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Seasonal variation characteristics of hydroxyl radical pollution and its potential formation mechanism during the daytime in Lanzhou

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ABSTRACT

Hydroxyl free radicals (OH radicals) play the main role in atmospheric chemistry and their involving reactions are the dominant rate determining step in the formation of secondary fine particulate matter and in the removal of air pollutants from the atmosphere. In this paper, we studied the seasonal variation characteristics of OH radicals during the daytime in Lanzhou and explored the potential formation mechanism of high concentration OH radicals. We found that the OH radicals in four seasons was 2.7×10^6 , 2.6×10^6 , 3.1×10^6 , and $2.2 \times 10^6 \text{ cm}^{-3}$, respectively. Since the rainfall was concentrated in summer, the wet deposition had a significant effect on removing OH radicals. Among the four pollutants (including ozone (O_3), volatile organic compounds (VOCs), nitrogen dioxide (NO_2) and fine particulate matter ($\text{PM}_{2.5}$)), the variation of OH radicals were closely related to ozone concentration especially in spring and summer. In autumn, the correlation between $\text{PM}_{2.5}$ and OH radicals were the closest among the observing pollutants and its formation mechanism was different conventional regeneration pathway. In Event 1, high concentration of ozone was the main source of OH radicals; under the high humidity condition, except for ozone, the multiple factors including VOCs, NO_2 and $\text{PM}_{2.5}$ interplayed and led to the Event 2.

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Introduction

Lanzhou city is one of the most polluted cities in China, with haze episodes in which particulate number concentration (diameter $< 2.5 \mu\text{m}$) can increase tenfold within a few hours. High number concentrations of Particle matter can reduce visibility, indirectly affect global climate change and cause strong adverse effects on human health (Elser et al., 2016;

Yao et al., 2018; Li et al., 2019a); compared to PM_{10} (coarse particles), the fine particle (diameter $< 2.5 \mu\text{m}$) can enter the human circulatory system and has higher biological toxicity (Zhang et al., 2016; Nan et al., 2017). The nucleation and formation of these fine particles are closely related with the capacity of atmospheric oxidation which is controlled by free radicals (Wang et al., 2017; Tan et al., 2019a).

Free radicals are the most important chemical intermediate or agent of the atmosphere and influenced by thousands of reactants. They are colorless, odorless species and not easy to perceive by body, or even some instruments. They include hydroxyl radical, hydrogen peroxy radical, nitrate radicals

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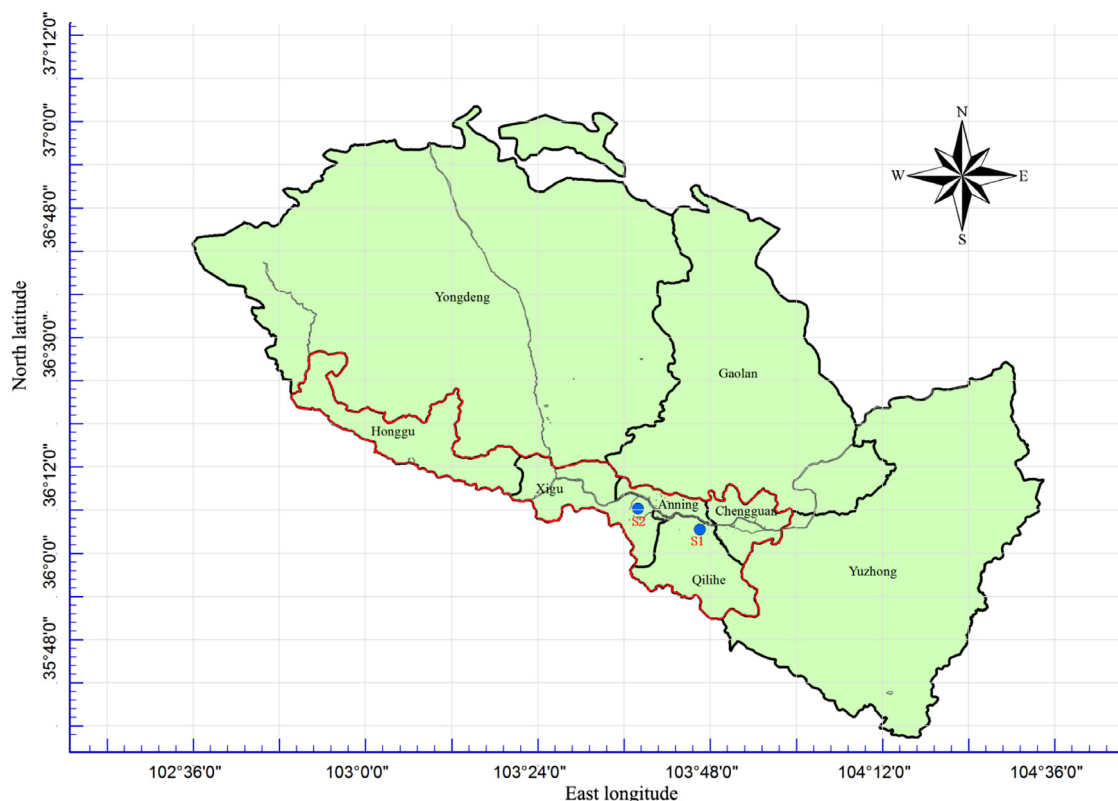


