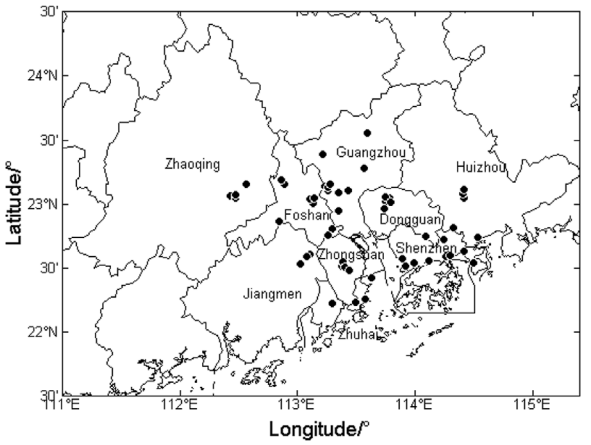

FIGURE 1 | Distribution of national control stations in the Pearl River Delta.

Research Methods

Li et al. (2020) used the following research methods to analyze the coordinated increase of ozone and secondary aerosols in typical Chinese cities: First, the daily maximum 1 h average concentration of ozone (O_3-max) was used to classify the atmospheric photochemical reactivity level. O_3-max < 100 μg/m^3 was defined as a low level of photochemical reactivity (O_{3L}), and 100 μg/m^3 ≤ O_3-max < 160 μg/m^3 was defined as a light level of photochemical reactivity (O_{3LH}). 160 μg/m^3 ≤ O_3-max < 200 μg/m^3 was defined as a moderate level of photochemical reactivity (O_{3M}), and O_3-max ≥ 200 μg/m^3 was defined as a high level of photochemical reactivity (O_{3H}). Then, CO was used as a tracer of the primary emission source, assuming that the structure of the emission source is basically stable; the larger the ratio of $PM_{2.5}$/CO mass concentration is, the larger the proportion of secondary components in $PM_{2.5}$ is (Chang and Lee, 2007; Zhang et al., 2015). Specific equations are as follows:

$$(PM_{2.5})_{p,LH,t} = CO_{LH,t} \times (PM_{2.5}/CO)_{p,L}, \quad (1)$$

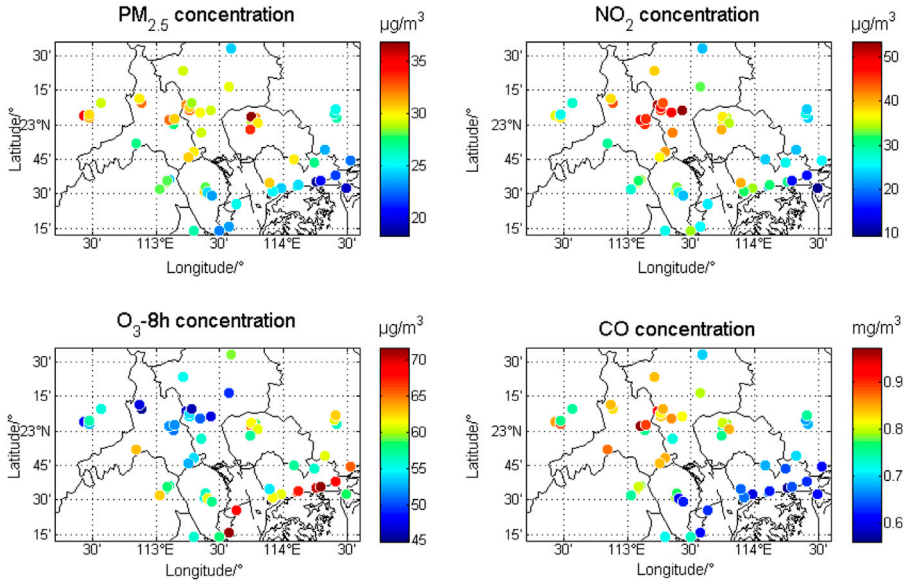

FIGURE 2 | Mean concentrations of $PM_{2.5}$, NO_2, O_{3-8h}, and CO at various stations.

$$(PM_{2.5})_{p,M,t} = CO_{M,t} \times (PM_{2.5}/CO)_{p,L}, \quad (2)$$

$$(PM_{2.5})_{p,H,t} = CO_{H,t} \times (PM_{2.5}/CO)_{p,L}, \quad (3)$$

$$(PM_{2.5})_{sec,LH,t} = (PM_{2.5})_{obs,LH,t} - (PM_{2.5})_{p,LH,t}, \quad (4)$$

