



Measurement of gas-phase total peroxides at the summit of Mount Tai in China

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ARTICLE INFO

Article history:

Received 10 July 2008

Received in revised form

3 December 2008

Accepted 15 December 2008

Keywords:

Photochemical production

Gas-phase peroxides

Principal component analysis

Acid rain

Mt. Tai

ABSTRACT

Measurement of ambient gas-phase total peroxides was performed at the summit of Mount Tai (Mt. Tai, 1534 m above sea level) in central-eastern China during March 22–April 24 and June 16–July 20, 2007. The hourly averaged concentration of peroxides was 0.17 ppbv (± 0.16 ppbv, maximum: 1.28 ppbv) and 0.55 ppbv (± 0.67 ppbv, maximum: 3.55 ppbv) in the spring and summer campaigns, respectively. The average concentration of peroxides at Mt. Tai, which is in a heavily polluted region, was much lower than hydrogen peroxide measurements made at some rural mountain sites, suggesting that significant removal processes took place in this region. An examination of diurnal variation and a correlation analysis suggest that these removal processes could include chemical suppression of peroxide production due to the scavenging of peroxy and hydroxy radicals by high NO_x , wet removal by clouds/fogs rich in dissolved sulfur dioxide which reacts quickly with peroxides, and photolysis. These sinks competed with photochemical sources of peroxides, resulting in different mean concentrations and diurnal pattern of peroxides in the spring and summer. A principal component analysis was conducted to quantify the major processes that influenced the variation of peroxide concentrations. This analysis shows that in the spring photochemical production was an important source of peroxides, and the major sink was scavenging during upslope transport of polluted and humid air from the lower part of the planetary boundary layer (PBL) and wet removal by synoptic scale clouds. During the summer, highly polluted PBL air (with high NO_x) was often associated with very low peroxides due to the chemical suppression of HO_2 by high NO_x and wet-removal by clouds/fogs in this sulfur-rich atmosphere, especially during the daytime. Higher concentrations of peroxides, which often appeared at mid-nighttime, were mainly associated with subsidence of air masses containing relatively lower concentrations of NO_y .

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1. Introduction

Peroxides (hydrogen peroxide and organic hydroperoxides) are products of photochemistry in both clean and polluted atmosphere. They are present in both gas and aqueous phase and play an important role in aqueous phase chemistry (Lazrus et al., 1986; Claiborn and Aneja, 1991). Among the total peroxides, hydrogen peroxide (H_2O_2) is a primary component, accounting for 70–90% of

the total peroxides (Lazrus et al., 1986; Heikes, 1992; Tanner and Schorran, 1995). Due to its high solubility in water with a Henry's law constant of $\sim 10^5 \text{ M atm}^{-1}$, H_2O_2 plays a key role in the oxidation of SO_2 to sulfate in clouds and aqueous aerosols (Penkett et al., 1979; Martin and Damschen, 1981; Lee et al., 1986; Weathers et al., 1986; Lind et al., 1987; Dutkiewicz et al., 1995; Husain et al., 2000; Rattigan et al., 2000). This is especially true when pH is 4.5 or lower and other aqueous S(IV) oxidation pathways become slow. Therefore H_2O_2 is closely linked to acid rain and global climate change via its role in the formation of sulfate (Charlson et al., 1992; Lelieveld and Heintzenberg, 1992). Moreover, peroxides are strong oxidants, like ozone, and can damage vegetation (Hewitt et al., 1990; Hewitt and Terry, 1992).

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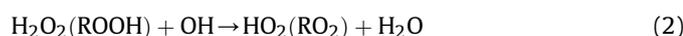
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Peroxides are mainly formed during gas-phase photochemical processes. The following reaction (1) is believed to be the principal gas-phase source of peroxides:



It shows that H_2O_2 is produced through the bimolecular combination of HO_2 , and when organic peroxy radical (RO_2) reacts with hydroperoxy radical (HO_2), organic peroxides are formed. In polluted air, photolysis of formaldehyde (HCHO) is the major source of HO_2 radicals (Calvert and Stockwell, 1983), whereas in the pristine atmosphere HO_2 is mainly formed by the photolysis of ozone (Kleinman, 1986). H_2O_2 and organic peroxides can also be formed from non-photochemical reaction of O_3 or NO_3 radical with biogenic hydrocarbons, e.g., isoprene, alkenes and terpenes (Becker et al., 1990, 1993; Hewitt and Kok, 1991; Simonaitis et al., 1991; Sauer et al., 1999).

Major sinks of peroxides are heterogeneous loss (cloud scavenging, wet and dry deposition) and gas-phase reactions involving OH radical (reaction (2)) and photolysis (reaction (3))



Atmospheric gas-phase H_2O_2 has been extensively measured in the past decades (Sakugawa et al., 1990; Sakugawa and Kaplan, 1993; Watanabe et al., 1995, 1996; Balasubramanian and Husain, 1997; Weinstein-Lloyd et al., 1998; Das and Husain, 1999; Lee et al., 2000 and references therein; Takami et al., 2003; Sówka et al., 2004). The gas-phase H_2O_2 concentrations ranged from the detection limits of the peroxide analyzers (typically 20–50 pptv) to several ppbv. Some measurements of H_2O_2 and organic peroxides were reported in urban Beijing and Guangzhou in China (Qi et al., 1998; Zhang et al., 2001; Zuo et al., 2003; Hua et al., 2008) and also at rural Mount Lushan (Su et al., 1989) in southern China and at remote Mount Waliguan (Tang et al., 2002) in western China.

