

A new method for quantitatively characterizing atmospheric oxidation capacity

CHENG YanLi^{1,2}, WANG XueSong^{1†}, LIU ZhaoRong¹, BAI YuHua¹ & LI JinLong¹

¹ College of Environmental Sciences and Engineering, Peking University, Beijing 100871, China;

² Chinese Academy of Meteorological Sciences, Beijing 100081, China

Based on atmospheric chemical kinetics, the rate constant of overall pseudo-first order oxidation removal of gaseous pollutants ($K_{por,T}$) is proposed to characterize the atmospheric oxidation capacity in troposphere. Being a quantitative parameter, $K_{por,T}$ can be used to address the issues related to atmospheric oxidation capacity. By applying this method, the regional oxidation capacity of the atmosphere in Pearl River Delta (PRD) is numerically simulated based on CBM-IV chemical mechanism. Results show the significant spatio-temporal variation of the atmospheric oxidation capacity in PRD. It is found that OH initiated oxidations, heterogeneous oxidation of SO₂, and photolysis of aldehydes are the three most important oxidation processes influencing the atmospheric oxidation capacity in PRD.

atmospheric oxidation capacity, quantitative characterization, air quality model, pseudo-first order oxidation reaction rate constant

A large amount of pollutants emitted by natural processes and human activities to the atmosphere, such as sulfur dioxide (SO₂), nitrogen oxides (NO_x), carbon monoxide (CO) and hydrocarbons (RH), are converted from reduced forms to oxidized forms, such as sulfate, nitrate, carbon dioxide and various oxidized organics by oxidation processes, and then removed from the atmosphere through dry and wet deposition. These oxidation reactions are sometimes referred to as atmospheric cleansing process, and the rate of cleansing trace substances by oxidations indicates atmospheric oxidation capacity^[1-4], which is the essential feature of the atmosphere^[5].

In recent years, along with rapid economic development and urbanization in China, regional air pollution complex appears in more and more fast developing areas^[6-8]. Atmospheric oxidation capacity is the driving force of air pollution, and also influences climate change as well as human health^[9]. Atmospheric oxidation capacity is a key point in many researches on air pollution complex, therefore, it is very important to quantitatively characterize the oxidation capacity in troposphere.

In a sense, oxidants determine the lifetimes and contents of trace substances in the atmosphere, and the concentrations of oxidants are usually used as the measure of atmospheric oxidation capacity^[1,10]. Important oxidants involved in the tropospheric chemical processes include ozone (O₃), OH radical, peroxy radicals (HO₂ and RO₂), peroxides (H₂O₂ and ROOH), as well as NO₃ radical and halogen radicals. Because of reacting with hundreds of species, OH is referred to as the “tropospheric vacuum cleaner” and is usually taken as the indicator of atmospheric oxidation capacity. Some techniques have been developed to determine ambient OH concentrations^[4,11-15]. Besides, total oxidant Ox (approximately equal to O₃+NO₂) is an alternative way to indicate atmospheric oxidation capacity. OH plays a key role in tropospheric daytime chemistry, while NO₃, N₂O₅ and O₃ become important in nighttime chemistry^[16]. However, it is quite difficult to accurately determine the

Received June 29, 2007; accepted November 20, 2007

doi: 10.1007/s11426-008-0119-z

†Corresponding author (email: xswang@pku.edu.cn)

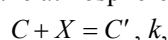
Supported by the National Basic Research Program of China (Grant Nos: 2005CB422204, 2002CB410802, and 2002CB410801)

spatio-temporal variations of OH and NO₃ due to their high chemical reactivities, low concentrations and short lifetimes in ambient air. Therefore, it is especially important to explore other methods to quantitatively characterize atmospheric oxidation capacity. In this paper, we propose a new method for the quantitative characterization of atmospheric oxidation capacity based on the principles of atmospheric chemical kinetics, and then conduct a preliminary application in the numerical simulation study on regional air pollution in Pearl River Delta (PRD).

1 Methodology

If oxidation reactions removing reduced trace substances in tropospheric atmosphere are referred to as the oxidation removal process of the atmosphere, the rate of the removal process or the average lifetime of reduced species in the atmosphere may be used as a measure of the strength of atmospheric oxidation capacity^[17]. The strong oxidation capacity of the atmosphere would result in the fast removal, i.e. the short residence time in the air, of reduced species.