$$(PM_{2.5})_{sec,M,t} = (PM_{2.5})_{obs,M,t} - (PM_{2.5})_{p,M,t}, \quad (5)$$

$$(PM_{2.5})_{sec,H,t} = (PM_{2.5})_{obs,H,t} - (PM_{2.5})_{p,H,t}, \quad (6)$$

where p is the primary pollutant, sec is a secondary pollutant, and obs is observed $PM_{2.5}$ concentration. t is the specific time of the day. L, LH, M, and H represent O_{3L}, O_{3LH}, O_{3M}, and O_{3H}, respectively. $CO_{LH,t} \times (PM_{2.5}/CO)_{p,L}$ is 25% of the hourly $PM_{2.5}$/CO in O_{3H}. It is the reference value of the primary aerosol for the calculation of different levels of photochemical reactivities. Finally, since ozone concentrations in eastern China generally peak between 14:00 and 16:00, the phenomenon of $PM_{2.5}$ and ozone concentration increasing simultaneously and continuously for no less than 2 h from 11:00 to 19:00 is defined as the coordinated increase of $PM_{2.5}$ and ozone. In this article, the aforementioned methods are used to estimate the hourly concentration of $PM_{2.5\text{-}sec}$ under different photochemical reactivities and to calculate the time for the coordinated increase of $PM_{2.5\text{-}sec}$ and ozone. More details can be found in Li et al. (2020).

DISTRIBUTION CHARACTERISTICS OF AIR POLLUTANT CONCENTRATION IN THE PEARL RIVER DELTA

Annual Average Variations

Figure 2 shows the mean concentrations of $PM_{2.5}$, NO_2, O_{3-8h}, and CO at various stations in the PRD in 2019. The air pollutants have obvious spatial variation characteristics. Concentrations of $PM_{2.5}$, NO_2, and CO are higher in the central and northern parts of the PRD (e.g., Guangzhou, Foshan, and Dongguan), whereas they are lower in coastal areas. The maximum annual mean concentrations of $PM_{2.5}$, NO_2, and CO appear in Dongguan (37 μg/m^3), Guangzhou (54 μg/m^3), and Foshan (980 μg/m^3), respectively. The average ozone concentrations in coastal areas (e.g., Zhuhai, Shenzhen, and Huizhou) are higher than those in other areas, and the maximum appears in Shenzhen with a value of 72 μg/m^3.

Seasonal Variations

Table 1 shows the seasonal variations of air pollutants in the PRD in 2019. The average concentrations of $PM_{2.5}$, CO, and NO_2 in the PRD appear the highest in winter and the lowest in summer, whereas the concentrations of O_{3-8h} appear the highest in autumn and the lowest in winter. The concentrations of $PM_{2.5}$, NO_2, and CO in the northern part of the PRD are higher than those in the southern part, whereas the distributions of O_{3-8h} appear vice versa. **Figure 3** shows the variations of $PM_{2.5}$ and ozone with temperature and humidity during autumn and winter in the PRD. The high-level $PM_{2.5}$ in autumn mainly occurs in the environment with humidity over 80%, but there is no similar distribution in winter. High ozone concentrations in autumn and winter appear under high-temperature and low-humidity conditions. According to the 10 m average wind field and cumulative rainfall distribution in the PRD (**Figure 4**), the prevailing wind directions in spring and summer are southeast and southwest, which bring clean marine air mass. Meanwhile, abundant precipitation is also conducive to pollutant removal. In autumn and winter, the prevailing wind changes to the northeastern direction, leading to inland polluted air masses influencing the air quality of the PRD, and the precipitation decreasing significantly compared with that in

TABLE 1 | Seasonal variations of air pollutants in the PRD.

City	Pollutant[a]	Spring	Summer	Autumn	Winter	Average	City	Pollutant	Spring	Summer	Autumn	Winter	Average
Dongguan	$PM_{2.5}$	26.6	18.7	40.7	42.8	32.2	Foshan	$PM_{2.5}$	25.6	17.6	37.8	39.1	30
	NO_2	35.9	28.4	39.5	43.3	36.8		NO_2	41.9	28.5	44.3	49.9	41.2
	$O_{3-8\ h}$	49.4	60.6	89.1	44.9	61.0		$O_{3-8\ h}$	38.2	53.1	82.8	34.7	52.2
	CO	0.767	0.689	0.781	0.92	0.789		CO	0.837	0.733	0.813	1.043	0.857
Guangzhou	$PM_{2.5}$	24	18.1	37	38.8	29.5	Huizhou	$PM_{2.5}$	20.5	14.4	31.3	33.8	25
	NO_2	44	32	45	50.1	42.8		NO_2	22.7	19.9	26.5	29.1	24.6
	$O_{3-8\ h}$	39.4	51.9	79	37.4	51.9		$O_{3-8\ h}$	60.9	50.9	84	50.6	61.6
	CO	0.794	0.664	0.795	1.013	0.817		CO	0.636	0.563	0.672	0.855	0.682
Jiangmen	$PM_{2.5}$	22.8	15.4	34.6	36	27.2	Shenzhen	$PM_{2.5}$	19.7	13.2	31.7	32.3	24.2
	NO_2	28.6	17.4	36.7	46.5	32.3		NO_2	22.9	20.1	26.5	32.4	25.5
	$O_{3-8\ h}$	43.6	53.6	98.2	41.4	59.2		$O_{3-8\ h}$	60.5	49.7	90.7	51.6	63.1
	CO	0.744	0.6	0.781	1.033	0.79		CO	0.599	0.545	0.625	0.743	0.628
Zhuhai	$PM_{2.5}$	19.2	11.9	31.6	35.4	24.5	Zhaoqing	$PM_{2.5}$	29.8	19	35.6	41.3	31.4
	NO_2	27.6	15.4	25.1	42	27.5		NO_2	32.5	21.2	34.2	39	31.7
	$O_{3-8\ h}$	55.5	52	96	51.3	63.7		$O_{3-8\ h}$	38.6	53.1	83	40	53.7
	CO	0.67	0.541	0.617	0.86	0.672		CO	0.829	0.66	0.8	0.963	0.813
Zhongshan	$PM_{2.5}$	20.5	12.9	34.3	38.6	26.6	Average	$PM_{2.5}$	23.2	15.7	35	37.6	27.9
	NO_2	23.8	14.1	34.4	46.4	29.7		NO_2	31.1	21.9	34.7	42.1	32.4
	$O_{3-8\ h}$	46.5	55.4	91.9	38.1	58		$O_{3-8\ h}$	48.1	53.4	88.3	43.3	58.3
	CO	0.656	0.558	0.681	0.895	0.698		CO	0.726	0.617	0.729	0.925	0.749