Fig. 1 – Location of the study site in Lanzhou. S1 and S2 refer to sampling sites 1 and 2, respectively.

and organic peroxy radicals, derived transition state species intermediate species and excited state species of chemical molecules. Among all kinds of free radicals, OH radicals composed of a hydrogen atom bonded to an oxygen atom have highly chemical reactivity and readily steal hydrogen atoms from other molecules to form water molecules (Gligorovski et al., 2015). Because the OH radical reactivity is typically more than $5\text{--}10\text{ sec}^{-1}$, the OH radicals lifetime is much less than 1 sec (Mao et al., 2010). It is well known that the oxidative capacity of the atmosphere is governed by the reactions that involve OH radicals. The OH radical reactions are the dominant rate determining step in the formation of secondary fine particulate matter and in the removal of air pollutants from the atmosphere (Wang et al., 2019; Arangio et al., 2016).

The OH radicals, known as the “detergent” of the atmosphere, are key oxidant species responsible for the oxidative capacity of the atmosphere (Levy et al., 1971). Although atmospheric OH radicals play a pivotal role in removing primary air pollutants emitted from human beings as well as those from the biosphere, serious secondary air pollution incidents can occur due to fast oxidation of the primary pollutants (Lu et al., 2019). Their vertical profiles are controlled only by the local concentrations of longer-lived species such as ozone (O_3), volatile organic compounds (VOCs), and nitrogen oxides (NO_x) (Gligorovski et al. 2015; Stone et al., 2012). In cleaner and polluted atmosphere, the source/sink mechanisms of OH radicals are different as well as complex. OH radicals are produced in the cleaner atmosphere by the reaction of water vapor with ozone by solar radiation at wavelengths below 320 nm. In polluted lower atmosphere, OH radicals can also be efficiently produced by the photolysis of nitrous acid (HONO), which occurs at wavelengths smaller than 400 nm (Tan et al., 2019b). Additionally, the photolysis of nitrogen dioxide (NO_2) leading to the formation of ozone and the fast reaction of electroni-

cally excited NO_2 and water vapor can indirectly produce the OH radicals (Rohrer et al., 2006; Villena et al., 2011). In the presence of OH radicals, the atmospheric trace gases from natural and anthropogenic emissions would be oxidizing to produce secondary pollutants including CO_2 , SO_3 , NO_2 and highly oxidized organic molecules (HOMs) (Prinn et al., 2003). Since the removal of atmospheric trace gases strongly consume the OH radicals, large global changes in OH radical concentrations are possible (Lelieveld et al., 2004). However, the monitoring data indicates that the OH radicals still remain median concentration level in haze days. The possible reason for this phenomenon could be the regeneration of OH radicals in unique environment. In an aqueous suspension, the environmentally persistent free radical in fine particulate matter ($\text{PM}_{2.5}$) can generate significant level of OH radicals (Gehling et al., 2014); HOMs is positively correlated with the formation of radicals in aqueous $\text{PM}_{2.5}$ extracts (Tong et al., 2019). In recent years, the particulate matter-induced regeneration of the OH radicals have attracted more attention. However, we have not found the accurate chemical mechanism which is inhibiting the process of air pollution control. So far, the annual observation and modelling studies for OH radicals are rarely reported in China. Therefore, more experimental studies in field environment need to put into force in future in order to fully understand the source/sink mechanism of OH radicals.