As part of China's National Basic Research Program (the 973 Program) on acid rain pollution and control, we conducted two intensive measurements of trace gases, aerosols, and cloud and rain water composition at the summit of Mount Tai (Mt. Tai, 36.251° N, 117.101° E, 1534 m above sea level) in central-eastern China in spring and summer of 2007. The experiments aimed to characterize the photochemistry, gas-particle-cloud interactions, and their impacts on acid rain in eastern China. Shandong Province, where Mt. Tai is situated, has the highest emission of SO_2 in China (~1967 Gg per year, representing approximately 10% of total emission in China) (http://www.cgrrer.uiowa.edu/EMISSION_DATA/anthro/table/so2_2000_final.htm). Being the highest point in the

North China Plains where high concentrations of ozone and acid rain have been observed (Gao et al., 2005; Li et al., 2007; Ding et al., 2008; Wang et al., 2008), the summit of Mt. Tai provides a unique place to study regional/long-range transport, and cloud processes related to photochemical and acid rain pollution. In this work, we analyze observations of gas-phase peroxides from the two-phase experiments at the summit of Mt. Tai. We first report observed concentration ranges of peroxides and their relation to other relevant trace gases, and then discuss the major chemical and dynamical processes affecting peroxide concentrations and their variability.

2. Experiment description

2.1. Measurement site and general weather condition

The experiment was conducted at the Meteorological Observatory located on the summit of Mt. Tai (in Fig. 1). The site overlooks the city of Tai'an (population: ~500,000) 15 km to the south. The city of Ji'nan (capital of Shandong province, population: 2.1 million) is situated 60 km to the north. As a famous tourism spot, Mt. Tai receives a large number of visitors in the summer months (June–September), and there are some local emissions from small restaurants and temples. Access to the mountain summit, however, is by cable car or foot. No roads or vehicles are present. Our measurement site is situated in the less frequently visited eastern part of the summit away from most of the local pollution sources. The same site has been used for a pilot study of ozone and for three-year sampling of rainwater chemistry (Gao et al., 2005; Wang et al., 2008).

The experiments were conducted in two periods: a spring campaign, from March 22 to April 24, and a summer campaign, from June 16 to July 20. To illustrate the general weather conditions during the two periods, Fig. 2a and b show the averaged geopotential height and wind streams at 850 hpa, a level corresponding to the elevation of the summit, and wind rose plots using the data collected at Mt. Tai Meteorological Observatory. A comparison of the two figures shows a large difference in the weather conditions during the two seasons. Due to the impact of the winter monsoon which is caused by a strong equator-ward movement of the Asian continental High (see Fig. 2a), cold fronts frequently passed the study region in the spring campaign, bringing in cold and dry air masses. Two strong dust storms were observed on March 31–April 2 and April 20–21. During the summer campaign, the interior Asian continent was dominated by a wide low-pressure system, and the stronger Pacific High (see right-bottom of Fig. 2b) carried more humid air from southern China and from the East China Sea to the North China Plains, giving rise to more cloudy and stormy weather. Wind rose analysis also shows

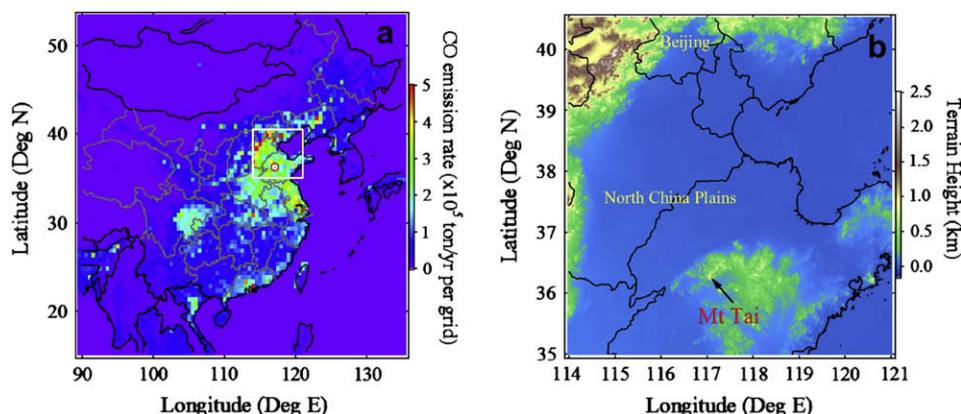


Fig. 1. Map showing the study area with (a) CO emission intensity (data from http://www.cgrrer.uiowa.edu/EMISSION_DATA_new/index_16.html) and (b) topography.

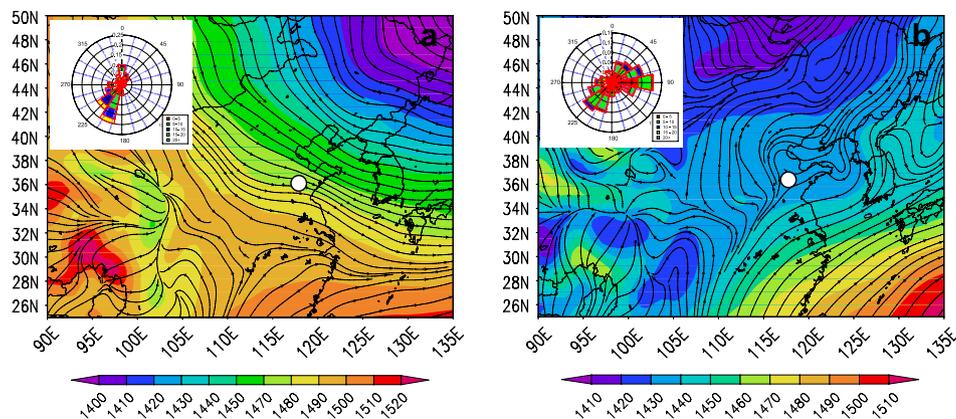


Fig. 2. Mean geopotential height (unit: m) and streamlines, and wind rose plots (unit for wind speed: m s^{-1}) at Mt. Tai during (a) spring campaign and (b) summer campaign.

more easterly winds during the summer campaign. On average wind speeds were larger in spring. Wind rose plots also indicated frequent southerly/southwesterly winds during the two periods. An examination of weather charts suggests that the southerly winds in the spring were due to the influence of troughs on the prevailing westerlies, while in summer the southerly winds generally occurred due to the influence of mountain–valley breezes along the southern slope of the mountain.

