Distribution and regeneration of hydroxyl free radicals in gaseous and particulate phases of pollutants in near-ground ambient air

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HIGHLIGHTS

- Distribution of hydroxyl free radicals in near-ground ambient air.
- Hydroxyl free radicals exist in flowing air phase & particulate phase.
- Excited electrons (e^-) and holes (h^+) pairs promoting regeneration of. OH
- Environmentally persistent free radicals promote chain reaction of free radicals

GRAPHICAL ABSTRACT
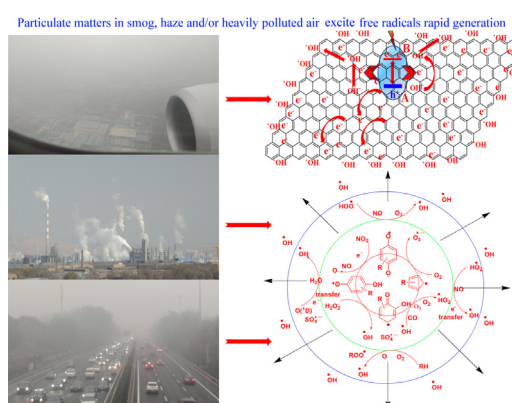
ARTICLE INFO

ABSTRACT

Hydroxyl free radicals play the main role in atmospheric oxidative capacity. The formation of secondary fine particulate matter and the degradation of gaseous pollutants in the troposphere are dominated by hydroxyl free radical reactions. The harmful effect of particulate matters to human health is closely related to the free radicals distributed in the particulate matter phase. In this paper, the distribution of hydroxyl free radicals in near-ground ambient air was studied. The hydroxyl free radicals exist not only in the gaseous phase but also in the particulate phase, especially during heavy haze pollution. It is noteworthy that the concentration of hydroxyl free radicals in the particulate phase is about two times higher than that in the gaseous phase. The possible regeneration mechanisms are proposed. The excited electrons (e^-) and holes (h^+) formed e^- - h^+ pairs in particulate matters are identified to play a key role in promoting the regeneration of hydroxyl free radicals in particulate phase. Environmentally persistent free radicals in particulate phase could also further promote the chain reaction of free radicals and ultimately result in explosive regeneration in an environment that has been excited. The correlation between radical concentrations in gas species, particulate phases and particulate number concentration has been summary based on the actual monitoring site including Thermal power plant, Yumen street and Chemical street sites.

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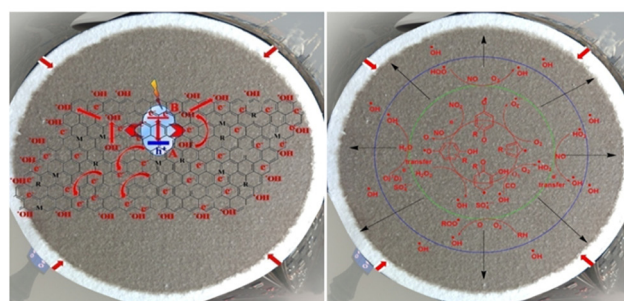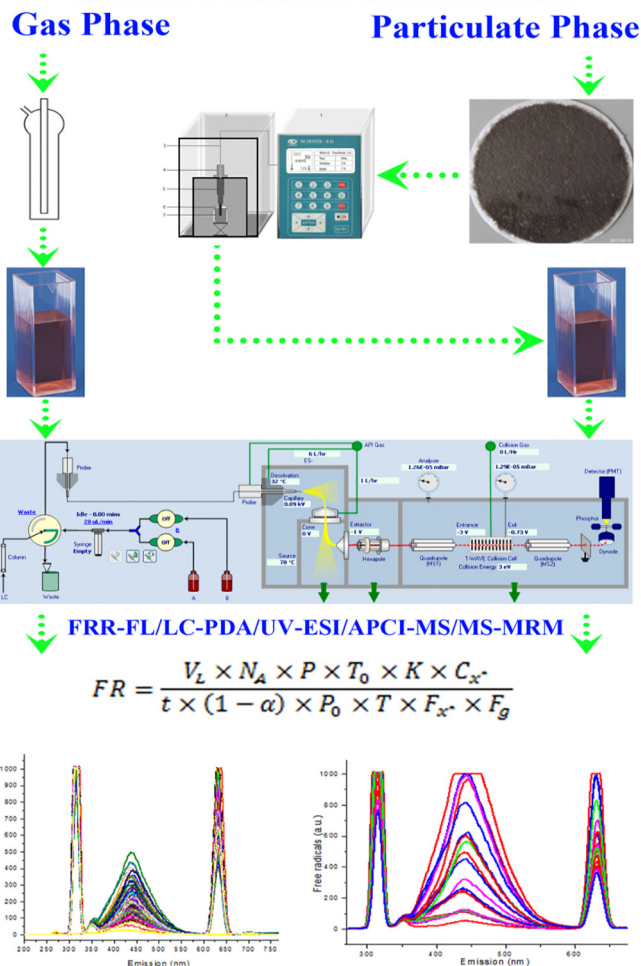   E-mail address: shigaofeng@lut.cn (G. Shi).

1. Introduction

The central role of hydroxyl free radicals in atmospheric chemistry was recognized by Levy, Hofzumahaus, Rohrer and Zhang (Levy II, 1971; Hofzumahaus et al., 2009; Rohrer et al., 2014). It is now widely accepted that the hydroxyl free 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 (Arangio et al., 2016; Khachatryan et al., 2014; Li et al., 2019; Lu et al., 2018; Nan et al., 2017; Ferracci et al., 2018; Stone et al., 2012). In the conventional theory, hydroxyl free radicals are produced in the troposphere by the reaction of water vapor with ozone by solar UV photolysis. The hydroxyl free radicals generated are then converted to organic peroxy radicals (ROO•) and to hydroperoxy radicals (HOO•) by reactions with volatile organic compounds (VOCs). When nitrogen oxides are present, ROO• are converted to HOO• through reaction with •NO. The HOO• further react with •NO, ultimately recycling hydroxyl free radicals (Rohrer et al., 2014; Ehhalt, 1999). Hydroxyl free radical recycling enhances the efficiency of atmospheric oxidation. Near-ground hydroxyl free radical chemistry has been studied in a number of field campaigns (Arangio et al., 2016; Khachatryan et al., 2014; Hofzumahaus et al., 2009; Rohrer and Berresheim, 2006, Li et al., 2019; Levy II, 1971). The hydroxyl free radical regeneration pathways and mechanisms, as well as the subsequent organic radical reactions, are diverse and introduce enormous complexity into tropospheric chemistry. These reactions are far from fully explored (Hofzumahaus et al., 2009; Khan et al., 2009; Goldstein and Galbally, 2007). More experimental studies in different chemical environments are necessary to understand the various factors related to hydroxyl free radical regeneration pathways and mechanisms. In this paper, we find the distribution of hydroxyl free radicals between the flowing air phase and the particulate matter phase in near-ground ambient polluted air. The field investigations show that the observed hydroxyl free radical concentrations in the particulate matter phase can be higher than expected in the air flow phase by up to a factor of three. Based on the previous research (Hofzumahaus et al., 2009; Rohrer et al., 2014; Tan et al., 2001; Lelieveld et al., 2008; Whalley et al., 2015; Lu et al., 2014) and the regeneration processes excited by particulate matter, we find a new regeneration source of hydroxyl free radicals in polluted air. Possible regeneration mechanisms of hydroxyl free radicals excited by particulate matter in local polluted air are proposed. The flowchart of the experimental implementation process is shown in Scheme 1.