In this paper, we explore the seasonal variation characteristics of OH radicals and its potential formation mechanism in unique conditions. The field investigations show that the observed OH radicals concentrations in the gas phase have strong correlation with ozone especially in spring and summer; the appearance of high concentrations in autumn need to do further research for deeply understanding regeneration of the OH radicals.

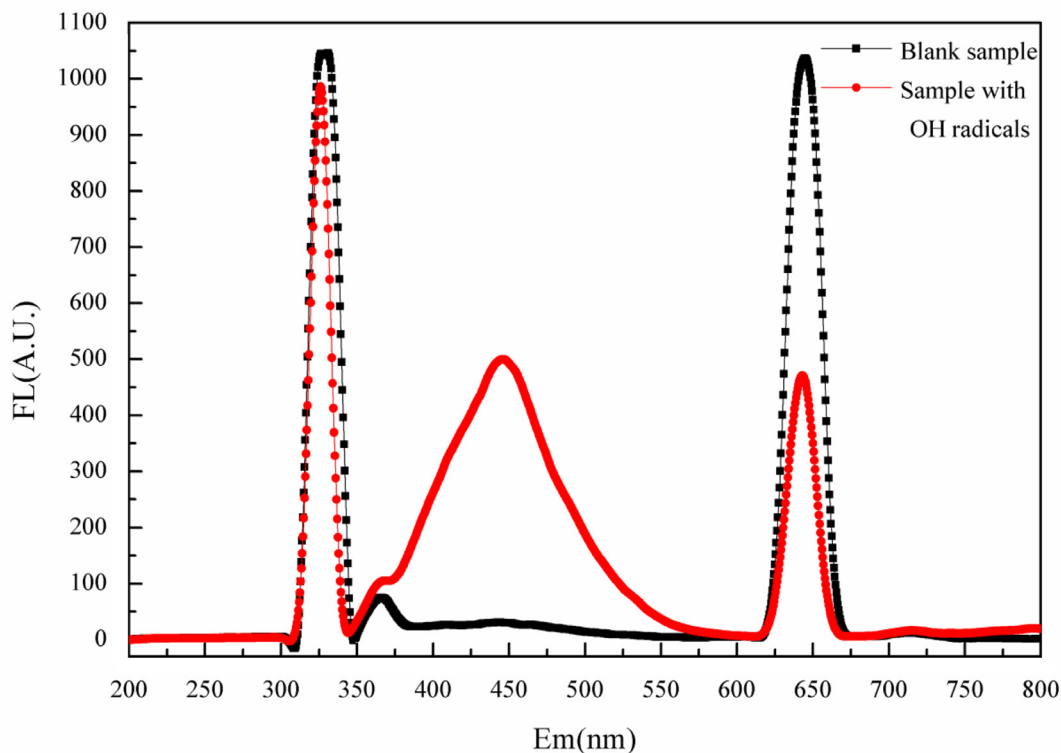


Fig. 2 – Fluorescence signal changes (FL) before and after free radical reaction in the field environment. Em: emission wavelength; A.U.: arbitrary unit.

1. Materials and methods

1.1. Site description

Lanzhou, the capital of Gansu Province, is situated in semi-arid region of northwest China and has unique geographical conditions and climatic factors. It is located in a long (40 km) but narrow (2–8 km) northwest–southeast-oriented valley basin, with Baita Mountain to the north and Gaolan Mountain to the south. And its climatic condition is characterized by low rainfall, high evaporation, low wind speeds, high frequencies of calm wind and a thick inversion layer. Due to the unique geographical conditions and climatic factors, the air pollutants in Lanzhou are hard to diffuse and form severe air pollution especially in winter. These unique conditions make it an ideal natural laboratory for research on OH radicals. The campaigns were carried out in Lanzhou during 2018. As shown in Fig. 1, the main sampling site 1 (S1) was situated at the Qilihe district (36.0622°N, 103.7852°E, Altitude 1594 m), which was 7 km away from Chengguan commercial district. The sampling site 2 (S2) was situated at the Xigu industrial area (36.1028°N, 103.6341°E, Altitude 1517 m), which is 16 km away from the sample site 1. To a considerable extent, it can represent the atmosphere pollutants level in Lanzhou.