2.2. Instruments

Gas-phase total peroxides were measured using a fluorometric analyzer based on the principle of the para-hydroxyphenylacetic acid (POPHA) and horseradish peroxidase derivatization and fluorescence detection method (Lazrus et al., 1986). This instrument was run using a dual-channel configuration to measure H_2O_2 in previous studies (Rattigan et al., 2000, 2001). In this work we used one channel measuring total soluble peroxides. Previous studies in other places indicate that the total peroxide signal is typically dominated by hydrogen peroxide due to its abundance and higher solubility (Lazrus et al., 1986; Heikes, 1992; Tanner and Schorran, 1995; Qi et al., 1998; Takami et al., 2003; Hua et al., 2008).

The peroxides instrument and other trace gases analyzers were housed in a room on the top floor of the Observatory. The sample inlets were located approximately 6.4 m above the ground. A PFA Teflon line (length: 9 m; $\frac{1}{4}$ inch outside diameter) was used as the sample line for the peroxides analyzer. The relatively long sample line had to be used to avoid the obstruction of air flow by the building roof. A new line was installed before each measurement period. An in-line particulate filter was used to prevent particles from entering into the instrument and replaced every 4 days. A bypass pump was used to get total flow rate of 4 standard liters per minute (SLPM), and 2 SLPM was for the peroxides analyzer. The air entered a 26-turn coil which is used to strip the peroxides out of the air and into a liquid phase by water (0.42 mL/min). The air and liquid then entered an air/liquid separator where the liquid was sucked through a 10-turn coil (0.42 mL/min) at which buffer (potassium hydrogen phthalate (KHP, Fisher Scientific) and tetrasodium ethylenediaminetetraacetate (Na_4EDTA , Fluka Scientific)) and fluorescence (POPHA (Fluka Scientific), horseradish peroxidase (Sigma Chemical Co.), KHP, and Na_4EDTA) solutions were added, both at the rate of 0.16 mL/min to form the POPHA dimer. Then the liquid entered a pH booster cell that contained 30% ammonium hydroxide (Sigma Chemical Co.) to adjust solution pH from 6 to approximately 10. After going through a debubbler (0.42 mL/min), where the bubbles were removed, the fluorescence of the dimer was detected using a fluorimeter (Spectrovision FD-100, Groton

Technology Inc., Concord, MA) with excitation and emission wavelength of 326 nm and 400 nm, respectively.

The analyzer was calibrated every two days using a series of aqueous phase standards, which were made by diluting a 3% H_2O_2 solution which was made from commercially available 30% wt. H_2O_2 (Sigma–Aldrich). The H_2O_2 standards were freshly prepared on-site immediately before calibrations to avoid any losses due to H_2O_2 decomposition. The uncertainty of these calibrations at 1.0 ppbv was $\pm 10\%$ (at the 95% confidence level). The minimum level of detection of the instrument, defined as a signal-to-noise ratio of 2 (2σ), was estimated to be ~ 0.02 ppbv with a precision higher than 2% RSD. 1-min averages were recorded by a data logger. In this paper we use 5-min or hourly averages.

It is important to point out that peroxides can experience losses within the sample tubing by reacting with deposited materials during periods of high relative humidity (Lee et al., 1991; Watkins et al., 1995). Lee et al. (1991) showed that at a relative humidity of 86%, the loss was about 11% for a residence time of 0.6 s in the sampling line. With a longer residence time of 1.7 s in our study, the losses of H_2O_2 could be larger at the same relative humidity.

The setup, precisions and accuracies of the instruments measuring other trace gases have been described previously (e.g. Wang et al., 2003, 2006; Gao et al., 2005). Briefly, O_3 was measured with a commercial UV photometric analyzer (TEI, Model 49C) with a detection limit of 2 ppbv and precision of ± 2 ppbv; CO was measured with a gas filter correlation, non-dispersive infrared analyzer (API Model 300E) with a detection limit of approximately 30 ppbv for a 2-min average; SO_2 was measured using a pulsed UV fluorescence analyzer (TEI, Model 43C). Nitric oxide (NO) was measured with a chemiluminescence analyzer (TEI Model 42i), and total reactive nitrogen (NO_y) was measured with another chemiluminescence analyzer equipped with an externally placed molybdenum oxide (MoO) catalytic converter (TEI, Model 42Cy). Meteorological measurements (wind speed and direction, temperature, relative humidity, and pressure) were routinely made by the Observatory. Total solar radiation was measured by our group using a LI-200SA Pyranometer Sensor.

3. Results and discussion

3.1. Overviews of results and comparison with other sites

The overall statistics of hourly averaged concentrations of total peroxides measured in both spring and summer study campaigns are summarized in Table 1, and the frequency distributions of peroxide and ozone concentrations are shown in Fig. 3. The averaged concentration of total peroxides was significantly higher in the

Table 1

Summary of ambient gas-phase peroxide concentrations (ppbv) at the summit of Mt. Tai for the spring and summer measurement periods in 2007. The daytime period corresponds to the period from 06:00–17:00 LT for the spring study and 05:00–19:00 LT for the summer study.

Period	N ^a	Mean	SD	Median	Max.	Min.
Spring campaign	696	0.17	0.16	0.14	1.28	<LOD ^b
Days	350	0.17	0.15	0.14	1.28	<LOD
Nights	346	0.18	0.17	0.12	0.90	<LOD
Summer campaign	670	0.55	0.67	0.32	3.55	<LOD
Days	421	0.45	0.47	0.30	2.97	<LOD
Nights	249	0.72	0.89	0.34	3.55	<LOD

^a Number of data samples.