2. Experiments and observation

2.1. Collection and measurement of free radical samples from gas phase and particulate matter phase

In the collection of gas phase free radical samples, the benzene pentacarbonic acid aqueous solution 0.2 mg/ml was put into gas sampling tubes, the airflow was introduced into the benzene pentacarbonic acid aqueous solution at a flow rate of 0.8 L/min, and the total sampling time was 2.5 h. The reaction solution was then filtered through a 0.22 μm filter membrane and transferred to a liquid chromatography sample bottle and a fluorescent cuvette after diluting to volume. Finally, the fluorescence spectrum and liquid chromatography combined with photodiode array & ultraviolet-visible detector and atmospheric pressure chemical & electrospray ionization and tandem mass spectrometry multiple reaction monitoring positive/negative ions analysis method (FL/LC-PDA/UV-APCI/ESI-MS^n-MRM) was used to determine the content of free radicals in the airflow phase.

In the collection of particulate phase free radical samples, the total particle collection was carried out using a glass fiber sampling membrane, and then the particulate matter was dissolved in an aqueous solution of benzene pentacarbonic acid, diluted to volume and filtered through a 0.22 μm filter, and transferred to a liquid chromatography

Gas Phase   **Particulate Phase**

FRR-FL/LC-PDA/UV-ESI/APCI-MS/MS-MRM

$$FR = \frac{V_L \times N_A \times P \times T_0 \times K \times C_{x^\cdot}}{t \times (1-\alpha) \times P_0 \times T \times F_{x^\cdot} \times F_g}$$

Possible mechanisms of radicals regeneration toward the particulate matters in polluted air

Scheme 1. The hydroxyl radicals in gaseous and particulate phases and possible regeneration mechanisms.

sample bottle and a fluorescent cuvette for FL/LC-PDA/UV- APCI/ESI-MS^n-MRM analysis, to measuring the content of free radicals in the particulate phase.

Specific monitoring sites are mainly located in Xugu and Qilihe of Lanzhou during 2016 and 2019. Particulate matter was collected on glass fiber filters and electrostatic spinning membranes by a high-
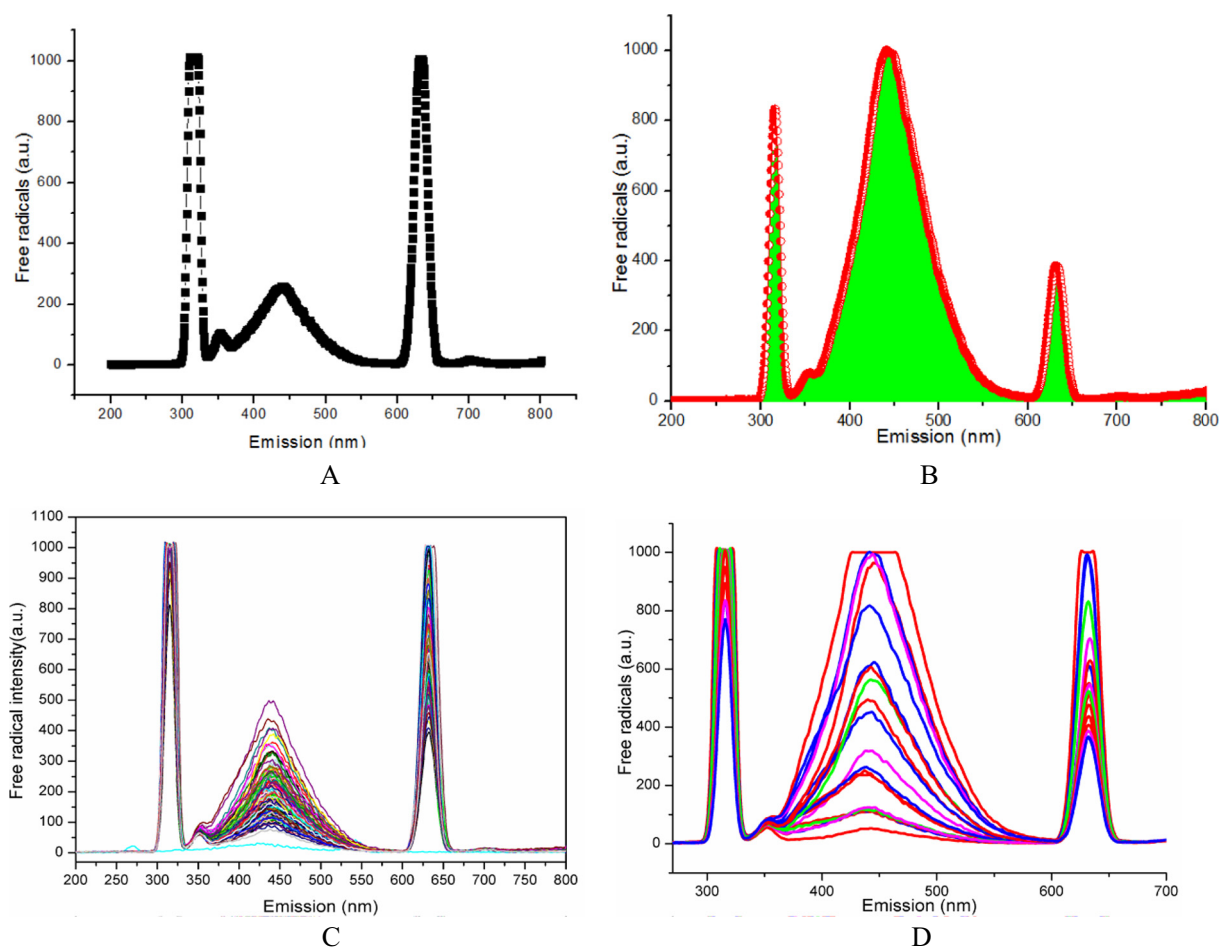
A

B

C

D

Fig. 1. Overall distribution trends of hydroxyl free radicals in two phases (flowing air phase and particulate matters phase).

volume particle sampler at a 100 L/min flow. Nearby, concentrations of OH were measured at the experimental platform. Experimental details of the measurement processes are provided below.