The elementary oxidation reaction removing a reduced species, C , in the atmosphere is given below:



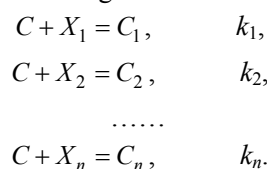
where X is the oxidant in the reaction, C' represents the product, and k is the reaction rate constant. The time rate of change of concentration of C is calculated as

$$\frac{dC}{dt} = -k[X][C]. \quad (1)$$

Consider the above removal of C as a pseudo-first order process, $k[X]$ is the rate constant of the pseudo-first order oxidation reaction, expressed as K_{por} , of which the reciprocal is the lifetime of C in the atmosphere (also called residence time, expressed as τ),

$$K_{por} = k[X] = \frac{1}{\tau}. \quad (2)$$

If C reacts with more than one kind of oxidants in the atmosphere, the following hold:



Then the overall removal rate of C by all the above oxidation reactions in the atmosphere is equal to the sum

of every specific oxidation reaction rate:

$$\frac{d[C]}{dt} = -\sum_{i=1}^n k_i[X_i][C], \quad (3)$$

where X_i represents the i th oxidant, and k_i is the rate constant of the i th oxidation reaction. Consider the removal of C as a pseudo-first order process:

$$\frac{d[C]}{dt} = -K_{por}[C]. \quad (4)$$

By combining eq. (3) with eq. (4), the rate constant of the overall pseudo-first order oxidation reaction removing C is obtained:

$$K_{por} = \sum_{i=1}^n k_i[X_i]. \quad (5)$$

In general, more than one kind of reduced species exists in the atmosphere. The total concentration of reduced species in the atmosphere, $[C]_T$, is calculated as

$$[C]_T = \sum_{j=1}^m [C_j], \quad (6)$$

where C_j represents the j th reduced species, and m is the number of kinds of reduced species. In ambient air, the overall removal rate of all reduced species by oxidation reactions is equal to the sum of that of every specific reduced species:

$$\begin{aligned} \frac{d[C]_T}{dt} &= \sum_{j=1}^m \left\{ \frac{d[C_j]}{dt} \right\} = \sum_{j=1}^m \left\{ -K_{por,j} \cdot [C_j] \right\} = \\ &= -\sum_{j=1}^m \left\{ [C_j] \cdot \sum_{i=1}^n k_{ij}[X_i] \right\}, \end{aligned} \quad (7)$$

where k_{ij} represents the rate constant of the reaction of the j th species with the i th oxidant, and $K_{por,j}$ that of the pseudo-first order oxidation reaction removing the j th species.

Consider the overall removal of all the above reduced species as a pseudo-first order process:

$$\frac{d[C]_T}{dt} = -K_{por,T} \cdot [C]_T = -K_{por,T} \cdot \sum_{j=1}^m [C_j], \quad (8)$$

where $K_{por,T}$ represents the rate constant of overall pseudo-first order oxidation reaction removing reduced species in the atmosphere. Combining eqs. (7) and (8), we obtain

$$K_{por,T} = \frac{\sum_{j=1}^m \left\{ [C_j] \cdot \sum_{i=1}^n k_{ij}[X_i] \right\}}{\sum_{j=1}^m [C_j]}. \quad (9)$$

According to eq. (9), the rate constant of overall

pseudo-first order oxidation reaction ($K_{por,T}$) is essentially the concentration weighted average of the pseudo-first order oxidation removal rate constant ($K_{por,j}$) of every specific reduced species (C_j). $K_{por,T}$ directly describes the rate of the removal of trace substances by oxidations in the atmosphere and reflects the atmospheric oxidation capacity.

$K_{por,T}$ describes the atmospheric oxidation capacity from three aspects. First, $K_{por,T}$ reflects the influence of ambient oxidant concentrations on the oxidation capacity. According to eq. (9), $K_{por,T}$ increases as oxidant concentrations (i.e. $[X_i]$) increase, which is consistent with the method using the concentrations of one or several kinds of oxidants, such as OH or O_x, to indicate atmospheric oxidation capacity. Second, the atmospheric oxidation capacity depends on not only the concentrations of oxidants, but also the kinetic mechanism of oxidation reactions. $K_{por,T}$ also describes the chemical processes and kinetic features of the removal of trace substances (through k_{ij}). Since oxidation rate constants (i.e. k_{ij}) are affected by temperature and radiation, $K_{por,T}$ actually involves the influence of meteorological conditions on atmospheric oxidation capacity. Third, even with the same oxidants (composition and concentrations) and meteorological conditions, the atmospheric oxidation removal processes may vary greatly with the composition of reduced substances (e.g. urban ambient air with elevated NO_x and VOCs emitted by a large amount of anthropogenic sources, polluted air with high level of SO₂, or air in remote areas with much biogenic VOCs). $K_{por,T}$ can reflect the influence of the composition of reduced species on atmospheric oxidation capacity. Therefore, $K_{por,T}$ is a more comprehensive physical parameter to characterize atmospheric oxidation capacity.