[a]*Concentration of air pollutants: ① $PM_{2.5}$, μg/m^3, ② NO_2, μg/m^3, ③ ozone-8h, μg/m^3, and ④ CO, mg/m^3.*

spring and summer, thus forming high levels of $PM_{2.5}$, NO_2, and CO in autumn and winter. In addition, concentrated human activities in the central PRD (e.g., Guangzhou, Foshan, and Dongguan) cause the local levels of primary air pollutants to be higher than those in the coastal areas. For the secondary pollutants (e.g., ozone), the northeast wind in autumn brings polluted air masses from the upwind direction in the PRD (Dongguan, Foshan, and Guangzhou), and the air masses mix with the local pollution, forming ozone enhancement in the southern and coastal areas. In summer, under the conditions of high temperature and strong radiation, a large number of local photochemical reactions cause ozone concentrations to be slightly higher than those in spring and winter.

PHOTOCHEMICAL REACTIVITY BACKGROUND AND COORDINATED INCREASE CHARACTERISTICS IN THE PEARL RIVER DELTA REGION

Regional Distribution Characteristics of Photochemical Reactivities

A previous study showed that air pollutants in the PRD have significant temporal and spatial variation characteristics. To explore the differences of photochemical reactivities in various cities, the day distributions of different photochemical reactivities at each station are presented in **Figure 5**. In 2019, the PRD mainly experienced O_{3L} and O_{3LH} for an average of 151 and 115 days, respectively, totally accounting for 74.9% of the year, whereas it experienced 46 days of O_{3M} and 43 days of O_{3H}. Most stations in Shenzhen, Zhuhai, Huizhou, and Zhaoqing experience more days of low- and light-photochemical reactivities than the median in the PRD (264 days). **Figure 6** shows the cumulative time of the coordinated increase between $PM_{2.5}$ and ozone and the mean values of $PM_{2.5}$/CO in the PRD. The cumulative time of the coordinated increase is 511–1,048 h, in accordance with the results of Li et al. (2020) in Guangzhou from April to October 2017 (580 h). The high values of cumulative time are mainly concentrated in Jiangmen, Zhongshan, and Dongguan. The ratio of $PM_{2.5}$/CO is between 0.030 and 0.045, which is lower than that in Beijing and Shanghai in 2017 and comparable to that of Guangzhou in 2017 (Li et al., 2020). The high values are concentrated in Dongguan and Shenzhen.

Seasonal Variation of the Coordinated Increase of $PM_{2.5}$ and Ozone

Figure 7 shows the monthly averaged days of different photochemical reactivities and average hours of the coordinated increase in 2019. O_{3M} and O_{3H} mainly concentrate from August to November, among which the maximum O_{3M} days appear in November (10.1 days), whereas the maximum O_{3H} days appear in September (11.7 days). What is more, the trend of coordinated increase time is basically opposite to that of O_{3L} days. Therefore, a coordinated increase of $PM_{2.5}$ and ozone mainly occurs under more significant oxidation backgrounds.