2.2. Hydroxyl free radicals regeneration measurement

Static measurements: the particulate matter in polluted air was collected using a Wuhan Tianhong sampler TH-150, TH-3150, TH-150 SMV equipped with $PM_{2.5}$, PM_{10}, and TSP fractionators. The flow rate was 100 L/min, and particulate matter samples were collected on a glass fiber membrane with a 90 mm diameter filter with a polypropylene supported ring. Particulate matter samples were accumulated to capture particulate matter in different time periods. Then, the collected particulate matter was dissolved in benzene pentacarbonic acid solutions and analyzed by the detection systems after through 0.22 μm filter membrane. The free radical signals excited by particulate matter can be effectively captured and amplified by the fluorescence and/or liquid chromatography atmospheric pressure chemical electrospray ionization and by the tandem mass spectrometry multiple reactions monitoring positive/negative parent/daughter ions/ion-pairs signal amplification technique. Dynamic measurements: the particulate matter in polluted air was continuously directed into scrubbing solutions, with mass flow rates of 0.8–1.0 L/min. Where the hydroxyl free radicals (•OH radicals) were reacted with the benzene pentacarbonic acid molecule system, pulsed excitation energy at a wavelength of 200–800 nm, optimal wavelength 335 nm, the resulting •OH radical emission signals were subsequently detected and identified by FL/LC-

PDA/UV- ESI/APCI-MS^n-MRM. In the •OH static and dynamic regeneration measurements, the reactions of •OH resulted in the electron transfers within the reaction system, and such that the reactive molecule structure was changed. On this basis, the signal difference in the
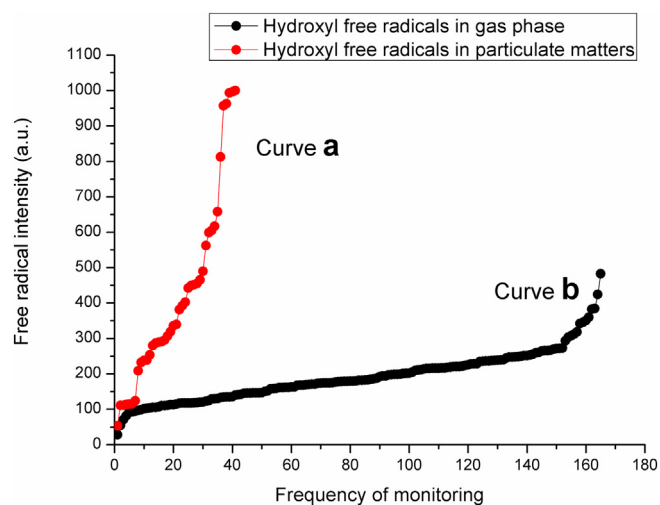

Fig. 2. Variation tendency of hydroxyl free radicals between gas phase and particulate matter phase.
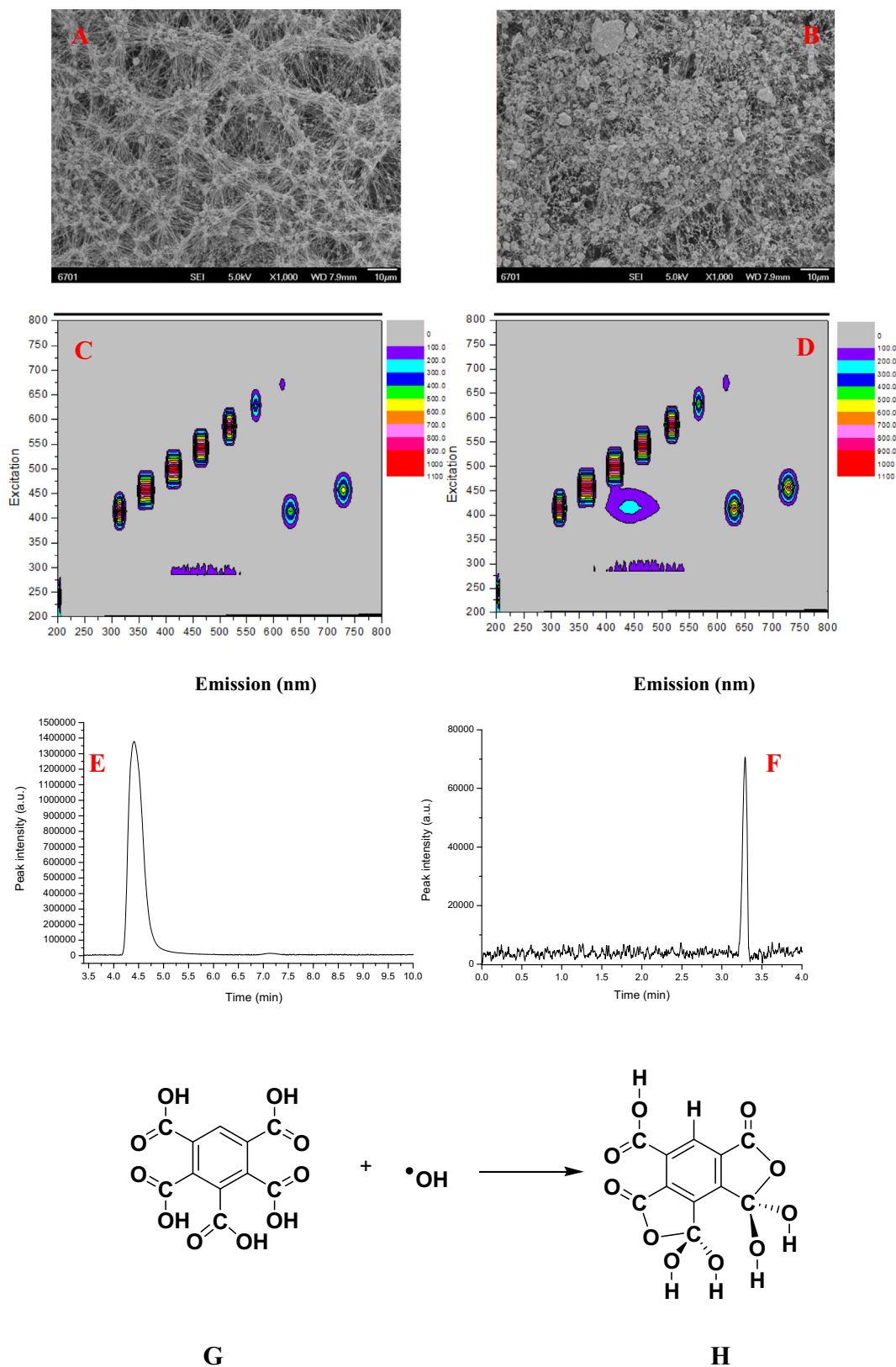
Fig. 3. Analysis of signal changes before and after free radical reaction in ambient polluted air (A and B: Scanning electron micrograph; C and D: Three-dimensional fluorescence spectroscopy; E and F: High performance liquid chromatograms; G and H: Reaction and/or addition mechanism of a large amount of hydroxyl free radicals with benzene pentacarbonic acid molecules). Note: A, C, E, and G represent before reaction with free radicals; B, D, F, and H represent after reaction with free radicals.