^b Level of detection (~ 0.02 ppbv).

summer campaign (mean: 0.55 ± 0.67 ppbv) than the spring campaign (mean: 0.17 ± 0.16 ppbv) (Table 1). The summer maximum value also substantially exceeded the spring maximum (3.55 vs. 1.28 ppbv). These differences are not surprising and can be attributed to more active photochemistry in summer. Ozone also showed increased concentrations in summer (see Fig. 3b, average concentrations of 71.6 ppbv in summer and 62.8 ppbv in spring). It is interesting to note that in summer peroxide concentrations during daytime were, on average, lower than at night (0.45 vs. 0.72 ppbv). Since photochemical production occurs during daylight hours, the decreased daytime concentrations suggest that some processes acted to remove gas-phase H₂O₂ during daytime in air mass arriving at the site. We will further discuss possible mechanisms below.

In Table 2 we compare our results with H₂O₂ or methylhydroperoxide (MHP) concentrations measured at rural mountainous and surface sites in previous studies. Only summer data are compared as most of the previously reported data were from summer. It can be seen that the concentrations of total peroxides at Mt. Tai were comparable to or a little higher than hydrogen peroxide concentrations measured at some rural or remote surface sites, such as Tabua (mean: 0.27 ppbv) and Sonia (mean: 0.41 ± 0.51 ppbv for 1991, and 0.35 ± 0.51 ppbv for 1992), but were lower than those measured at mountain sites: Gibbs (mean: 0.76 ± 0.57 ppbv) and Whitetop (mean: 0.8 ppbv), even less than half of the average H₂O₂ concentration at Whiteface (mean: 1.15 ± 0.64 ppbv) and Waliguan (mean: 1.8 ppbv). Note that our results are for total peroxides and represent an upper limit to concentrations of hydrogen peroxide at Mt. Tai. The lower concentrations at Mt. Tai suggest that some processes may be occurring to suppress peroxide formation in the regional atmosphere and/or to remove those peroxides that are formed.

3.2. Diurnal variation

To understand factors that might influence the concentrations of gas-phase peroxides at different times of day, we examine the

diurnal patterns of peroxide concentrations together with those for other trace gases, including O₃, CO, NO_y, and SO₂, and those for key meteorological parameters, including relative humidity (RH), air temperature (T), and wind, for the spring and summer campaigns (Fig. 4a and b).

From Fig. 4a, it can be seen that in spring, on average, gas-phase peroxide concentrations showed a small diurnal variation with a small peak in late afternoon (at approximately 15:00 local time (LT)), corresponding roughly to the daily ozone peak (at 16:00 LT). CO, SO₂ and NO_y all exhibited a broad afternoon peak corresponding with the ozone peak. The enhanced concentrations of these gases during afternoon have been explained by the transport of emissions in the PBL by upslope flow and stronger daytime vertical mixing of the PBL (Gao et al., 2005). The simultaneous increase of peroxides and O₃ in late morning and early afternoon suggests that photochemical production is an important factor affecting the peroxide concentrations compared with removal processes such as photolysis, cloud scavenging, and deposition. The somewhat different diurnal patterns of peroxide and O₃ concentrations suggest that their sources/sinks are different, although they both are products of photochemistry. One important difference in this environment is the large sink for peroxides represented by aqueous phase reaction in clouds. With average SO₂ concentrations in the 10 to 20 ppbv range throughout the day, the formation of clouds will result in rapid depletion of the small amount of peroxides present through reaction with dissolved SO₂ (present as H₂SO₃, HSO₃⁻, and SO₃²⁻ in solution).

The summer campaign showed a different diurnal pattern of peroxides. Fig. 4b shows that the peroxide concentrations were higher at night (20:00–04:00 LT) and showed a broad minimum during the daytime. Similar diurnal behavior has been observed at many other mountain sites (e.g., Claiborn and Aneja, 1991; Sakugawa and Kaplan, 1993; Watanabe et al., 1995; Das and Husain, 1999; Tang et al., 2002), but the reason(s) for the pattern can be different from site to site. At our site, the high and relatively stable nighttime concentrations of peroxides can be explained by several factors: First, because the summit of Mt. Tai was frequently above the top of the PBL at night, strong winds and air subsidence due to nighttime valley breezes could transport aged regional-scale pollution from the residual PBL or the free troposphere over the North China Plains. Second, removal processes were reduced at night. Photochemical destruction of peroxides could be minimized at night, and cloud scavenging and dry deposition could also be minimized. Third, there could be a possible chemical source of peroxides at night. Previous studies have suggested that peroxides also can be produced from non-photochemical reactions like oxidation of isoprene, alkenes or terpenes by O₃ (or NO₃ radical) under humid conditions at night (Cantrell et al., 1986; Becker et al., 1990; Platt et al., 1990; Simonaitis et al., 1991; Das and Aneja, 1994;

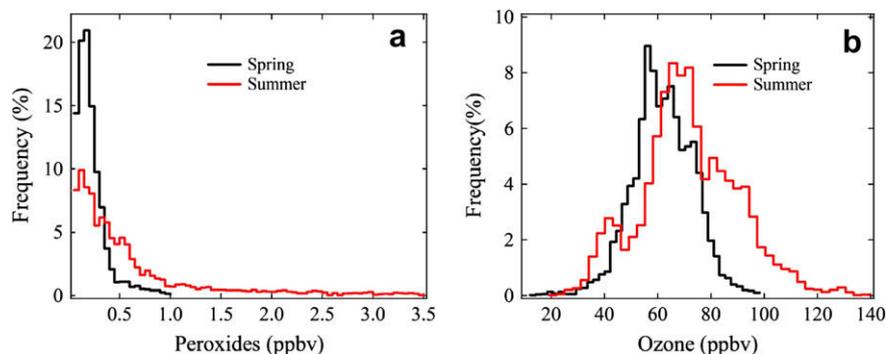


Fig. 3. Frequency distributions of 5-min averaged concentrations of (a) gas-phase peroxides and (b) O₃ at the summit of Mt. Tai.