In order to obtain $K_{por,T}$, the concentrations of oxidants and reduced substances as well as the rate constants of oxidation reactions are needed. However, measuring ambient concentrations of some species like reactive free radicals is quite difficult. At present, air quality modeling can solve the above problem. While conducting numerical simulation, the adopted numerical model, chemical mechanism, as well as oxidants and reduced species involved in the calculation will influence the value of $K_{por,T}$; however, when the above conditions are fixed, $K_{por,T}$ can be used as a measure to describe the spatio-temporal variation of the atmospheric oxidation capacity on global, regional or urban scales. According to eq. (9), relative contributions by different

oxidants, different oxidation processes, or different reduced substances may be calculated to reveal their relative importance to atmospheric oxidation capacity.

The factors influencing atmospheric oxidation capacity are quite complicated, some oxidation processes, such as heterogeneous oxidation reactions, are still under research. The calculation of $K_{por,T}$, can easily involve newly discovered oxidation processes, which shows the compatibility of the proposed method to new oxidation mechanisms.

In this paper, a two-dimensional air quality model is adopted to simulate $K_{por,T}$, and then $K_{por,T}$ is used to study the atmospheric oxidation capacity on a region scale. $K_{por,T}$ has dimensions of reciprocal of time, and is given in units of min⁻¹ in the following discussion. For the convenience of quantifying atmospheric oxidation capacity, the value of $K_{por,T}$ is multiplied by 10⁴, expressed as K'_{por} :

$$K'_{por} = 10000K_{por,T} \quad (10)$$

2 A preliminary application in PRD

The rapid economic development and serious air pollution problems make PRD an important area focused by many air quality researches in China. In recent years, PRD has been considered a typical region in China with air pollution complex which characterized by co-existence of high concentrations of O₃ and PM_{2.5} as well as severe visibility degradation. In this paper, based on the simulation of the air pollution complex in PRD, the method developed in this paper (see Section 1) is applied to study the features of atmospheric oxidation capacity in this area.

The horizontal modeling domain selected in PRD is a region measuring 225 km × 225 km with the origin point of 113°36'25"E, 22°4'19"N and the grid resolution of 15 km. The simulation period covers from October 18 to October 24, 2004 with the first two days as spin-up.

2.1 A brief model description

The 2-D air quality model adopted in this paper has been introduced in detail elsewhere^[18]. The revised Carbon Bond IV (CBM-IV) chemical mechanism^[19] is used to describe gaseous chemical reactions, including the oxidation processes removing reduced pollutants such as CO, SO₂, NO_x, and primary and secondary hydrocarbons. A total of 15 reduced species and 7 oxidation pathways are listed in Table 1. Preparations of source emissions and meteorological input data as well as ini-

Table 1 Reduced species and the removal pathways by oxidations in CBM-IV mechanism

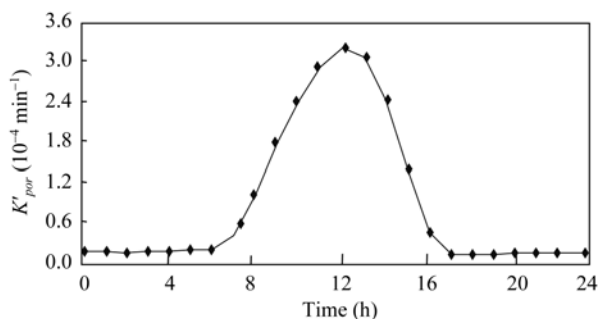
Species ^{a)}	Photolysis of aldehydes	Oxidations by OH	Oxidations by O ₃	Oxidations by NO ₃	Oxidations by O	Oxidations by NO ₂	Other oxidations ^{b)}
NO ₂		√					
CO		√					
PAR		√					
ETH		√	√		√		
OLE		√	√	√	√		
FORM	√	√		√	√		
ALD2	√	√		√	√		
XYL		√					
TOL		√					
ISOP		√	√	√	√	√	
APIN		√	√				
BPIN		√	√	√			
CRP		√					
HUM		√					
SO ₂		√					√

a) PAR stands for paraffin, ETH ethylene, OLE the alkenes other than ethylene, FORM formaldehyde, ALD2 the aldehydes other than formaldehyde, XYL xylenes, TOL toluene, ISOP isoprene, and APIN, BPIN, CRP and HUM represent α -pinene, β -pinene, phellandrene and humulene emitted by biogenic sources, respectively. b) Heterogeneous oxidation reaction of SO₂^[19].

tial and boundary conditions for the 2-D air quality model are also described in [18].