integration of peak areas was used to quantify the •OH radicals in the atmospheric particulate matter. The integral areas changed with the change of •OH concentrations in particulate matter, while for the samples without •OH radicals excited capacity, there was no change in their peak area. The detail method of the quantitative analysis for radical concentration followed the Eq. (1). The integral peak area of •OH radical
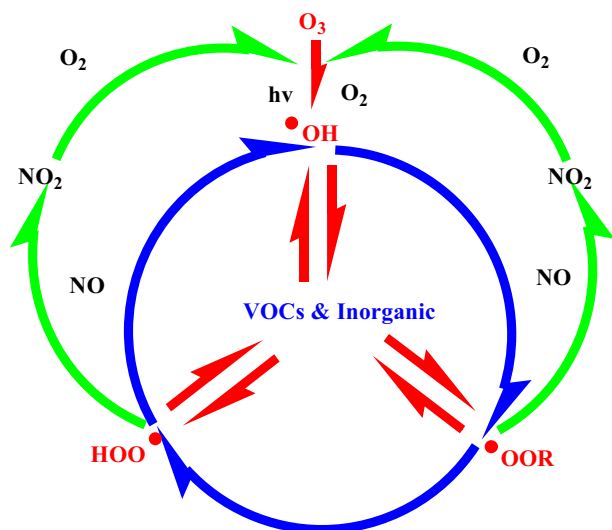
Fig. 4. Main pathway for the formation of hydroxyl free radicals in atmosphere.

signal is substituted into the equation to obtain the concentration of •OH radical (/cm^{-3}).

$$
\begin{aligned}
&\text{$^{\cdot}$OH radical concentration } (/cm^{-3}) \\
&= (K * C_x * V_L * N_A * P * T_0)/(F_X * F_g * t * (1-\alpha) * P_0 * T),
\end{aligned}
\tag{1}
$$

where K: Correction factor, C_x: Concentration of free radical adducts produced in solution samples (mol/L, Peak area), V_L: The absorbed liquid volume after sampling (L), F_X: Yield of free radical adducts (%), F_g: Air sample flow rate (cm^3/min), α: The product loss rate when the sample enters the reactive system of the active molecule (%), P_0: Standard atmosphere (1 atm), P: Working atmosphere (atm), T_0: Standard temperature (273 K), T: Actual temperature (K), t: Sampling time (min), N_A: Avogadro's constant.

2.3. Liquid chromatography tandem mass spectrometry separation and analysis

Particulate matter collected from heavily polluted air excites free radical formation. The generation processes were also measured by liquid chromatography tandem mass spectrometry. The separation and analysis were done on a Hypersil GOLD C_{18} column (3.0 μm, 150 × 2.1 mm i.d.) (Thermo Electron Corporation, USA) with a photodiode array detection system under the following isocratic and gradient elution conditions: flow rate 0.2–0.5 mL/min; column temperature 35–45 °C; sample manager room temperature 4 °C; detection wavelength 190 nm - 800 nm (3 D-plots were recorded); acquiring sample mode: partial loop with needle overfill; solvent A, 5.0% methanol (HPLC purification grade) and 1.0% formic acid (HPLC purification grade) in ultrapure water; solvent B, acetonitrile; isocratic elution: 95% A and 5% B, run time 40 min; gradient elution: starting from 3% to 20% B in 35 min, from 20% to 30% B in 40 min, from 30% to 40% B in 45 min, from40% to 60% in 55 min, and keeping constant for 5 min; then from 60% to 80% B for 65 min and from 100% to 3% B for 1 min and keeping constant for 9 min for reconditioning the column. The detection and identification were done on a LC-MS/MS system equipped with a multi-mode ESI/APCI ion source operating in both positive ion mode and negative mode. LC-MS/MS conditions were set as follows: ion mode: ESI-negative mode; discharge voltage: 3.6 kV; capillary temp: 150 °C; vaporizer Temp: 350 °C; desolvation gas flow: 66 arb; cone gas flow: 20 arb; collision energy: 25–70 V; cone gas and desolation gas: high-purity nitrogen; collision gas: high-purity argon; capillary voltage (v) -6; tube lens offset (v) 6; isolation width (m/z) 1–2; normalized collision energy(%) 50. All the samples were passed through 0.22

μm filters in advance and then were used for LC-PDA/UV-ESI/APCI-MS/MS analysis.

Details of field measurements. TVOC, CO, NO_2, O_3, $PM_{2.5}$, PM_{10}, and SO_2 measurements began in December 2016. The monitoring realized 24 h online continuous detection. Samples for free radicals detection were acquired from December of 2016 to Februry of 2019 at Lanzhou by offline detection processes. The TVOC, CO, NO_2, O_3, $PM_{2.5}$, PM_{10}, and SO_2 were measured using a continuous automatic on-line monitoring system in the monitoring sites, and there are parallel reference monitoring sites around. The particulate numbers were also measured with the particulate counter using 6 particle size channels of simultaneous counting.