Table 2
Summary of ambient gas-phase hydrogen peroxide or organic peroxide concentrations at various sites.

	Measurement site	Altitude	Period	Mean concentration or data range (ppbv)	References
Mountain site	Mt. Tai	1534 m	Jun–Jul 2007	0.55 ± 0.67 (max. 3.55)	This study
	Oku-Nikko Observation station	1500 m	Jul–Aug 1998–2000	0.2–1.6, MHP ^a mean: 0.1	Takami et al., 2003
	Mt. Waliguan (36°17' N, 100°54' E)	3810 m	Jul 1996	1.8 (0.5–4.0)	Tang, et al., 2002
	Mt. Whiteface (44°23' N, 73°51' W)	Summit: 1483 m Lodge: 620 m	Jul–Aug 1997	Summit: 1.15 ± 0.64 (0.26–4.30) Lodge: 1.14 ± 0.75 (0.06–4.57)	Das and Husain, 1999
	Mt. Whiteface	1483 m	Jul 1995	1.61 ± 0.90 (1.5–5.15)	Balasubramanian and Husain, 1997
	Mt. Norikura, Japan	2770 m	Jul–Sep 1993	0.1–4.5	Watanabe et al., 1995
	Mt. Gibbs, at Mt. Mitchell	2006 m	May–Sep 1988	Summer: 0.76 ± 0.57 (max. 4.18) Fall: 0.20 ± 0.26 (max. 1.22)	Claiborn and Aneja, 1991
	Mt. Whitetop	1689 m	1986	Summer: 0.80 (0.02–2.6) Fall: mean 0.15 (0.02–0.57)	Olszyna et al., 1988
Ground site	University of Nevada	10 m	Jun–Dec 1999	0.012–2.74	Liu et al., 2003
	Beijing (urban)	9 m	May–Jun 1997	0.78 (max. 2.65), MHP ~ 0.07 (max. 0.28)	Qi et al., 1998
	Tabua, Portugal (40°19.5' N, 1°03' W)	Ground level	Jun 1994	0.27 (max 0.63), MHP ~ up to 0.1	Jackson and Hewitt, 1996
	Meadview, AZ (remote location)	850 m	Jul–Aug 1992	Total peroxides: 1–4, H ₂ O ₂ (max. 2.9)	Tanner and Schorran, 1995
	Sonia (rural) (35.26° N, 79.84° W)	170 m	Jul–Aug 1991	1991: 0.41 ± 0.51 (max. 2.19)	Das and Aneja, 1994
			Jun–Jul 1992	1992: 0.35 ± 0.51 (max. 1.6)	

^a Methyl hydroperoxide.

Sauer et al., 1999). However, we believe that this source should not be a major contributor at Mt. Tai because biogenic emissions are difficult to transport to the mountain top due to the strong subsidence and also due to lower water content (see low RH) of the nighttime air above the PBL.

For daytime, the peroxide concentrations showed a sharp drop during summer in the early morning (5:00–7:00 LT) with a concurrent but small increase in RH (see Fig. 4b). O₃ concentrations also show a continuous drop in the morning. This indicates possible break-up of nighttime surface inversions on the mountain slopes or transport of air masses of different origin. The quick drop of peroxides was probably due to the removal by aqueous aerosols or morning fogs/clouds within the nighttime boundary layer (NBL). In the afternoon when upslope mountain breezes typically

developed (see the change in wind vectors), O₃ concentrations increased by about 10 ppbv with obvious enhancement of other trace gas concentrations (CO, SO₂ and NO_y). Average peroxide concentrations during afternoon, by contrast, showed rather constant and low values. These low levels may reflect a combination of scavenging and chemical destruction by fog/clouds and also suppression of peroxide formation by high daytime NO_x levels which scavenge peroxy radicals (Calvert and Stockwell, 1983; Jackson and Hewitt, 1996). Indeed orographic clouds/fogs were frequently observed in the afternoon during summer at Mt. Tai, in contrast to springtime with its relatively dry air masses. With average SO₂ concentrations typically an order of magnitude higher than average peroxide concentrations in summer, aqueous destruction of peroxide by reaction with S(IV) will be very quick.