2.2 Results

2.2.1 Diurnal variation of K'_{por} in PRD. The above air quality model is used to obtain the value of K'_{por} from October 20 to October 24, 2004 in PRD. The average diurnal variation of K'_{por} during the episode on domain-wide scale is then calculated (see Figure 1). K'_{por} increases at 6:00 LST, and reaches peak value around 12:00 LST, then gradually decreases to a relatively low level at 17:00 LST, and keeps the low level during the nighttime. The maximum hourly value of K'_{por} in a whole day is $3.2 \times 10^{-4} \text{ min}^{-1}$.

**Figure 1** Diurnal variation of K'_{por} in PRD.

2.2.2 Spatial distribution of K'_{por} in PRD. The simulated results on October 22, 2004 are taken as an example to characterize the spatial distribution of K'_{por} in PRD (Figure 2). The value of K'_{por} is very low in the whole domain at 3:00 LST, and experiences a certain increase in Guangzhou, Dongguan, Shenzhen, Hong Kong, Zhuhai, Zhongshan and Foshan at 9:00 LST, reaches peak value of the whole day at noon. The K'_{por} is found to be highest in the coastal areas of southern PRD and to be low in the northeast and northwest. Hereafter, K'_{por} gradually decreases to a very low level in the evening. In general, K'_{por} is higher in southern PRD than in northern areas in the daytime.

The spatio-temporal variation of K'_{por} in PRD is related to that of oxidants in ambient air. The simulated results show that the peak concentration of OH radical usually appears at noon (Figure 3(a)), and that of ozone occurs around 14:00 LST (Figure 3(b)). Because of the large emissions of precursor pollutants in Guangzhou, Shenzhen, Dongguan and Hong Kong and the transport by dominant northerly wind, the elevated OH and ozone usually occur in Pearl River Estuary and southern coastal areas during the episode, while the concentrations are relative low in northern areas of PRD. The spatio-temporal variation of K'_{por} is consistent with that of