3. Results and discussion

3.1. Two-phase distribution of hydroxyl free radicals between flowing air phase and particulate matter phase

The hydroxyl free radicals, which are the most important chemical cleaning intermediate of the atmosphere, play the main role in the atmosphere's oxidative capacity. The free radicals almost control the removal and/or secondary formation of nearly all gaseous atmospheric pollutants. The local transformation characteristics of hydroxyl free radicals in the atmosphere were monitored and analyzed. The concentration of hydroxyl free radicals is linearly dependent on solar ultraviolet radiation during the daytime (Rohrer and Berresheim, 2006). In some local areas, a high variability of hydroxyl free radical concentrations usually occurs, and during some monitoring periods high variability of hydroxyl free radicals prevents the observations of possible trends in the concentration of hydroxyl free radicals in the atmosphere (Rohrer and Berresheim, 2006). After long-term measurements of hydroxyl free radicals from 2016 to 2018 at the Lanzhou, Baiyin and Xining test locations and in northwest China and Beijing, we found that the hydroxyl free radical distribution in polluted air was not only in the flowing air phase (Fig. 1 A, C) but also in the particulate matter phase (Fig. 1 B, D). According to the monitoring data of outer filed sites, the distribution of hydroxyl free radicals in the particulate phase of pollutants in near-ground ambient air become the main sources of hydroxyl free radicals in polluted air. The contrast between the gaseous and particulate phases shows a significant change in the trend of hydroxyl free radicals. In the particulate phase, the concentration of hydroxyl free radicals is higher, accounting for a much larger percentage. (Fig. 2, Curve a). The particulate phase concentration is approximately two times higher than that in the gaseous phase. Long-term observations over the past three years suggest that the overall change in concentration of hydroxyl free radicals in the gaseous phase is lower. The highest concentration in gaseous phase is 482.7102 a.u. (peak area after integration), that's the same thing as the number of free radicals 3.5660E+06 /cm^{-3} (Fig. 2, Curve b). The concentration of hydroxyl free radicals in the particulate phase, however, can reach the highest value of 996.0218 a.u., 1.4193E +07 /cm^{-3}. Moreover, the relative concentration of the hydroxyl free radicals in the particulate phase exhibits high oscillation.

The reaction mechanism of a large amount of hydroxyl free radicals with benzene pentacarbonic acid molecules was confirmed and the results are shown in Fig. 3. By contrast, significant changes in the apparent structure of the membrane after sampling can be shown on the membrane (Fig. 3 A, B). The oxidative addition process of the hydroxyl free radicals occurs. In the three-dimensional fluorescence spectrum, it can be clearly seen that there is a significant free radical addition fluorescence characteristic region (Fig. 3 D) within the excitation wavelength range from 350 nm to 450 nm and within the emission wavelength range from 380 nm to 510 nm. In the blank group, detection before sampling, no changes appear in the three-dimensional fluorescence signals (Fig. 3 C). Furthermore, the similar signals of hydroxyl free radicals can also be detected by liquid chromatographic analysis. A significantly increased peak appear in the chromatogram with a retention time
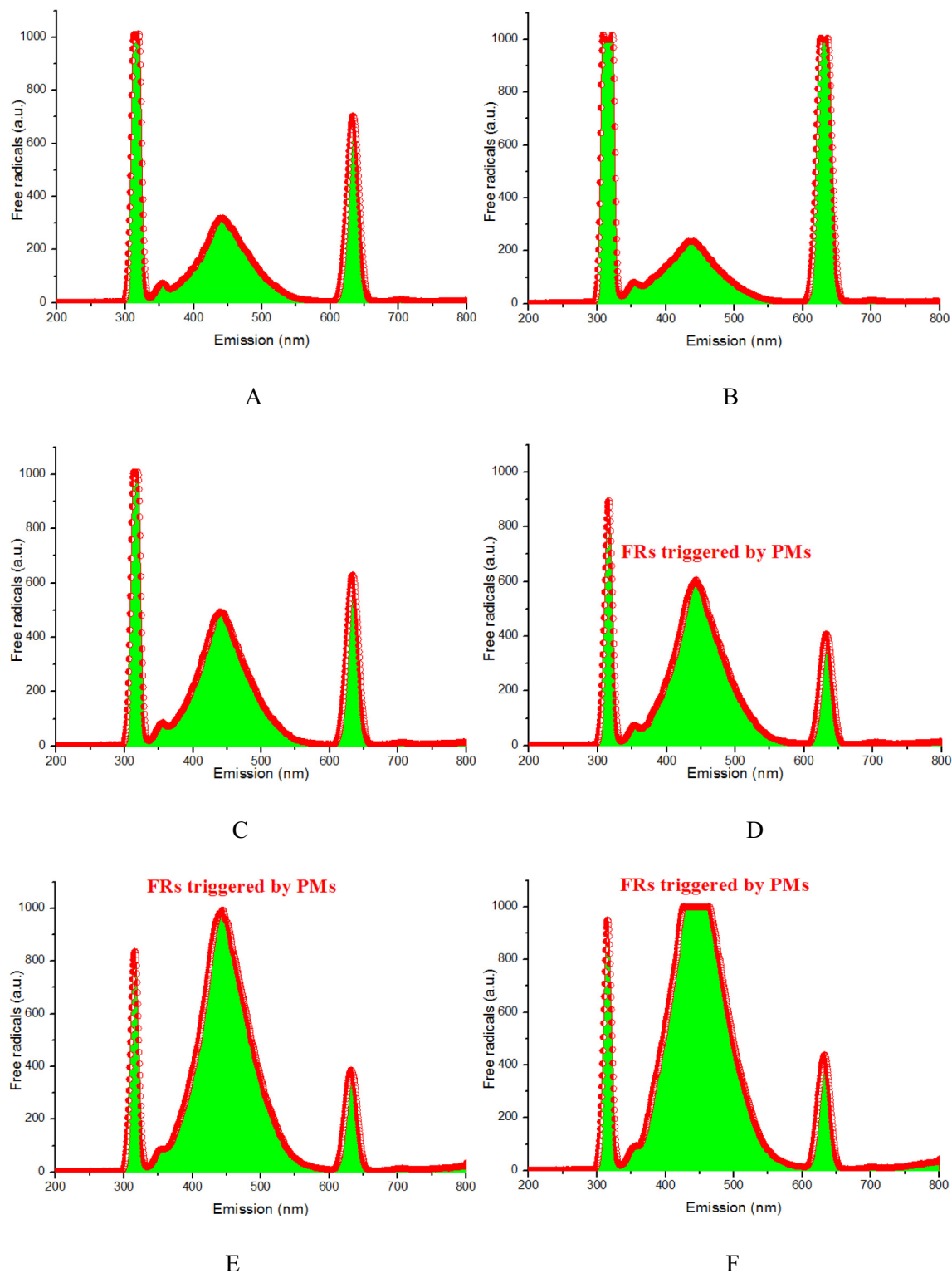
Fig. 5. Typical PMeFR regeneration in polluted air (Free radicals, FRs; Particulate matters, PMs).

between 3.2 min and 3.4 min and an integral area of 302,502.1 a.u. (Fig. 3 F). The reaction and/or addition mechanism of a large amount of hydroxyl free radicals with benzene pentacarbonic acid molecules are elucidated in Fig. 3 G. The formation of a rigid plane enhances (Fig. 3H)the three-dimensional excitation fluorescence effect (Fig. 3 D) and provides accurate, sensitive and reliable data for the detection of free radicals in the gas phase and particulate phase.