In general, photochemical reactivities in the PRD have obvious spatial and temporal variation differences. In terms of spatial variations, photochemical reactivities appear high in central and western regions but low in eastern regions and high in inland regions but low in coastal regions. In terms of seasonal variations, moderate and high levels of photochemical reactivities mainly

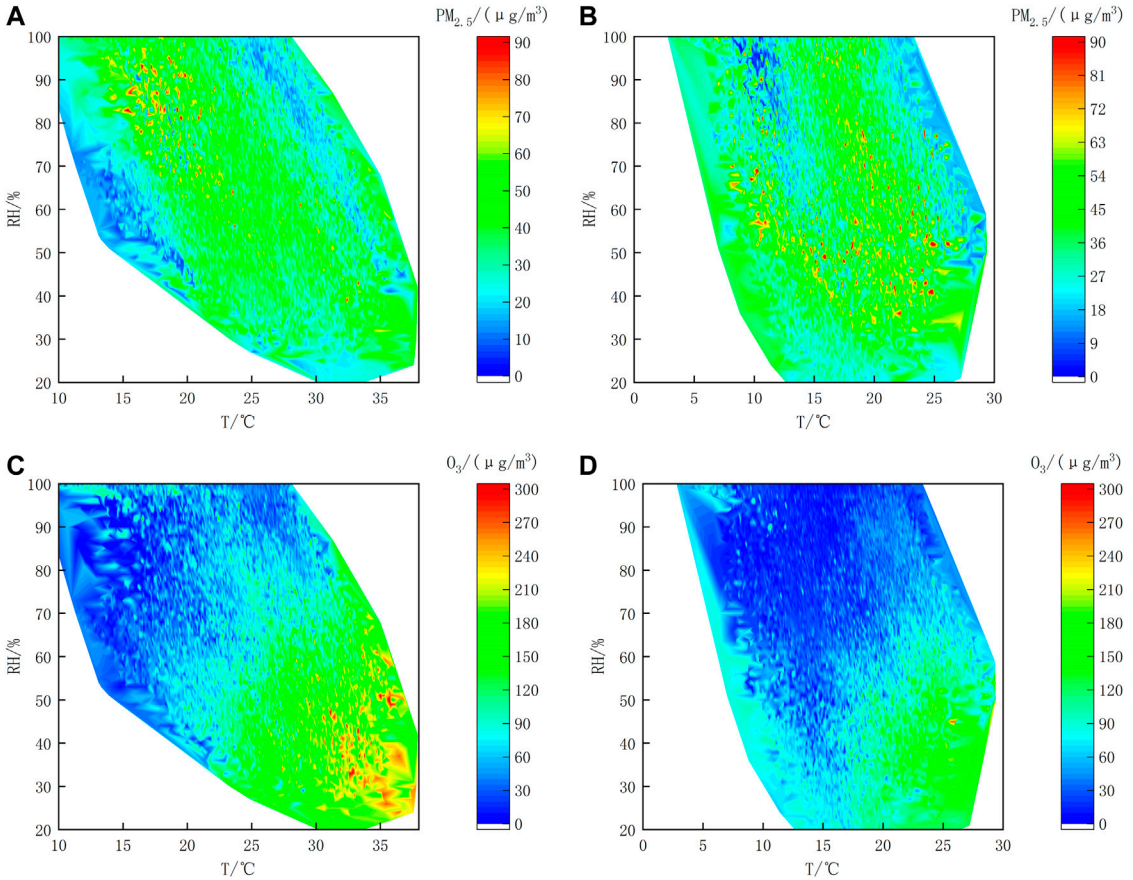

FIGURE 3 | Variations of $PM_{2.5}$ and ozone with temperature and humidity in autumn and winter. **(A)**. $PM_{2.5}$ in autumn, **(B)**. $PM_{2.5}$ in winter, **(C)**. ozone in autumn, and **(D)**. ozone in winter.

appear in autumn. In general, higher levels of photochemical reactivities are more conducive to the coordinated increase of $PM_{2.5}$ and ozone, and the proportions of secondary aerosols in $PM_{2.5}$ are also higher. However, some coastal stations in Shenzhen and Zhuhai have a long-term coordinated increase or a high $PM_{2.5}$/CO value, which requires further research.

DISTRIBUTION CHARACTERISTICS OF $PM_{2.5\text{-SEC}}$ UNDER DIFFERENT PHOTOCHEMICAL REACTIVITY BACKGROUNDS

Temporal and Spatial Variation Characteristics of $PM_{2.5\text{-sec}}$

Figure 8 shows the seasonal variation of the average $PM_{2.5\text{-sec}}$ concentration at each station. The concentration in autumn is significantly higher than that in other seasons, and the concentration varies from 6 μg/m^3 to 13 μg/m^3, with the maximum appearing at Jida station in Zhuhai. $PM_{2.5\text{-sec}}$ concentrations are the highest in autumn, during which the regional discrepancies appear the most significantly with the highest levels in the southern areas. High concentrations of $PM_{2.5\text{-sec}}$ and ozone occur in the southern areas in autumn, indicating that the atmospheric oxidation background promotes the formation of $PM_{2.5\text{-sec}}$.