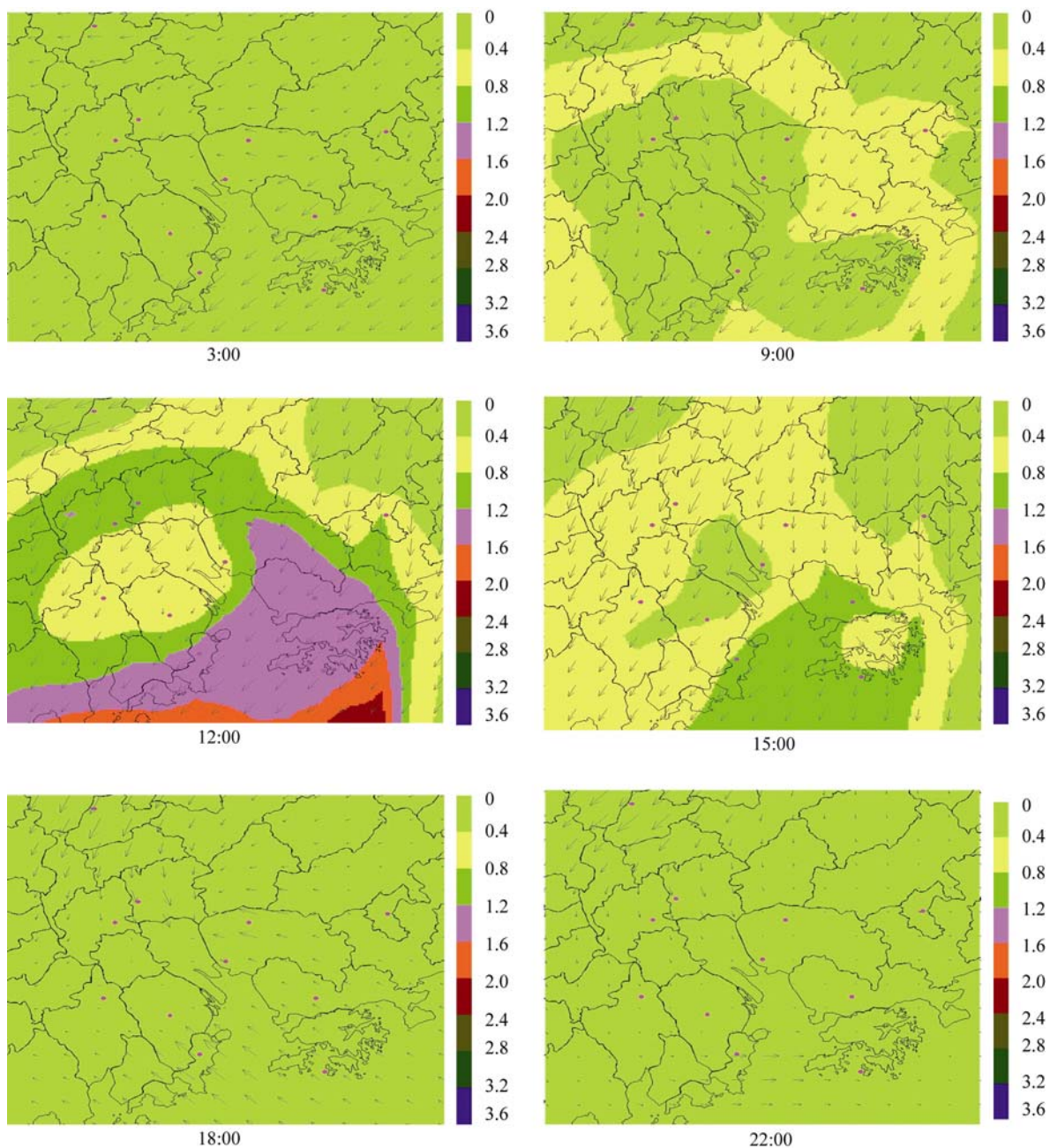


Figure 2 Spatial distribution of K'_{por} in PRD on October 22, 2004 (Unit: 10^{-4} min^{-1}).

oxidants, suggesting the influences of reactive oxidants on K'_{por} .

2.2.3 Influences of oxidants on K'_{por} . Figure 4 shows the time series of domain-wide average K'_{por} and simulated concentrations of OH, NO_3 , O, O_3 and O_x , to assess the influences of different oxidants on atmospheric oxidation capacity. Both K'_{por} and the concentrations of OH and O reach the corresponding peaks at around 12:00 LST, while peak concentrations of O_3 usually ap-

pear at around 14:00 LST. The peak O_x in the daytime occur with the similar timing as that of O_3 , and O_x also show high levels in the nighttime due to the accumulation of NO_2 . The elevated NO_3 generally appear at nightfall.

The contributions of seven kinds of oxidation reactions to K'_{por} are calculated by applying Counter Species Method^[20], shown in Table 2. In PRD, the oxidation reactions initiated by OH radicals are the most important

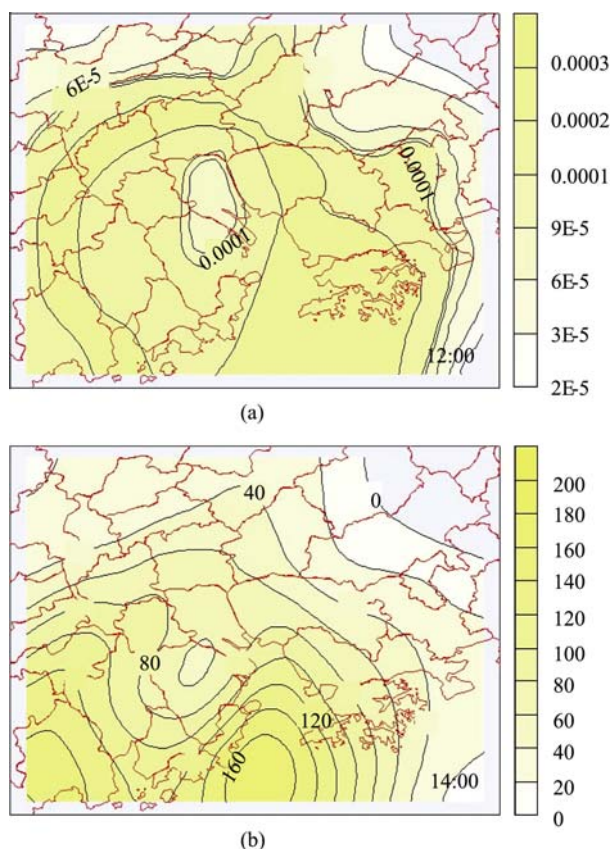


Figure 3 Spatial distributions of elevated concentrations of oxidants in PRD on October 22, 2004 (Unit: $\text{mg}\cdot\text{m}^{-3}$). (a) OH at 12:00 LST; (b) O_3 at 14:00 LST.