3.2. Possible regeneration pathways and mechanisms of hydroxyl free radicals in particulate matter phase

The understanding of the chemistry of hydroxyl free radicals (•OH) in gas phase has been largely confirmed by ground-based field studies in polluted environments and in clean air (Anderson, 1987; Hofzumahaus et al., 2009). We outline a summary of the main pathway

for the formation of hydroxyl free radicals (Fig. 4). In addition to the traditional regeneration pathway of hydroxyl free radicals, we have also found a new regeneration pathway of hydroxyl free radicals in local polluted air (Figs. 5 and 6). The hydroxyl free radicals in local polluted air can not only create tiny particles but can also excite chain reactions of hydroxyl free radicals. That is, hydroxyl free radicals in local polluted air can easily be excited again by particulate matter and then regenerated through the new particulate matter pathway. Here, we define the excited radicals regenerated in local polluted air as particulate matter excited free radicals (PMeFR).

Fig. 5 A, B, C, D, E and F show the PMeFR regeneration processes excited by particulate matters in local polluted air. Here, we present direct dynamic evidence in the flowing air phase (Fig. 5 A, B and C) and static evidence in the particulate matter phase (Fig. 5 D, E and F) of the regeneration of PMeFR excited by particulate matter in local polluted air. Those reactions suggest new regeneration mechanisms for the recycling of PMeFR in local polluted air, especially when the concentration of particulate matter is high in local polluted air (e.g., ~ above 150 $\mu g\,m^{-3}$).

Two possible regeneration mechanisms for the recycling of PMeFR in local polluted air are proposed. The evidence of the regeneration of hydroxyl free radicals excited by particulate matters in local polluted air is elucidated based on the detection results of PMeFR from the Lanzhou. The same phenomenon was also found at monitoring sites set up in Baiyin, Xinning and Beijing. In all the field campaigns in different regions and sources, especially in haze-fog pollution periods and regions, we find PMeFR regeneration can easily be excited by particulate matter. The rapid generation processes of hydroxyl free radicals excited by particulate matter were demonstrated in all the field campaigns.

Obviously, this formation pathway will inevitably become the main pathway of non-traditional formation of hydroxyl free radicals in polluted air. Why does the polluted air produce so many hydroxyl free radicals in the particulate matter phase, and what is the formation mechanism? With these questions in mind, we have studied the formation mechanism of particulate matter based on field studies, laboratory dynamics research and theoretical calculation of quantum chemistry (Such as the formation of free radical adduct reaction pathway and structural optimization and frequency & energy calculations through quantum chemical computing software, Fig. 3 G and H). With the help of actual test data, combined with the idea of catalytic oxidation reaction and the "quasi-adsorption-desorption equilibrium equation"

(Eq. (1-1)) (Mowery et al., 1999; Schmal et al., 2000; Euzen et al., 1999; Fujimoto et al., 1998; Nomura et al., 1998), the possible mechanisms for the generation of hydroxyl free radical from particulate matter phase are proposed and shown below.

$$2OH* \rightleftharpoons H_2O(g) + O* + \square* \qquad (1-1)$$

The square in the equation represent surface hole.

Fig. 6 shows a new mechanism of PMeFR regeneration in the particulate matter phase in local polluted air. Here, we find strong correlation between levels of PMeFR and particulate matter in local polluted air. We confirmed dynamic and static evidence respectively in the air flow phase and the particulate phase of the regeneration of PMeFR excited by particulate matters in local polluted air. The regeneration mechanism of hydroxyl free radicals excited by particulate matters in haze-fog is shown in Fig. 6. In this new significant chemical mechanism (Fig. 6 a), in the particulate matter, a mixed system of inorganic carbon, organic carbon and metal oxide is formed to exert a catalyst-like effect, and an effect similar to a hole-electron pair occurs. The possible regeneration mechanism is described below. The electrons (e^-) in the valence band (A) of particulate matter components can be excited to the conduction band (B), leading to the formation of holes (h^+) in the ground state A band of particulate matters simultaneously. The particulate matters (including metal complexes, organic carbon, inorganic carbon) in local polluted air can promote the electrons transfer and effective separation of electrons (e^-) and holes (h^+) pairs. Furthermore, the excited electrons are then quickly transferred to the surface of the particulate matter. In the meantime, the excited holes are available to react with atmospheric water vapor to produce hydroxyl free radicals. The holes (h^+) excited in the A band upon excitation are readily transferred to the B band of particulate matter. The lifespan of holes is extended, and they excite the PMeFR regeneration process. The holes (h^+) in the A band of particulate matter have enough positive potential to excite hydroxyl radicals, hydroperoxyl radicals, alkyl peroxyl radicals, nitroxyl radicals, and biradical chain reactions of persistent free radicals derived from organic pollutants (Fig. 6 b). The excited electrons (e^-) and holes (h^+) formed e^- - h^+ pairs in particulate matter surface or internal structure. The e^- - h^+ pairs are identified as playing a key role in promoting the explosive increase of PMeFR in sever haze.
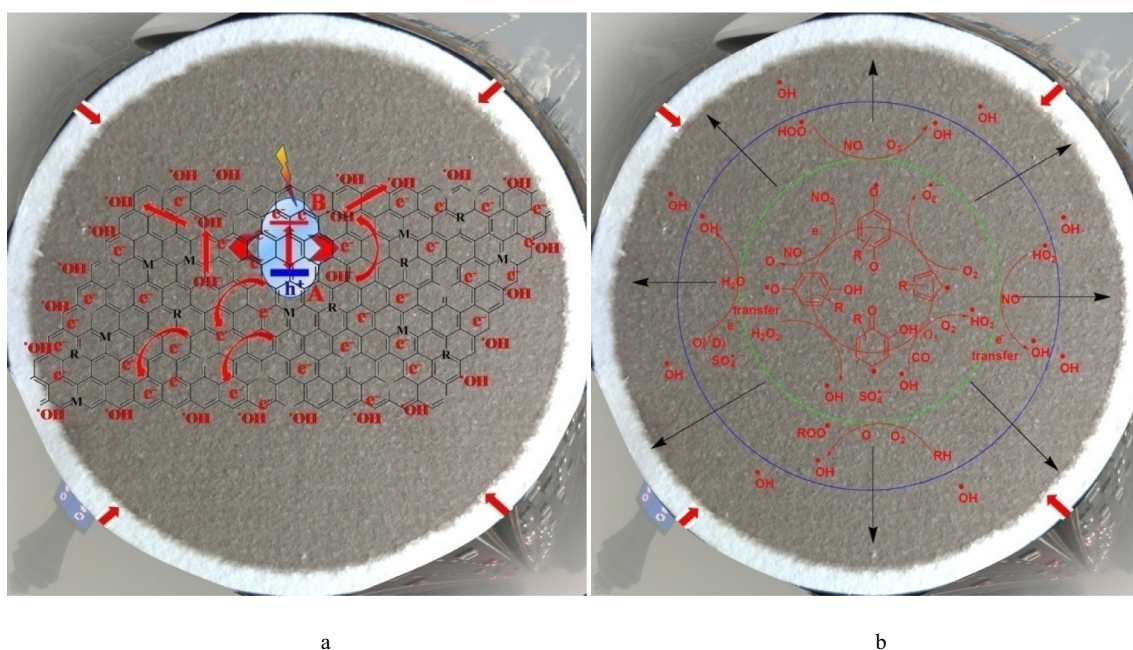