1.2. Sampling and measurement

From January 01 2018 to December 13 2018, we collected 956 samples in the main sampling site 1; at the same time, we collected 80 samples in the sampling site 2. Since the OH radical concentration was variable, the sampling period in daytime was divided into four parts (9:00–11:30, 11:40–14:10, 14:20–16:50, and 17:00–19:30). The OH radicals sample collections

from gas phase took place from 9:00 to 19:30, and the reaction between OH radicals and the benzene pentacarboxylic acid aqueous solution 0.2 mg/mL was carried out for 2.5 hr at a flow rate of 1.0 L/min. After the OH radicals in polluted air were reacted with the benzene pentacarboxylic acid molecule system, the resulting OH radicals emission signals can be detected and identified by fluorescence spectroscopy (FL signals) (Wang et al., 2019). Due to the change of reactive molecule structure, the FL signals of samples reacted with OH radicals would increase; while for the samples without oxidized adduct, there was no change in their peak area as shown in Fig. 2. The integration of peak area would change with the variation of OH radicals concentration and so we could apply the integration of peak area to quantify the OH radicals concentration in the atmospheric environment. Moreover, meteorological data and Environmental monitoring data were obtained by online monitoring equipment from Lanzhou Municipal Environmental Protection Bureau.

2. Results and discussion

2.1. Seasonal variation characteristics of OH radicals in field observations

Lanzhou is situated in northwest China and has unique climatic factors and geographical conditions. Since its urban area adjoins the largest oil refinery in western China, the ozone and VOCs concentrations in Lanzhou, especially in summer, are higher than surrounding areas. Additionally, the ozone is one of the most important predecessors for OH radicals and influences the formation rate of them. Lanzhou experiences more windless days (nearly 300 days per year) than other regions, and the percent of flow velocity (< 4.0 m/sec,

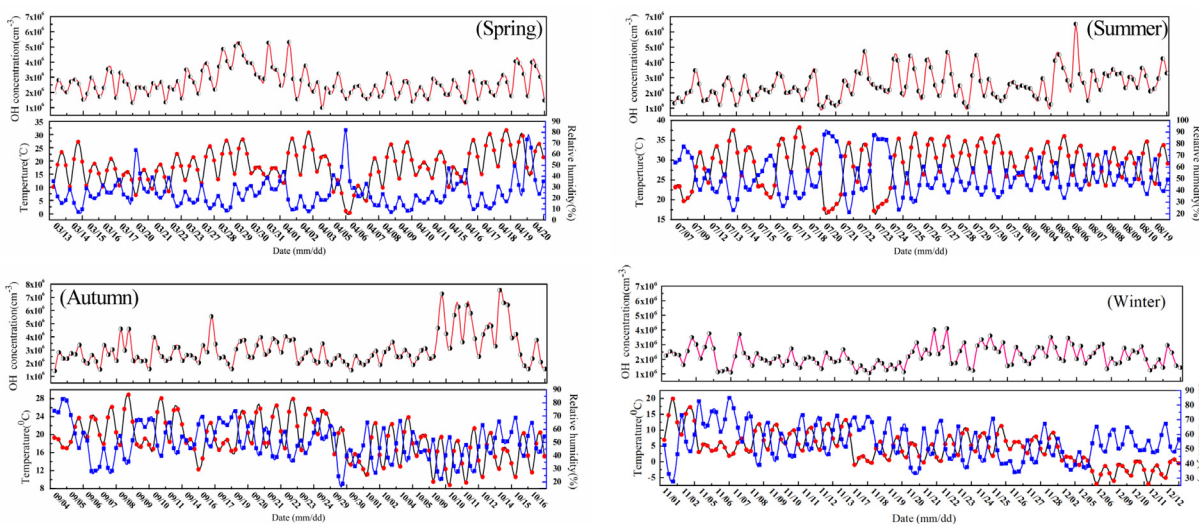


Fig. 3 – Variations of hydroxyl free radical concentration and meteorological data in different seasons.

Table 1 – Range of OH radicals in sampling period.