with an average contribution of 76% to K'_{por} , followed

Table 2 Contributions of seven kinds of oxidations to K'_{por} (%)

Sites	Photolysis of aldehydes($h\nu$)	Oxidations by OH	Oxidations by O_3	Oxidations by NO_3	Oxidations by O	Oxidations by NO_2	Other oxidations
Luhu	12.9	70.1	1.6	0.2	0.03	0.002	15.0
Conghua	13.7	82.6	2.7	0.3	0.01	0.001	0.7
Jinguowan of Huizhou	15.3	80.9	2.4	0.2	0.01	0	1.2
Wanqingsha	14.9	64.8	1.7	0.4	0.05	0.002	17.9
Quanwan	12.8	78.9	1.3	0.3	0.02	0.001	6.6
Dongyong	13.2	80.4	1.2	0.4	0.01	0.001	4.8
Tamen	11.8	82.5	1.3	0.2	0.01	0	4.2
Monitoring station of Guangdong	13.0	68.9	1.6	0.2	0.03	0.002	16.1
Xinken	14.9	69.4	1.6	0.5	0.04	0.001	13.5
Dongguan	11.9	79.6	1.8	0.5	0.01	0.001	6.1
Foshan	12.2	70.8	1.6	0.3	0.02	0.001	15.2
Huizhou	12.6	83.4	1.8	0.2	0.01	0	2.1
Jiangmen	12.9	74.5	1.7	0.6	0.02	0.001	10.2
Zhongshan	14.1	78.4	1.6	0.6	0.03	0.001	5.4
Zhuhai	13.4	81.9	1.2	0.5	0.01	0	2.8
Average	13.3	76.4	1.8	0.4	0.02	0.001	8.1

by photolysis of aldehydes with the contribution of 13%, and heterogeneous oxidation reaction of SO_2 with the contribution of 8% to K'_{por} , while all the contributions of oxidations by O_3 , NO_3 , O and NO_2 are less than 3%. The results suggest the significant differences in contributions of different oxidation processes to atmospheric oxidizing capacity, and are helpful to explain the occurrence of peak K'_{por} at noon. In general, the noontime is the period having the strongest solar radiation associated with the most active photochemical reactions in a day, in which OH radicals reach peak levels due to the fast generation from photolysis of O_3 , HONO and aldehydes. As a result of significant contributions of oxidations initiated by OH and photolysis of aldehydes, ambient air usually shows the strongest oxidation capacity in the noontime.

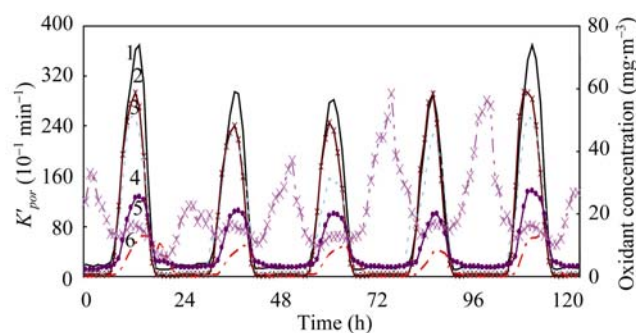


Figure 4 Temporal variations of domain-wide average K'_{por} and oxidants. 1, $K'_{por} \times 100$; 2, $\text{OH} \times 10^7$; 3, $\text{O} \times 5 \times 10^7$; 4, $\text{O}_3/5$; 5, $\text{O}_x/30$; 6, $\text{NO}_3 \times 5 \times 10^5$

In addition, the simulated results indicate the difference in relative importance of some kind oxidation to K'_{por} between daytime and nighttime (Figure 5). The oxidations by OH radicals dominate the atmospheric oxidation capacity in the daytime, while the heterogeneous oxidation of SO_2 becomes more important to K'_{por} in the nighttime. However, the absolute K'_{por} in the nighttime is an order of magnitude lower than that in the daytime.