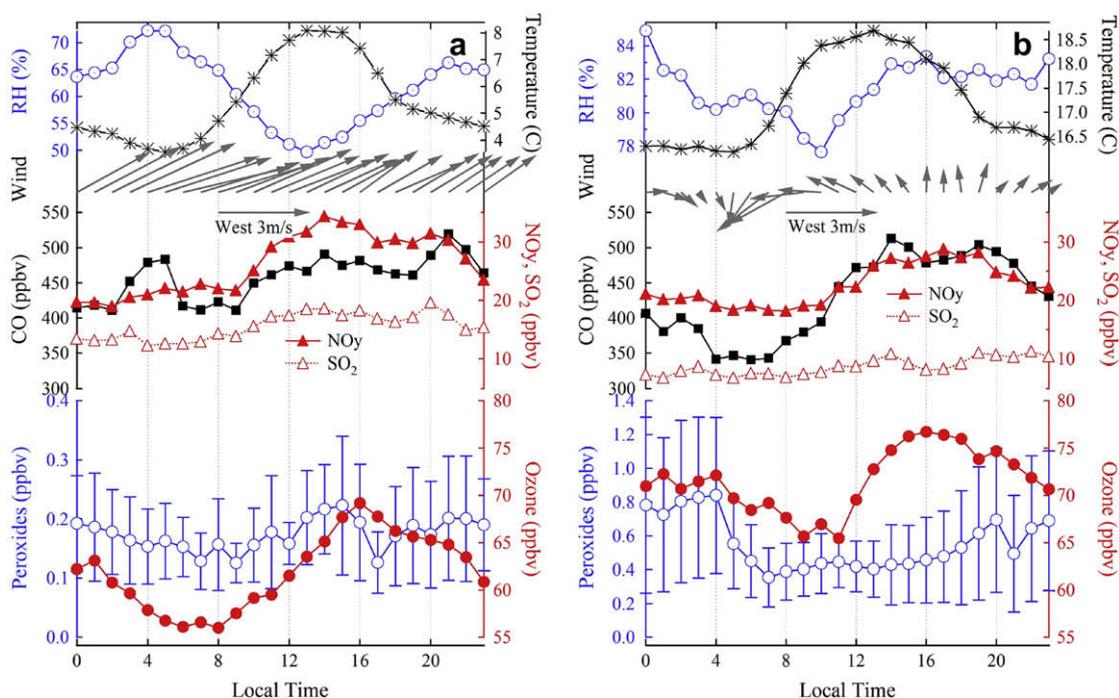


Fig. 4. Diurnal variations of gas-phase concentrations of total peroxides and other trace gases and meteorological parameters for (a) the spring campaign and (b) the summer campaign. The vertical bars show 0.5 standard deviation for peroxides.

Table 3
Correlation matrix of main trace gases and meteorological variables during the two measurement seasons.

	Spring campaign							Summer Campaign							
	Peroxides	O ₃	SO ₂	NO _y	CO	T	RH	Peroxides	O ₃	SO ₂	NO _y	CO	T	RH	
Peroxides															
O ₃	0.24							0.06							
SO ₂	0.01	0.24						0.01	0.48						
NO _y	-0.10	0.45	0.68					-0.43	0.59	0.55					
CO	-0.11	0.28	0.66	0.80				-0.47	0.28	0.45	0.58				
T	0.07	0.34	0.14	0.23	0.23			0.24	0.29	0.02	-0.05	-0.21			
RH	-0.11	0.20	0.18	0.51	0.56	-0.17		-0.69	-0.27	-0.15	0.38	0.48	-0.52		
SR	0.01	-0.09	0.04	0.02	-0.09	0.24	-0.25	-0.14	0.06	0.05	0.00	-0.04	0.57	-0.27	

Values in bold correspond to statistically valid correlation coefficients ($p < 0.01$).

3.3. Relationships between peroxides and other pollutants and meteorological parameters

To gain preliminary insight into how relevant chemical and meteorological factors might affect the observed variations of peroxide concentrations, we examined the inter-correlation of

peroxides, other trace gases (O₃, SO₂, NO_y, and CO) and key meteorological factors (T, RH and solar radiation). The matrix of correlation coefficients corresponding to the spring and summer campaigns is shown in Table 3. The correlation coefficients with a significance level above 99.9% (i.e. $p < 0.01$) are shown in bold. In addition, we also give the scatter plots and regression functions of