	Date (mm.dd)	Concentration (average (av.)) ($\times 10^6 \text{ cm}^{-3}$)				
		9:00-11:30	11:40-14:10	14:20-16:50	17:00-19:30	9:00-19:30
Spring	04.01	3.2	5.3	2.9	1.6	3.2
	03.29	5.1	5.2	4.4	3.9	4.7
	04.03	2.7	1.0	2.3	1.9	2.0
	04.10	1.	2.4	1.8	1.6	1.9
Summer	08.06	2.5	6.5	3.2	2.7	3.7
	07.20	3.4	3.3	4.7	2.9	3.6
	07.22	1.1	1.7	1.3	1.2	1.3
Autumn	07.07	1.3	1.7	1.4	2.0	1.6
	10.14	7.5	6.6	6.4	3.9	6.1
	10.09	3.1	5.6	6.3	3.6	4.7
	09.04	1.4	2.8	2.4	2.4	2.2
Winter	09.17	2.3	2.5	1.9	1.6	2.1
	11.22	2.8	4.1	1.7	1.7	2.6
	11.21	2.7	2.4	4.0	2.4	2.8
	11.17	1.1	1.6	1.2	1.1	1.2
	11.06	1.1	1.2	1.3	1.1	1.2

mostly < 2.0 m/sec) was almost 80% in the observation period. These factors can affect the seasonal variation of OH radicals in field observation.

Fig. 3 showed seasonal variations of OH radicals and meteorological data in Lanzhou during observation period. Except for relative humidity (RH), the temperature presented similar temporal variations to OH radicals. The relationship between OH radicals concentration and temperature showed positive correlation in spring and summer, while it was significantly weakened in autumn and winter. The curve of OH radicals in daytime often exhibited a single peak which usually appeared at 12:00–16:00; this was because, in the afternoon, high temperature and intense radiation made for the photolysis of HONO, HCHO and ozone so as to contribute significantly to the OH radicals production. But then the OH radicals concentration would decrease gradually with the weak solar radiation. The results were consistent with the monitoring data of other areas (Ren et al., 2003, 2006; Nan et al., 2017; Lu et al., 2013).

In Fig. 3a, the OH radicals in spring showed the highest concentration in April 01 followed by March 29 whereas the lowest

concentration was found in April 03; the concentration of OH radicals ranged from 1.0×10^6 to $5.3 \times 10^6 \text{ cm}^{-3}$ (average (av.) $2.7 \times 10^6 \text{ cm}^{-3}$). As shown in Fig. 3b, the OH radicals in summer showed the highest concentration in August 06 followed by July 22 whereas the lowest concentration was found in July 20; The concentration of OH radicals ranged from 1.1×10^6 to $6.5 \times 10^6 \text{ cm}^{-3}$ (av. $2.6 \times 10^6 \text{ cm}^{-3}$). In autumn, the OH radicals showed the highest concentration on October 14, 2018 followed by October 09 whereas the lowest concentration was found in September 04; concentrations of OH radicals ranged from 1.4×10^6 to $7.5 \times 10^6 \text{ cm}^{-3}$ (av. $3.1 \times 10^6 \text{ cm}^{-3}$), as shown in Fig. 3c. In winter, the OH radicals showed the highest concentration in November 22 followed by November 21 whereas the lowest concentration was found in November 17 in Fig. 3d; concentrations of OH radicals ranged from 1.1×10^6 to $4.1 \times 10^6 \text{ cm}^{-3}$ (av. $2.2 \times 10^6 \text{ cm}^{-3}$).

In view of the range of OH radicals listed in Table 1, the concentration in winter was much lower than three seasons due to multiple factor including temperature, radiation, and the precursor et al. The highest concentration of this campaign