a

b

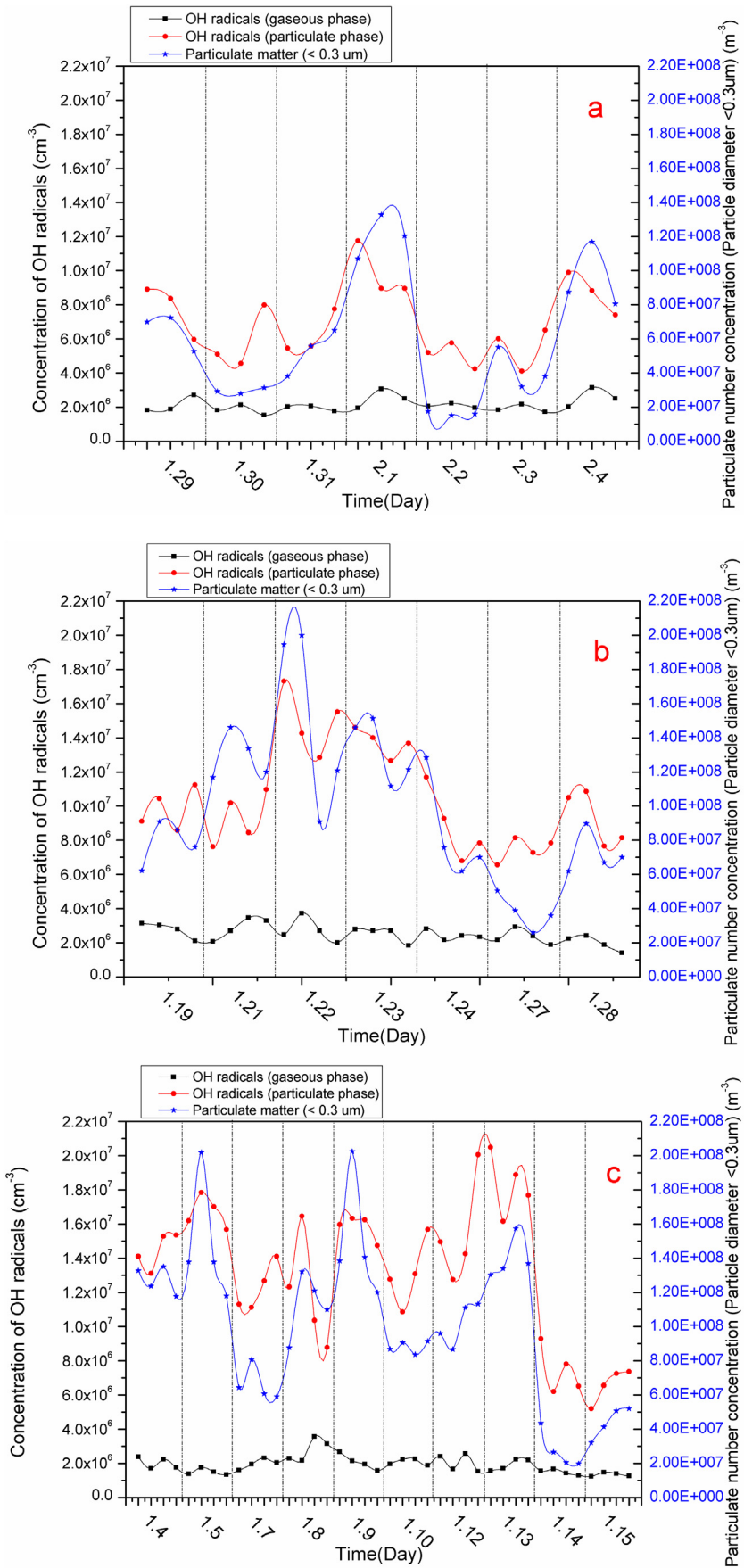Fig. 6. The possible mechanism of PMeFRs regeneration toward the particulate matters in polluted air.

Fig. 7. Summary of correlation between radical concentrations in gas species, particulate phases and particulate number concentration in field observation (a: Thermal power plan, b: Yumen street, c: Chemical street).

Another important possible contribution of PMeFR regeneration maybe comes from the environmentally persistent free radicals (Arangio et al., 2016; Khachatryan et al., 2014; Li et al., 2019) in particulate matter. The environmentally persistent free radicals could further promote the chain reaction of free radicals and ultimately will result in an explosive increase of hydroxyl free radical regeneration. Fig. 6 b shows the chain reaction of PMeFR excited by environmentally persistent free radicals derived from organic pollutants. All the chain reactions will eventually lead to the regeneration of hydroxyl free radicals. The chain reaction cycling of the adsorbed environmentally persistent free radicals was hypothesized as a source for short-lived free radical regeneration (Valavanidis et al., 2005; Valavanidis et al., 2008). The results of field observation showed that the short life and high activity free radicals generated from per milligram of particulate matter (contain persistent free radicals) were three times the expected concentration of free radicals in the gaseous phase, and finally presented in the form of hydroxyl radical regeneration in the overall atmospheric oxidation (Hydroxyl radicals are produced in the chain reaction pathway). The recycling process from particulate matter to hydroxyl radical indicates the existence of a catalytic cycle.