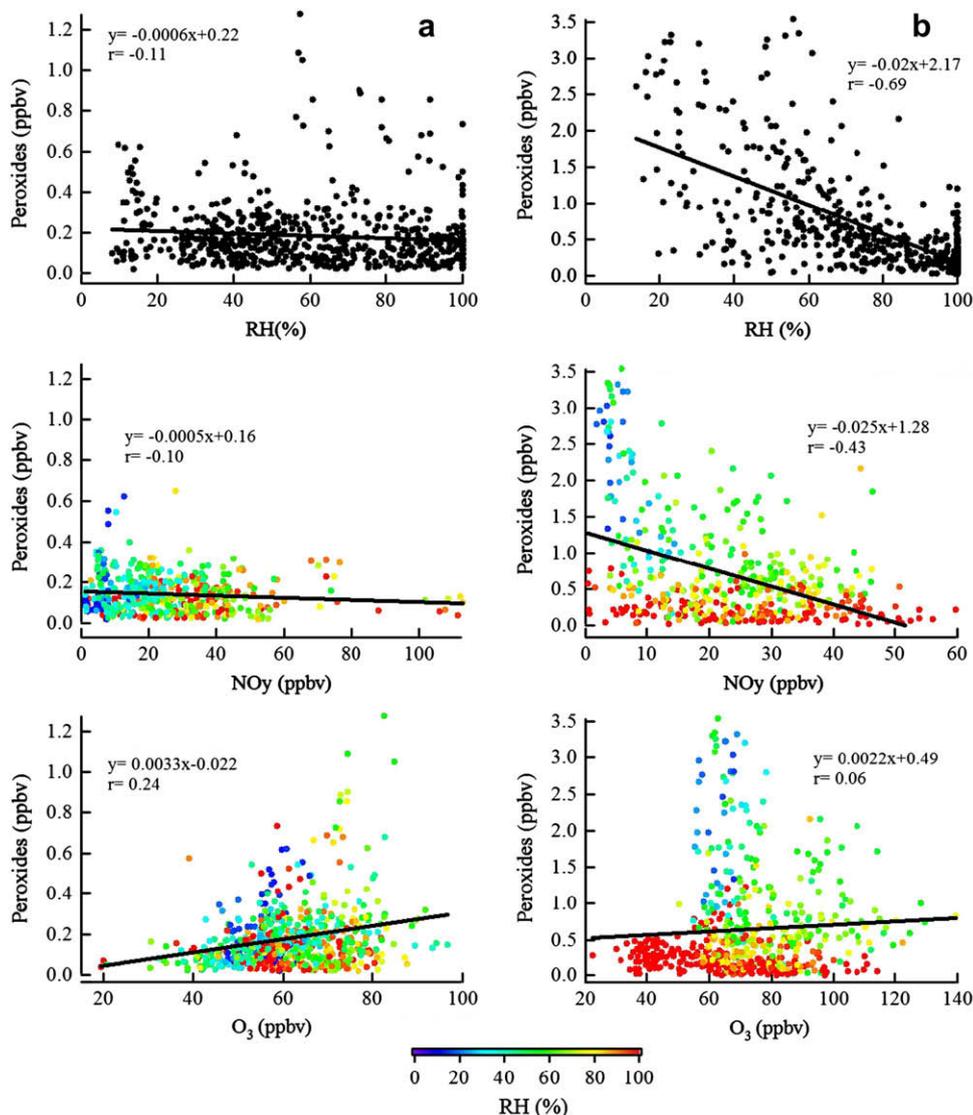


Fig. 5. Scatter plots of peroxides vs. RH, NO_y and ozone during (a) the spring and (b) summer field campaigns. Data points in the NO_y and O₃ plots are color coded by RH using the scale shown.

Table 4

Factor loadings from principal component analysis for data of spring campaign ($n = 448$, total explained variance 72%).

	Factor 1	Factor 2	Factor 3	Factor 4
Peroxides	-0.22*	-0.11*	(0.76)*	-0.05
O ₃	0.34	0.35	(0.54)	-0.27
SO ₂	(0.84)	0.05	-0.12	0.18
NO _y	(0.93)	0.13	0.12	-0.03
CO	(0.90)	0.15	0.08	-0.12
T	0.19	0.27	(0.75)	0.34
RH	(0.53)	(0.56)	-0.13	-0.39
Pressure	-0.10	(-0.51)	-0.29	0.09
SR	0.02	0.00	0.02	(0.92)
<i>u</i>	0.04	(0.85)	-0.08	0.20
<i>v</i>	0.12	(0.82)	0.12	-0.08
Variance	26%	20%	14%	12%

Values in parentheses indicate loading factors greater than 0.5. *u* and *v* indicate the *x*- and *y*- (latitudinal and longitudinal) components of wind, positive values of *u* and *v* represents the west and south vector, respectively.

*Coefficient statistically significant at the 95% confidence level ($p < 0.05$).

peroxides to RH, NO_y and O₃ for the spring and summer study phases in Fig. 5, as these parameters are thought to have major impact on the levels of peroxides.

Table 3 shows that peroxides had weak to moderate correlation with these parameters. For O₃, which is a product of VOC–NO_x photochemistry, similar to peroxide, a weak correlation ($r = 0.24$) was observed with peroxide concentrations in spring but almost no correlation ($r = 0.06$) was found in summer. This suggests that sources and sinks probably had different degrees of influence on the levels of peroxides and O₃.

Wet removal processes appear to have a major impact on peroxide concentrations in summer. Table 3 and Fig. 5 show an anti-correlation between peroxide concentrations and RH during summer. While a variety of peroxide concentration levels were seen during low RH periods, at higher RH peroxide levels clearly decreased. Here, we should note that the anti-correlation may in part be due to the loss of peroxides in the sample line at high RH. From Fig. 5, it can be seen that in summer, when RH was low (RH < 60%), peroxides showed a positive correlation with O₃, with a slope changing with RH.

Peroxide concentrations exhibited a negative correlation with NO_y, particularly during the summer measurement period. By

examining a scatter plot of peroxides vs. NO_y color-coded according to RH (see Fig. 5), it can be clearly seen that in summer when RH was high (80–100%) the peroxides remained below 1 ppbv, independent of the amount of NO_y, but in dry air (RH < 60%) peroxide concentrations were anti-correlated with concentrations of NO_y, consistent with the tendency of VOC-limited atmospheres to produce large amounts of NO_y while NO_x-limited environments tend to favor peroxide production.

Together, these results demonstrate the complex interaction of several factors and their influence on atmospheric peroxide concentrations. Both NO_x scavenging of hydroxy and peroxy radicals and peroxides scavenging and destruction in liquid water (clouds, fogs, and perhaps deliquesced aerosols) compete during summer at Mt. Tai with photochemical production of peroxides via termination reactions involving two peroxy radicals. In spring peroxide concentrations were much lower, likely reflecting lower overall photochemical activity, and relationships between peroxide concentrations and other measured parameters were less evident.

3.4. Principal component analysis of peroxides and case studies

In order to further identify the major factors that controlled the variation of peroxides, a principal component analysis (PCA) was carried out for the data during the measurement seasons. PCA is a statistical technique based on the assumption that the observed values of the variables can be represented as linear combinations of a set of mutually independent factors. It can provide a quantitatively simplified description of a system by reducing the original data matrix to a factor pattern matrix of a smaller number of variables/components (Johnson and Wichern, 1988; Das and Husain, 1999). We included peroxides, O₃, SO₂, NO_y, CO, T, RH, pressure, solar and *u*- and *v*-component of wind in the PCA. PCA was conducted using a commercially available software package (SPSS), and Varimax Rotation was utilized to determine the final factors.

Table 4 shows the results of four main components (factors) from PCA for the data collected in the spring campaign. Together the four factors account for 72% of the total variance in peroxide concentrations. The first factor, with the maximum explained variance (26%), has strong loadings from SO₂, NO_y, CO and RH (see