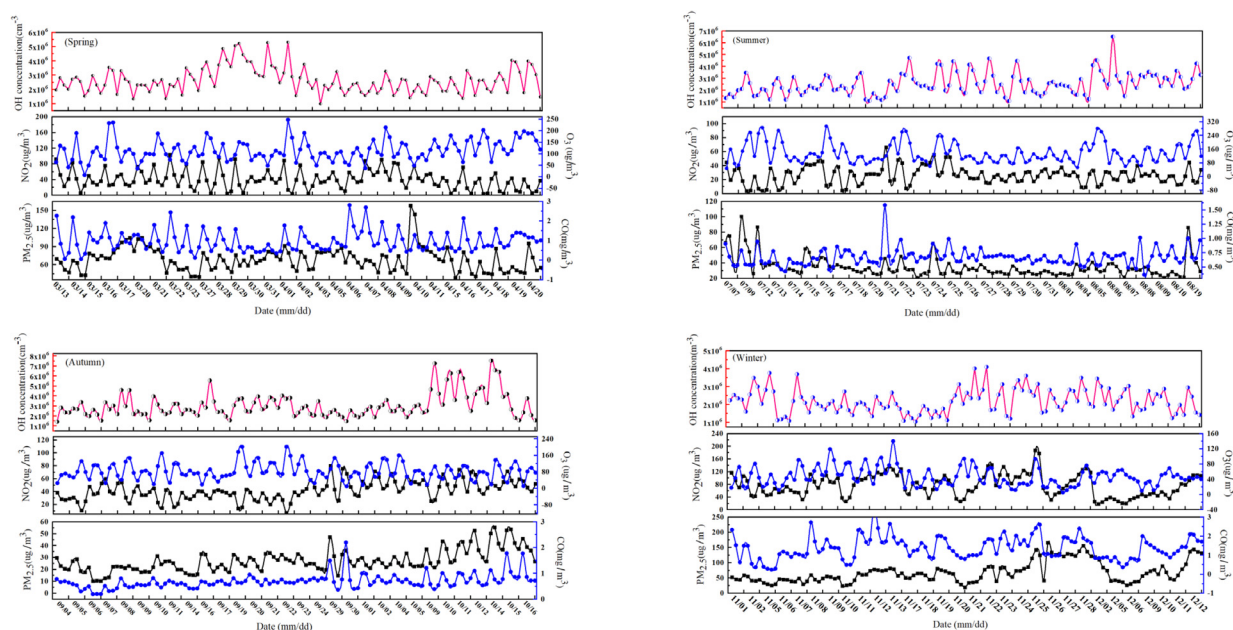


Fig. 4 – Hydroxyl free radical and pollutants data in different seasons.

Table 2 – Pearson correlation between pollutants and OH radicals in sampling period.

		Ozone	NO ₂	CO	PM _{2.5}
Spring	•OH	0.38	0.12	0.04	0.01
Summer	—	0.43	-0.32	-0.05	-0.06
Autumn	—	0.19	-0.07	0.04	0.37
Winter	—	0.25	0.024	-0.09	0.11

PM_{2.5}: the fine particles identified as particles with aerodynamic diameter less 2.5 μm.

was observed at 9:00–11:30 on October 14, 2018 and even its daily average concentration was also the highest. It was different from the conventional generation style of OH radicals and worthy to explore the potential mechanism.

2.2. Impact of environmental factor on OH radicals in daytime

The daytime OH chemistry and its abundance were determined by the concentration of VOCs and NO_x (Nan et al., 2017). The time series of observed OH radicals and pollutants including O₃, NO₂, PM_{2.5}, CO were shown in Fig. 4. Since the main sample site was located the campus of Lanzhou University of Technology without obvious pollutant emissions nearby, the OH radicals and pollutants were very close to the average level of Lanzhou city. In daytime strong sunlight was favorable for the generation of Ozone and the photolysis of nitrous acid (HONO) and aldehydes which maintained the high concentration of OH radicals.

From Fig. 4, the variation trend of ozone was very similar to the change profile of OH radicals from 9:00 to 19:30, which reached the maximum around noon time. It indicated that the ozone was not only one of the OH radicals generation source but also constantly associated with the OH radicals change (Wennberg, 2006). As shown in Table 2, the Pearson correlation between ozone and OH radicals in spring and

summer was 0.40 and 0.43, respectively; and with the decrease of PM_{2.5} concentration, the ozone prevention and control have attracted much attention from government and researchers. Compared to ozone, the correlation relationships between the other three pollutants and OH radicals were obviously much weaker since they were not the direct generation pathway of OH radicals and CO even consumed it to some extent. In summer, nitrogen dioxide would be oxidized and transferred into nitrates in the presence of high concentration of OH radicals; subsequently, it would nuclear and grow to new fine particle by a series of physical and chemical reactions (Lu et al., 2019). But a fraction of it could also transfer to HONO or electronic excitation of NO₂, as a pathway of producing OH radicals (Li et al., 2008). In autumn, the correlation relationships between PM_{2.5} and OH radicals enhanced significantly and it suggested that the particles from combustion sources including coal combustion, vehicle exhaust, and industry contribute to the OH radicals generation (Li et al., 2019a). But it was not constantly associated with the OH radicals change and there was about 2–5 hr delay (Wang et al., 2017). The chemical composition of PM_{2.5} also had a great effect on the process of producing OH radicals (e.g., Fe²⁺, organic carbon and elemental carbon). Under high relative humidity condition, as well-known Fenton reaction, divalent iron ions reacting with hydrogen peroxide can generate OH radicals (Kwan et al., 2003; Zhu et al., 2019). However, the accurate production of OH radicals per unit mass in atmosphere was unknown and worthy to explore in future.