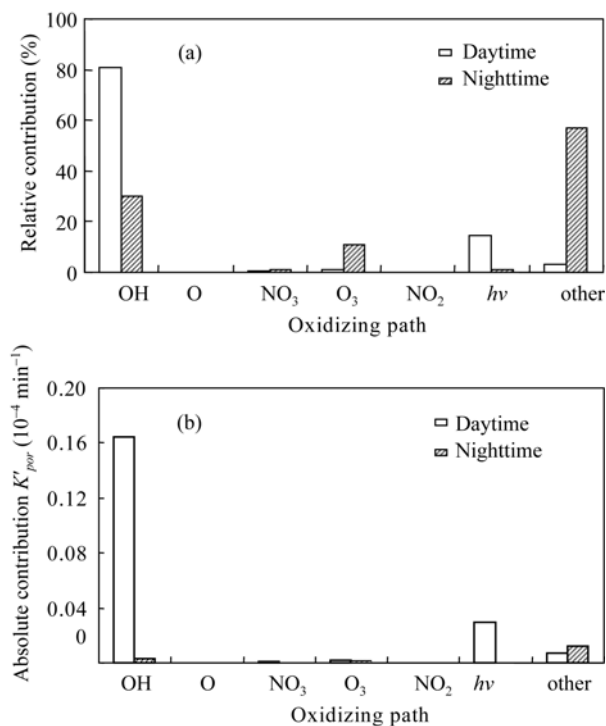


Figure 5 Contributions of seven kinds of oxidations to K'_{por} . (a) Relative contribution; (b) absolute contribution.

Various oxidations also show different relative importance to K'_{por} at different observation sites (Table 2). Especially, heterogeneous oxidation of SO_2 shows significantly different contributions in rural sites (e.g. Conghua, Jinguowan and Huizhou), urban sites (e.g. Guangdong Provincial Environment Monitoring Station) and downwind sites (e.g. Xinken and Wangqingsha), among which, the relative contribution in Conghua is smallest, only accounting for 0.7 percent, while that in Wangqingsha is 17.9 percent of K'_{por} .

3 Discussion

(1) Quantitative characterization of atmospheric oxidation capacity has been a difficult problem for quite a

long time, and $K_{por,T}$ is proposed as an alternative method to solve the above problem in this paper. The simulated results have shown that $K_{por,T}$ could be used to describe the spatio-temporal variation of the atmospheric oxidation capacity. Being a preliminary application, the oxidation processes removing SO_2 , CO, primary and secondary hydrocarbons are taken into account in the calculation of $K_{por,T}$. Due to the complexity of nitrogen oxides in chemical reactions, only the removal process of NO_2 oxidized by OH is considered in the application. The following work will involve more oxidation processes in characterizing atmospheric oxidation capacity.

(2) The results show that both peak $K_{por,T}$ and peak OH appear in the noontime, and the OH initiating oxidations play the most important role to $K_{por,T}$, which suggests that the proposed method here is consistent with the one using OH concentration to indicate atmospheric oxidation capacity. On the other hand, heterogeneous oxidation of SO_2 is the most important oxidation process in the nighttime, moreover, photolysis of aldehydes and heterogeneous oxidation reaction of SO_2 contribute more than 20 percent of regional average $K_{por,T}$, which suggests that $K_{por,T}$ gives us more comprehensive descriptions of atmospheric oxidation capacity than other methods.

(3) In this paper, only a five-day simulation on $K_{por,T}$ in PRD is conducted. In the following researches, more applications of the proposed method will be carried out to study the features of $K_{por,T}$ in different regions and in different seasons to understand in depth the relationship between atmospheric oxidation capacity and ambient air pollution complex.

4 Conclusions

(1) $K_{por,T}$, the rate constant of overall pseudo-first order oxidation removal of gaseous pollutants in tropospheric atmosphere, is proposed to characterize atmospheric oxidation capacity. Being a quantitative parameter, $K_{por,T}$ can be used to address the issues related to atmospheric oxidation capacity.

(2) In the preliminary application in PRD, it is found that $K_{por,T}$ has significant spatio-temporal variation, the peak value of which usually appears in the noontime, similar to the timing of occurrence of peak OH, and the elevated value of which also has similar spatial distribu-

tion to that of elevated OH and O₃. Among various oxidation processes, the OH initiating oxidations are the most important to atmospheric oxidation capacity in PRD, accounting for 76 percent of regional average $K_{por,T}$, followed by photolysis of aldehydes and heterogeneous oxidation of SO₂ with the contribution of 13% and 8% to $K_{por,T}$, respectively. Other processes only

explain a little portion of $K_{por,T}$. The OH initiating oxidations dominate the daytime oxidizing capacity, while the heterogeneous oxidation of SO₂ plays an important role in the nighttime.