Variation Characteristics of $PM_{2.5\text{-sec}}$ Under Different Photochemical Backgrounds

In addition to seasonal differences, there are also differences in $PM_{2.5\text{-sec}}$ concentrations and the proportions of $PM_{2.5\text{-sec}}$ in $PM_{2.5}$ under different photochemical reactivity backgrounds. **Figure 9** shows the regional variations of $PM_{2.5\text{-sec}}$ under different photochemical reactivities. With the enhancement of photochemical reactivities, $PM_{2.5\text{-sec}}$ levels increase significantly. Under the background of O_{3H}, the annual average $PM_{2.5\text{-sec}}$ concentrations at the coastal stations are generally above 13 μg/m^3 with a maximum of 20 μg/m^3 at some stations, whereas under the background of O_{3M}, the concentrations at the coastal stations are basically around 10 μg/m^3. Moreover, under the same photochemical reactivity background, $PM_{2.5\text{-sec}}$ concentrations in coastal areas are significantly higher than those in inland areas. **Figure 10** shows that the proportions of $PM_{2.5\text{-sec}}$

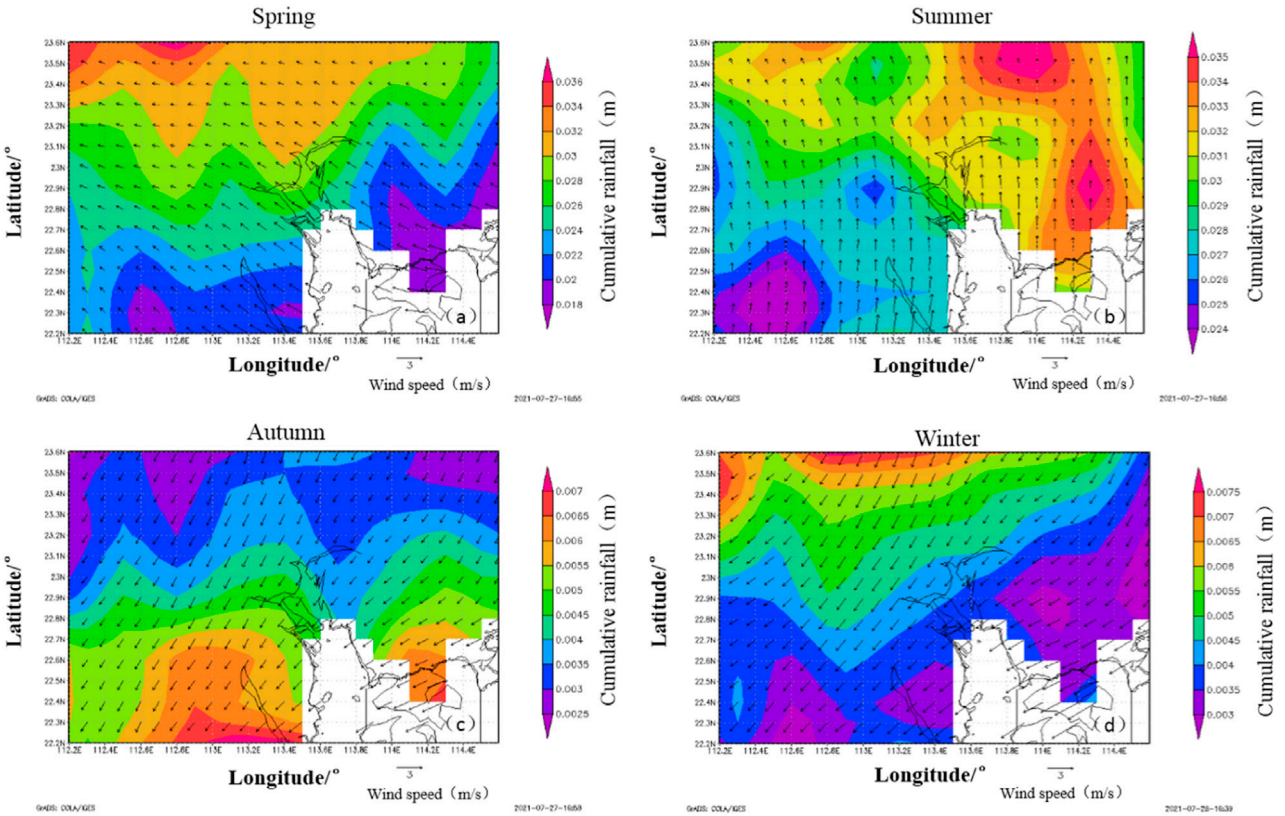

FIGURE 4 | 10 m wind field and accumulated rainfall in the PRD.