Wet deposition (including surface condensation and direct deposition), as an important environmental factor, can remove primary and secondary pollutants from the atmosphere and contributes significantly to the migration of pollutants. Since the rainfall in Lanzhou city focused on summer from June to August, we specifically studied the effect of rainfall on OH radical concentration. As shown in Table 3, we can find that the daily concentration of OH radicals in rainy days were much lower than average level in summer; moreover, most of them were only reached the 40%–70% of average level in summer. It indicated that the process of rainfall had a significant effect on the OH radical removal. The scavenging

Table 3 – OH radicals concentration in rainy days.

Date (mm.dd)	06.06	06.07	06.24	07.03	07.05	07.15	07.20	07.23	Average in summer
Weather	Light rain	Light rain	Shower	Light rain	Shower	Moderate rain	Light rain	Light rain	Normal
Concentration (av.) ($\times 10^6 \text{ cm}^{-3}$)	1.5	1.3	2.0	1.7	1.6	2.0	1.3	2.2	2.8

mechanisms of rainfall included in-cloud scavenging, diffusive and inertial collisions between aerosol and precipitation particles due to absorption of gases or inertial scavenging of aerosol particles larger than $1 \mu\text{m}$ (Polkowska et al., 2011). Furthermore, the solar radiation would also decrease and directly influence the rate of photochemical reaction. In a word, wet deposition was crucial to the variation tendency of OH radicals and related precursor.

2.3. Potential formation mechanism of OH radicals in unique conditions

The profiles of OH radicals in Lanzhou during 2018 are shown in Appendix A Fig. S1. When the OH radicals level over $4.5 \times 10^6 \text{ cm}^{-3}$ lasted more than 3 hr in daytime, we defined it as “The Event of high concentration”. Through the analysis and statistical treatments, we found that the event of high concentration appeared predominantly in May and October; thus they were divided into Event 1 and Event 2, respectively. The environmental parameters of Event 1 were different from Event 2 and their related data are shown in Appendix A Table S1.

As shown in Fig. 5, the green solid line represented positive correlation and the black dotted line represented negative correlation; in addition, the thicker the line was, the stronger the correlation was. The Pearson correlation between environmental parameters and OH radicals in Events 1 and 2 are in shown in Appendix A Table S2.

In Event 1, the correlation coefficient between OH radicals and ozone was 0.46, indicating medium positive correlation; the correlation coefficient between OH radicals and VOCs was -0.67, indicating strong negative correlation. The results suggested that the ozone contributed greatly to the production of OH radicals and then the oxidation of VOCs was a very important transformation pathway for OH radicals and ozone (Li et al., 2019b; Hong et al., 2019). In this period, the temperature and humidity of atmosphere make for the process that excited oxygen reacted with H_2O and then high concentration of ozone reacting with alkenes was also one of the pathways to produce OH radicals. Furthermore, the OH radicals and CO presented medium positive correlation which needed to analyze in-depth. In Event 1, the correlation coefficient between OH and $\text{PM}_{2.5}/\text{CO}$ was -0.47, indicating that the secondary part of $\text{PM}_{2.5}$ maybe consumed the OH radicals. However, the correlation coefficient between OH radicals and $\text{PM}_{2.5}/\text{CO}$ was only 0.01, which indirectly suggested that the ratio of secondary part of $\text{PM}_{2.5}$ to the total $\text{PM}_{2.5}$ may be bigger in Event 2. The formation mechanism of OH radicals in this period was closely related to environmental conditions and different from the main generation pathway. As the high concentration of VOCs and NO_2 occurred in Event 2, they could control the OH radicals production. In the presence of ozone, it reacted with NO_2 to generate the NO_3 radicals which would oxidize VOCs to form OH radicals; besides, the reaction of electronic excitation of NO_2 with water can be a major source of tropospheric OH radicals (Li et al., 2008). Under high humidity condition the secondary organic aerosols with Fe^{2+} ions also formed substantial amounts of OH radicals (Tong et al., 2016). Compared to Event 1, the correlation coefficient between OH radicals and CO significantly decreased in Event 2, indicating