The hydroxyl free radicals were most likely excited to the particulate matter's exterior. Increased PMeFR regeneration results from the synergistic effect of persistent quinoid and/or semiquinone radicals in ambient particulate matters. The direct role of stable environmentally persistent free radicals bound to particulate matter as a generator of short life span free radicals in local polluted air (Gehling et al., 2014; Anderson, 1987; Fang et al., 2013). This is also one of the most important sources of regeneration of free radicals in the air contaminated by secondary fine particles. The formed e^- - h^+ pairs and chain reactions of persistent free radicals derived from organic pollutants in the particulate phase together promote the PMeFR regeneration in the particulate matter phase and become the main potential regeneration mechanism of hydroxyl free radicals. These regenerative pathways and mechanisms have provided new evidence for the presence of higher levels of free radicals at night.

3.3. The summary of correlation among radical concentration in gas species, particulate phases and particulate number concentration

Comprehensive figures have been added in this section to summary the correlation between radical concentrations in gas species, particulate phases and particulate number concentration. The comparison data of the distribution of hydroxyl radicals in the two phases at the actual monitoring site, including Thermal power plant, Yumen street, Chemical street and the corresponding relationship with the concentration of particulate matter (number concentration) have been shown in Fig. 7 a (Thermal power plant), Fig. 7 b (Yumen street) and Fig. 7 c (Chemical street). The TVOC data around the monitoring sites are shown in Table 1.

In order to further explain the distribution trend of free radicals in the gaseous and particulate phases, and to verify the possible trigger mechanism, continuous observations were carried out in the outer filed. Observation sites include Thermal power plant, Yumen street and Chemical street in Xugu of Lanzhou. The observation time was from Jan. 4, 2019 to Feb. 4, 2019. At the same time, the free radicals in the gaseous and particulate phases collected from the same place were compared with the particulate concentration data of atmospheric particulates with a particle size of less than 0.3 µm during the same period. It can be seen that the data of the three sites have a certain positive correlation, especially at some obvious peaks.

Fig. 3a, b and c respectively show the changes of the three groups of data of the sites: Thermal power plant, Yumen street and Chemical street. It can be seen that during the monitoring process, the number of particles concentration value of atmospheric particles with particle size less than 0.3 µm, the signal value of hydroxyl free radicals in the particle phase and the signal value of hydroxyl free radical

Table 1
The TVOC data around the monitoring sites.

Monitoring period		TVOC (µg/m³)	Monitoring period		TVOC (µg/m³)	Monitoring period		TVOC (µg/m³)
1.4	A	276.2	1.14	A	251.0	1.28	A	634.4
	B	286.2		B	196.8		B	588.1
	C	259.5		C	192.5		C	418.5
	D	325.6		D	201.2		D	299.4
1.5	A	234.3	1.15	A	351.5	1.29	A	287.5
	B	269.3		B	321.2		B	258.1
	C	326.0		C	339.0		C	241.5
	D	467.5		D	424.3			
1.7	A	260.0	1.19	A	361.2	1.30	A	273.8
	B	271.8		B	336.2		B	249.4
	C	265.5		C	275.0		C	233.5
	D	270.6		D	330.6			
1.8	A	288.1	1.21	A	369.3	1.31	A	256.3
	B	307.5		B	386.8		B	231.9
	C	277.0		C	304.0		C	248.0
	D	359.3		D	369.4			
1.9	A	338.5	1.22	A	435.0	2.1	A	336.3
	B	355.6		B	310.6		B	326.3
	C	311.5		C	185.0		C	317.5
	D	288.7		D	351.3			
1.10	A	315.5	1.23	A	385.6	2.2	A	410.6
	B	284.3		B	351.9		B	366.3
	C	281.0		C	230.5		C	396.5
	D	443.7		D	425.0			
1.12	A	287.5	1.24	A	324.4	2.3	A	447.5
	B	290.0		B	214.4		B	396.3
	C	279.0		C	181.0		C	374.0
	D	415.6		D	188.1			
1.13	A	294.5	1.27	A	274.4	2.4	A	413.8
	B	284.3		B	243.0		B	410.0
	C	264.0		C	217.0		C	327.5
	D	385.0		D	223.8			

Note: A, 9:00–11:50; B, 11:50–14:00; C, 14:30–17:20; D, 17:20–20:00.

concentration in the gaseous phase all show a wave peak or trough at the same time. The change of signal value of concentration of hydroxyl radical in the gaseous phase is 2–3 h later than the peak time of the former two.

Fig. 3a shows the changes of the three data of petrochemical thermal power plant. On Jan. 29, Feb. 1, Feb. 2, Feb. 3 and Feb. 4, the OH radicals (gaseous phase), OH radicals (particulate phase) and particulate matters (less than 0.3 µm) have obvious positive correlation. Moreover, the signal of hydroxyl radical concentration in the gaseous phase monitored on Jan. 29, Feb. 1, Feb. 3 and Feb. 4 was 2–3 h later than that in the particulate phase at the same time.

Fig. 3b shows the changes of the three data of Yumen street. On Jan. 21, Jan. 22, Jan. 23, Jan. 24, Jan. 28, the OH radicals (gaseous phase), OH radicals (particulate phase) and particulate matters (less than 0.3 µm) have obvious positive correlation. Moreover, the signal of hydroxyl radical concentration in the gaseous phase monitored on Jan. 21, Jan. 22, Jan. 23, Jan. 27 was 2–3 h later than that in the particulate phase at the same time.

Fig. 3c shows the changes of the three data of Chemical street. On Jan. 4, Jan. 5, Jan. 8, Jan. 10, Jan. 12, Jan. 13, and Jan. 15, the OH radicals (gaseous phase), OH radicals (particulate phase) and particulate matters (less than 0.3 µm) have obvious positive correlation. However, the signal delay of hydroxyl radical concentration in the gaseous phase is not obvious.

To sum up, there is a positive correlation between the peak concentration of hydroxyl free radicals in the particulate phase, gaseous phase and particles with particle size less than 0.3 µm.

4. Conclusions

In summary, we have provided dynamic and static evidence of the generation of hydroxyl free radicals excited by secondary particulate matters. We proposed possible hydroxyl free radicals regeneration

mechanisms. A mechanism-1, excited state electrons from the secondary particulate matters excite an electron-hole pairs, and further promotes the production of free radicals in the electron-transfer center of secondary particulate matters collected from petrochemical industrial zone. A mechanism-2, environmentally persistent free radicals from the particulate matters excite chain reactions of hydroxyl free radical and then promote free radicals generation, eventually lead to the regeneration of hydroxyl radicals in particulate matters phase. The possible PMeFR generation mechanisms would play more important roles in the regulation and the control of explosive increase of secondary particulate matters, change of atmospheric oxidative capacity and the nucleation process of fine particles pollution in haze-fog in petrochemical industrial zone.

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