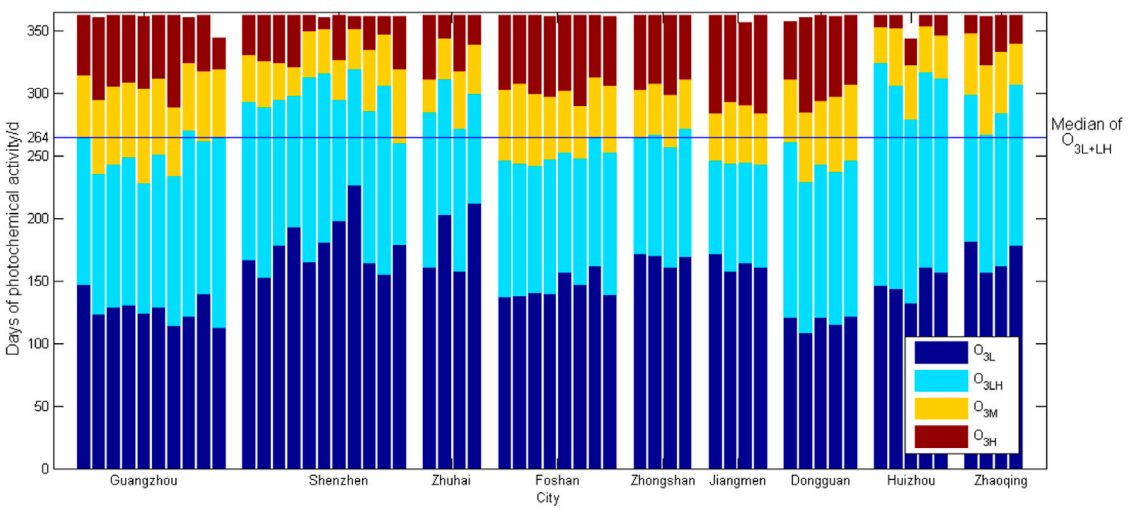

FIGURE 5 | Daily distribution of photochemical activities in the PRD.

in $PM_{2.5}$ have similar characteristics under different photochemical reactivity backgrounds. The ratios are about 10% in O_{3L}, 20%–30% in O_{3M}, and 20–50% in O_{3H}. Meanwhile, under the same photochemical background, the ratios of $PM_{2.5\text{-}sec}/PM_{2.5}$ in coastal areas are significantly higher than those in inland areas.

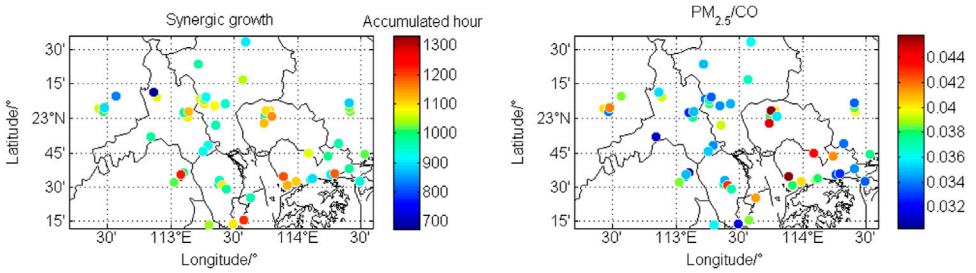

FIGURE 6 | Coordinated increase time and $PM_{2.5}$/CO distribution in the PRD.

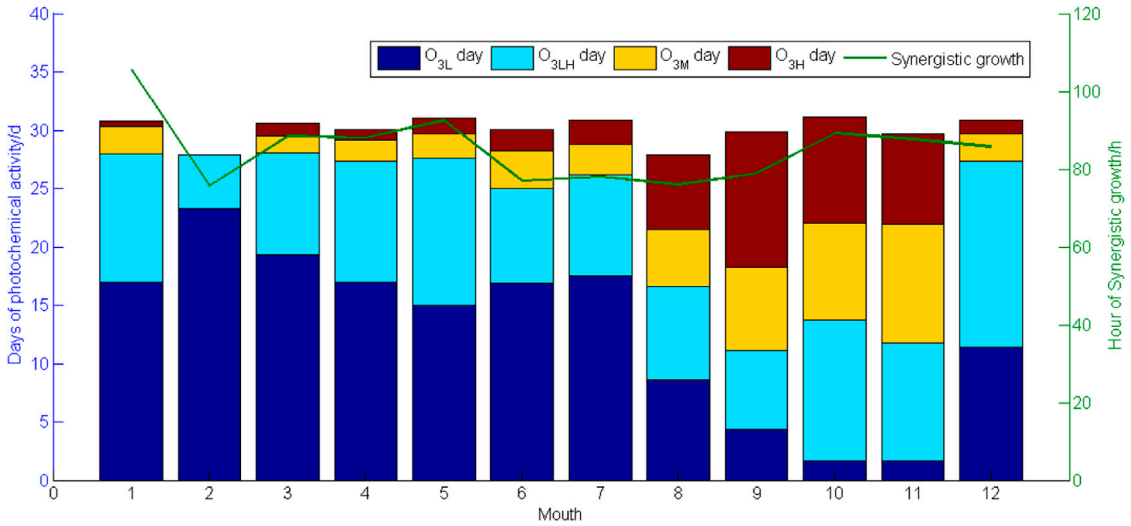

FIGURE 7 | Monthly averaged days of different photochemical reactivities and the average hours of coordinated increase.