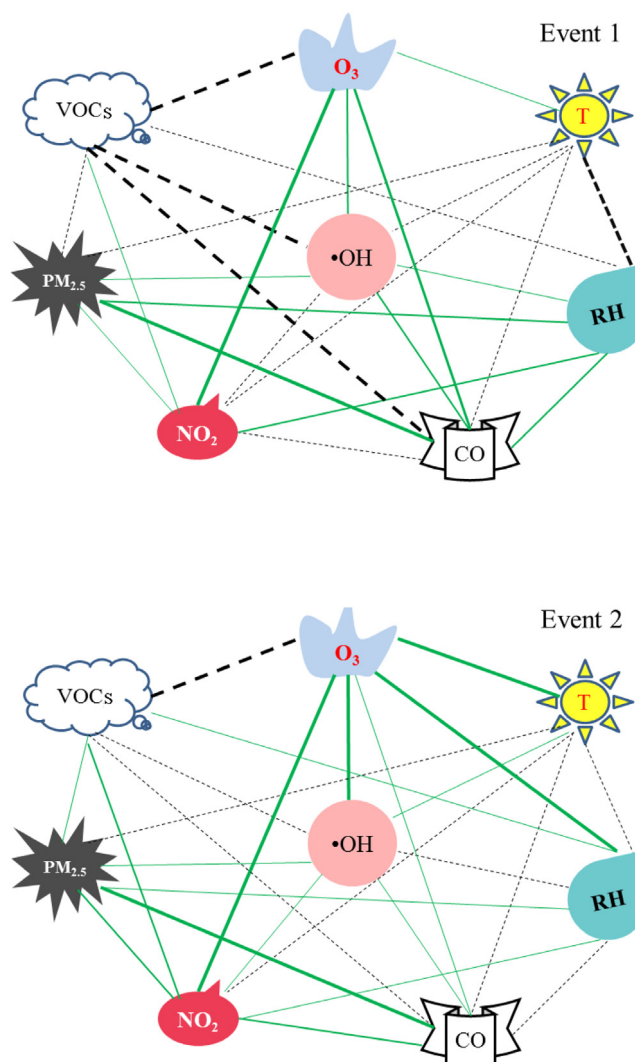


Fig. 5 – Relationship between hydroxyl radicals and environmental parameters in Event 1 and Event 2. VOCs: volatile organic compounds; RH: relative humidity; T: temperature.

that the higher concentration of CO would weaken the correlation. The OH radicals generation from environmentally persistent free radicals in $\text{PM}_{2.5}$ also should be pay more attention and this theory can explain why OH radicals remained high level in haze days.

3. Conclusions

To investigate OH radicals seasonal variation and generation mechanism during the daytime in Lanzhou, the benzene pentacarbonic acid molecule system was utilized to observe OH

radicals and other environmental pollutants data was obtained from online monitoring equipment of Lanzhou Municipal Environmental Protection Bureau. This campaign took place from January 01 to December 13, 2018 and the OH radicals concentration in four seasons was 2.7×10^6 , 2.6×10^6 , 3.1×10^6 , and $2.2 \times 10^6 \text{ cm}^{-3}$, respectively. Since the rainfall was concentrated in summer, the wet deposition had a significant effect on removing OH radicals. Among the four pollutants, the OH radicals variation was closely related to ozone concentration especially in spring and summer. In autumn, the correlation between $\text{PM}_{2.5}$ and OH radicals was the closest among the observing pollutants and its formation mechanism was different conventional regeneration pathway. From the profile of the OH radicals seasonal variation, we found that the high concentration OH radicals appeared in May and October and the pathway of producing OH radicals in Event was different. In Event 1, high concentration of ozone was the main source of OH radicals; under the high humidity condition, except for ozone, the multiple factors including VOCs, NO_2 and $\text{PM}_{2.5}$ interplayed and led to the Event 2.

Declaration of competing interest

None.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material associated with this article can be found in the online version at doi:10.1016/j.jes.2020.03.045.

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