The authors thank Panyu Meteorological Bureau for providing the meteorological data and Guangdong Provincial Center for Environmental Monitoring for providing source emission data.

- 1 Thompson A M. The oxidizing capacity of the Earth's atmosphere: Probable past and future changes. *Science*, 1992, 256: 1157–1165
- 2 Prinn G R. Ozone, hydroxyl radical and oxidative capacity. *Treatise Geochem*, 2003, 4: 1–19
- 3 Muller J F, Vinckier C, Peeters J, Arijis E. Anthropogenic and biogenic influences on the oxidation capacity of the atmosphere. *SPSD II-Part 2- Global Change, ecosystems and biodiversity*. 2005
- 4 Bloss W J, Evans M J, Lee J D, Sommariva R, Heard D E, Pilling M J. The oxidative capacity of the troposphere: Coupling of field measurements of OH and a global chemistry transport model. *Faraday Discuss*, 2005, 130: 425–436
- 5 Levy H. Normal atmosphere: large radical and formaldehyde concentrations predicted. *Science*, 1971, 173: 141–143
- 6 Zhang Y H, Shao K S, Tang X Y, Li J L. The study of urban photochemical smog pollution in China (in Chinese). *Acta Scientiarum Naturalium, Universitat is Pekinensis*, 1998, 34(2-3): 392–400
- 7 Wang S L, Zhang Y H, Zhong L J, Li J L, Yu Q. Interaction of urban air pollution among cities in Zhujiang Delta (in Chinese). *Chin Environ Sci*, 2005, 25(2): 133–137
- 8 Shao M, Tang X Y, Zhang Y H, Li W J. City clusters in China: Air and surface water pollution. *Front Ecol Environ*, 2006, 4(7): 353–361
- 9 Zhu T. *Air Pollution Complex at Urban and Regional Scale (Chemistry Progress Series—Environmental Chemistry)*. Beijing: Chemical Industry Press, 2005
- 10 Jacob D. Heterogeneous chemistry and tropospheric ozone. *Atmos Environ*, 2000, 34: 2132–2159
- 11 Holland F, Aschmutat U, Hessling M, Hofzumahaus A, Ehhalt D H. Highly time resolved measurements of OH during the POPCORN using laser-induced fluorescence spectroscopy. *J Atmos Chem*, 1998, 31: 205–225
- 12 Mauldin III R L, Frost G J, Chen G, Tanner D J, Prevot A S H, Davis D D, Eisele F L. OH measurements during the first aerosol characterization experiment (ACE 1): Observations and model comparisons. *J Geophys Res*, 1998, 103(D13): 16713–16729
- 13 Pan X M, Chen S M, Hou H Q. Determination of OH free radical concentration in atmosphere (in Chinese). *Shanghai Environ Sci*, 1999, 18(2): 59–61
- 14 Ren X R, Shao K S, Tang S Y. Measurement of gas-phase OH using liquid phase scrubbing and high performance liquid chromatography (in Chinese). *Environ Chem*, 2001, 20(1): 81–85
- 15 Shao M, Ren X R, Wang H X, Zeng L M, Zhang Y H, Tang X Y. Quantitative relationship between production and removal of OH and HO₂ radicals in urban atmosphere. *Chin Sci Bull*, 2004, 49(21): 2253–2258
- 16 Platt U, Winer A M, Biermann H W, Atkinson R, Pitts Jr J N. *Environ Sci Technol*, 1984, 18: 365–369
- 17 Prinn G R. The cleansing capacity of the atmosphere. *Ann Rev Environ Resour*, 2003, 28: 29–57
- 18 Cheng Y L, Bai Y H, Li J L, Liu Z R. A numerical simulation study of contribution of various anthropogenic sources to ozone formation in Pearl River Delta region. *Acta Scientiae Circumstantiae*, 2008, 28(4): 791–798
- 19 Gery M W, Whitten G Z, Killus J P. Development and testing of CBM-IV for urban and regional modeling. U S Environmental Protection Agency, EPA-600/3-88-012, 1988
- 20 Joseph A L, Seinfeld J H. Analysis of the characteristics of complex chemical reaction mechanisms: application to photochemical smog chemistry. *Environ Sci Tech*, 1984, 18: 280–287