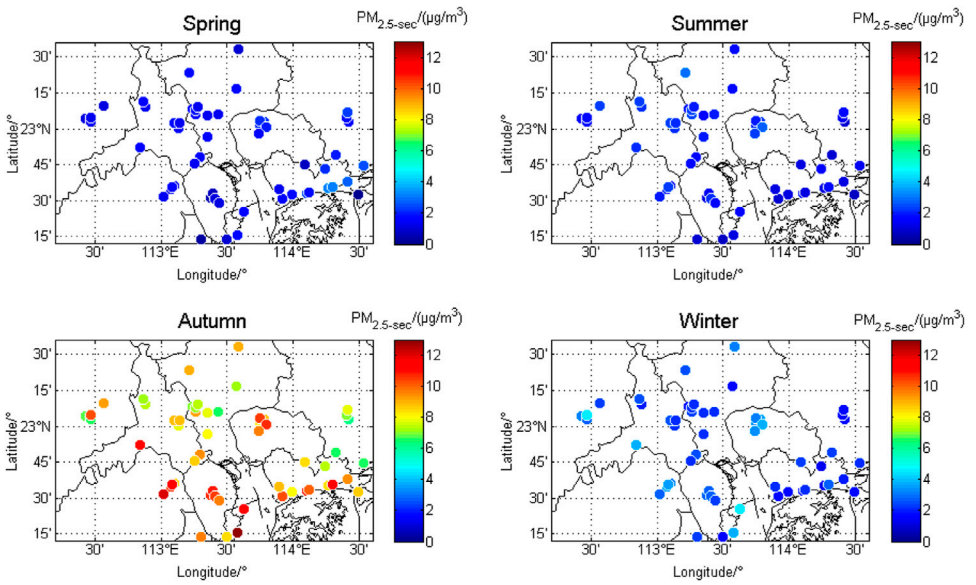

FIGURE 8 | Seasonal variations of $PM_{2.5\text{-sec}}$ in the PRD.

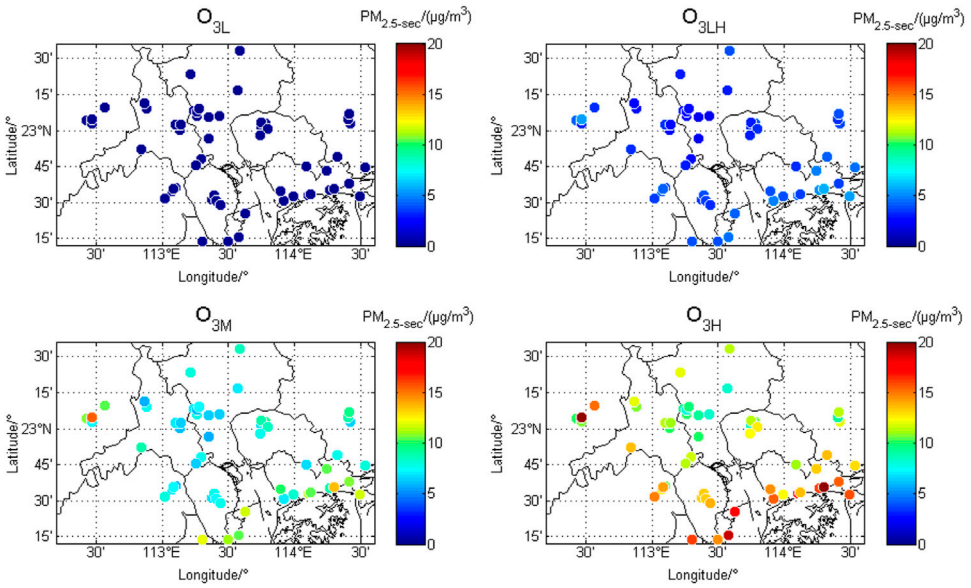

FIGURE 9 | $PM_{2.5\text{-}sec}$ variations under different photochemical backgrounds.

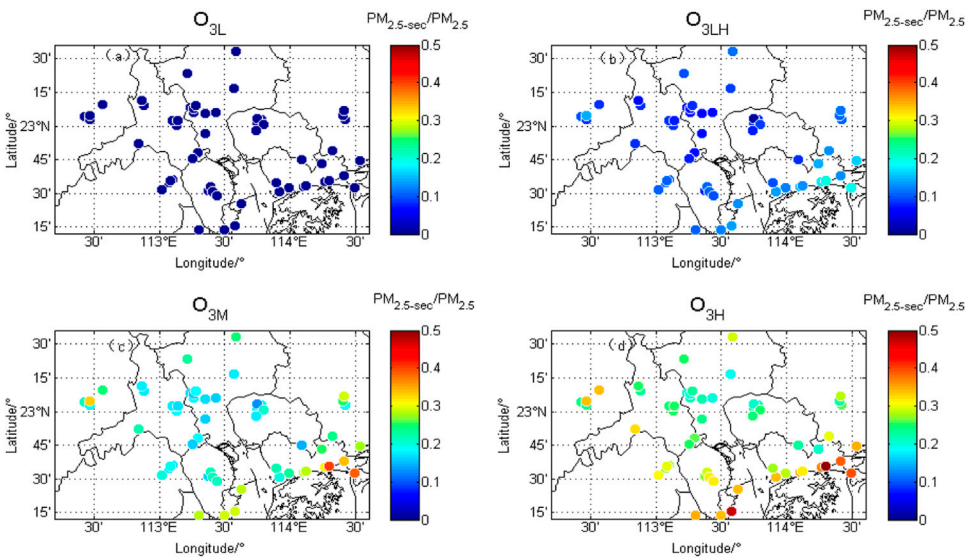

FIGURE 10 | Variations of the ratios in $PM_{2.5\text{-}sec}/PM_{2.5}$ under different photochemical backgrounds.

Diurnal Variation Characteristics

Because the stations in the PRD are widespread with significant background discrepancies, we refer to the standard of ozone pollution in the Ambient Air Quality Standard (GB3095-2012) and take MDA8-O_3 (daily maximum 8 h average value of O_3) ≥ 160 μg/m^3 as the classification standard. Then, the three stations with the most days exceeding the standard (located in Guangzhou, Foshan, and Dongguan) are identified as polluted stations, whereas the three stations with the least number (located in Zhuhai, Shenzhen, and Huizhou) are defined as clean stations. Finally, diurnal variations and standard deviations of $PM_{2.5\text{-}sec}$ and ozone are presented (**Figure 11**, the error bars depict the standard deviation). The concentrations of the two pollutants are higher in the daytime than at night, and their maximum concentrations for both appear at about 15:00. As for ozone, the variation at polluted stations is larger than that at clean stations because the maximum concentration of ozone at polluted stations (91 μg/m^3) is higher than that at clean stations (60 μg/m^3) due to the photochemical reactions of a large number of precursors in the daytime, whereas the minimum concentration

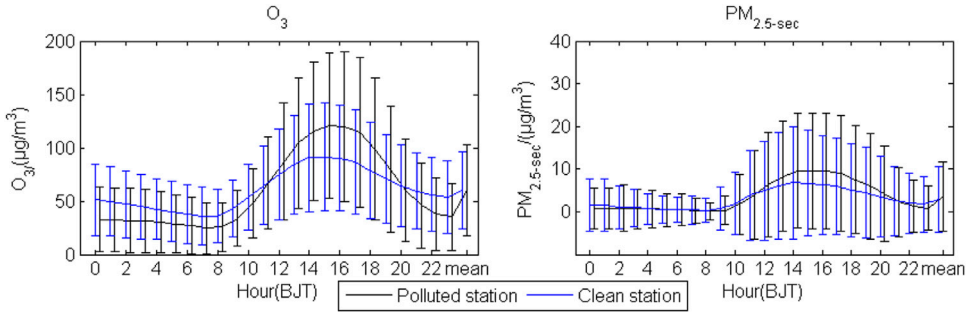

FIGURE 11 | Diurnal variations of ozone and $PM_{2.5\text{-sec}}$ under different photochemical backgrounds.

of ozone in polluted stations is lower than that in clean stations due to the consumption of a large number of NO in polluted stations at night. Under the background of high-photochemical reactivities, the concentration of $PM_{2.5\text{-sec}}$ at polluted stations is higher than that at clean stations from 12:00 to 20:00, which further reflects the promoting effect of the atmospheric oxidation background on $PM_{2.5\text{-sec}}$ formation.

CONCLUSION

Based on the observation data of environmental and meteorological stations in the nine cities of the PRD during 2019, the variations of $PM_{2.5\text{-sec}}$ and the coordinated increase of $PM_{2.5\text{-sec}}$ and ozone under different photochemical reactivity backgrounds in the PRD are revealed.

The trend of coordinated increase time is basically opposite to that of O_{3L} days, meaning that the coordinated increase of $PM_{2.5}$ and ozone mainly occurs under more significant oxidation backgrounds. The photochemical reactivities appear more significant in the central and western areas than in the eastern areas of the PRD and appear more significant in inland areas than in coastal areas. The days of moderate- and high-photochemical reactivities mainly appear from August to November.

The $PM_{2.5\text{-sec}}$ concentrations are the highest in autumn, during which the regional discrepancies appear the most significantly with the highest levels in the southern areas. With the enhancement of the photochemical reactivity background, the $PM_{2.5\text{-sec}}$ level at each station increases significantly, which appears significantly higher in coastal areas than that in inland areas. The ratios of $PM_{2.5\text{-sec}}/PM_{2.5}$ are as high as 30–50% under the high-photochemical reactivity background.

Both $PM_{2.5\text{-sec}}$ and ozone concentrations show single-peak variations, which appear higher in the daytime than at night with the peak occurring at about 15:00. As for each pollutant, the average maximum concentration appears higher for polluted stations than for clean ones, indicating that the atmospheric oxidation background is conducive to the formation of $PM_{2.5\text{-sec}}$.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material; further inquiries can be directed to the corresponding author.

AUTHOR CONTRIBUTIONS

XY contributed to data processing, mapping, analysis, and writing; YZ contributed to software and mapping; NL contributed to conceptualization and check on; and SY contributed to writing and editing.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

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