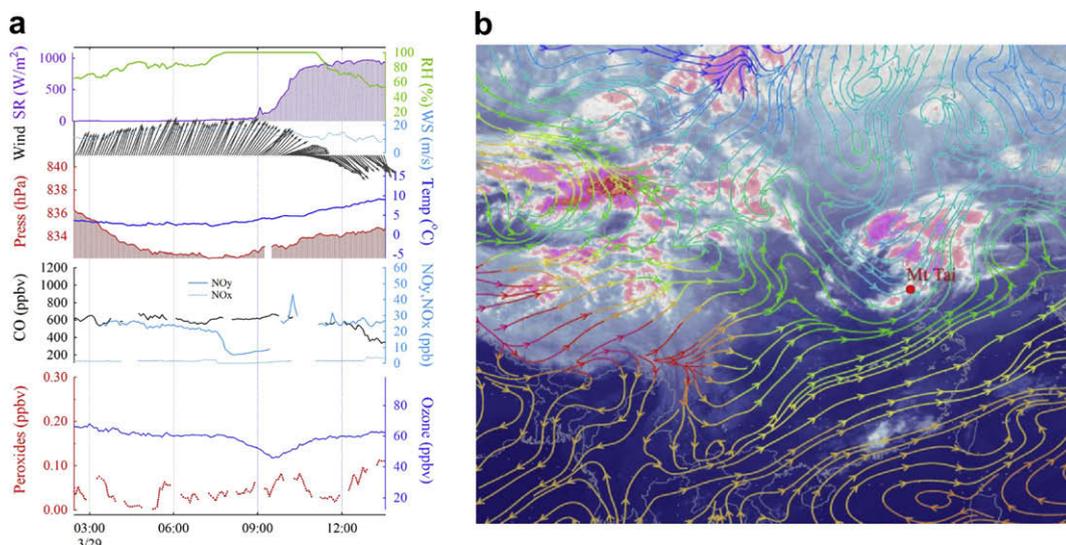


Fig. 6. (a) Time series of trace gases and meteorological parameters, and (b) stream lines at 850 hpa (using FNL data) and satellite observed infrared cloud photo (by FY2 satellite) for March 29.

Table 5
Same as Table 4 but for summer campaign ($n = 377$, total explained variance 75%).

	Factor 1	Factor 2	Factor 3	Factor 4
Peroxides	-0.11*	(0.90)*	-0.08	0.00
O ₃	(0.77)	0.16	-0.03	0.22
SO ₂	(0.82)	0.00	-0.01	-0.29
NO _y	(0.80)	-0.31	0.06	0.05
CO	(0.61)	(-0.53)	-0.19	-0.03
T	0.02	0.23	(0.89)	0.22
RH	0.09	(-0.78)	-0.48	0.07
Pressure	(0.50)	0.35	-0.14	(-0.58)
SR	-0.05	-0.06	(0.91)	-0.12
<i>u</i>	0.02	0.06	-0.01	(0.91)
<i>v</i>	0.29	0.43	0.03	0.38
Variance	24%	20%	17%	14%

Values in parentheses indicate loading factors greater than 0.5. *u* and *v* indicate the *x*- and *y*- (latitudinal and longitudinal) components of wind, positive values of *u* and *v* represents the west and south vector, respectively.

*Coefficient statistically significant at the 95% confidence level ($p < 0.05$).

values marked with parentheses in Table 4), representing humid and polluted air. This factor is related to decreases in peroxides (note negative peroxide loading) due to chemical suppression by high NO_x and wet scavenging as discussed above.

Factor 2 shows a strong loading from RH, pressure, and *u* and *v* wind. This factor appears to represent peroxide decreases associated with humid “background” air transported from the southwest (note that the positive *u* and *v* values represent westerly and southerly wind, respectively). This factor may represent the influence of synoptic clouds, which differ from the topography-induced cloud/fogs mentioned previously. The synoptic clouds were often associated with a low-pressure cyclone or a low-pressure trough (note the negative loading of pressure in Table 4). Fig. 6 shows a typical case observed on March 29. In the early morning peroxides remained at very low concentration (below 0.1 ppbv) for a half day (Fig. 6a) when a low-pressure system passed over Mt. Tai and brought in a lot of cloud (Fig. 6b) and humid air (see RH in Fig. 6a) from the southwest to the site.

The third factor has strong positive loadings of O₃, air temperature and peroxides, suggesting a photochemical production process, which is often strongly related to air temperature (Das and Husain, 1999). Finally, Factor 4 shows a very strong

loading from solar radiation but small negative loadings for peroxides and O₃. Das and Husain (1999) showed that photolysis was an important sink for H₂O₂ at Whiteface Mountain. It appears that this sink had only a minor impact on the variation of peroxides at Mt. Tai.

For the summer campaign, the PCA analysis yields four major factors accounting for 75% of the total variance (see Table 5). Only two factors (Factor 1 and Factor 2) have a statistically significant correlation with peroxides. The first factor has strong positive loadings from O₃, primary pollutants (SO₂, NO_y and CO) and pressure. This factor represents O₃ rich air from the PBL which had experienced strong photochemical processing under high-pressure conditions. Peroxides, however, had a negative weak correlation. Fig. 7a shows a case illustrating the impact of this factor. It shows that the peroxide concentrations could be low in the NO_x-rich air mass presumably due to the chemical suppression of NO on HO₂ radical concentrations, which can be very important in high air temperature conditions during summer (Watkins et al., 1995). Note in this case RH was fairly constant at ~60%. Factor 2 has a strong positive loading from peroxides and a negative one from RH and CO. Fig. 7b shows a multi-day case in early July indicating high peroxide concentrations associated with low RH and low primary pollutant concentrations. Examinations of summer concentration time series suggest that peroxides with concentrations >2 ppbv were most strongly associated with this factor, and they occurred mostly during the night.

4. Summary and conclusions

Ambient gas-phase total peroxides (hydrogen peroxide plus other soluble hydroperoxides) were measured at the summit of Mt. Tai in the North China Plains during spring and summer of 2007. We observed relatively lower levels of peroxides than observed previously at several other rural mountain sites, especially in summer. The concentrations of peroxides observed at Mt. Tai show a weak peak in late afternoon in spring, reflecting photochemical production, but a reverse pattern in summer. Principal component analysis suggests wet removal of peroxides and chemical suppression of peroxy radicals by NO_x were major sinks for peroxides at Mt. Tai. The wet removal appears due to scavenging by clouds and fogs, for

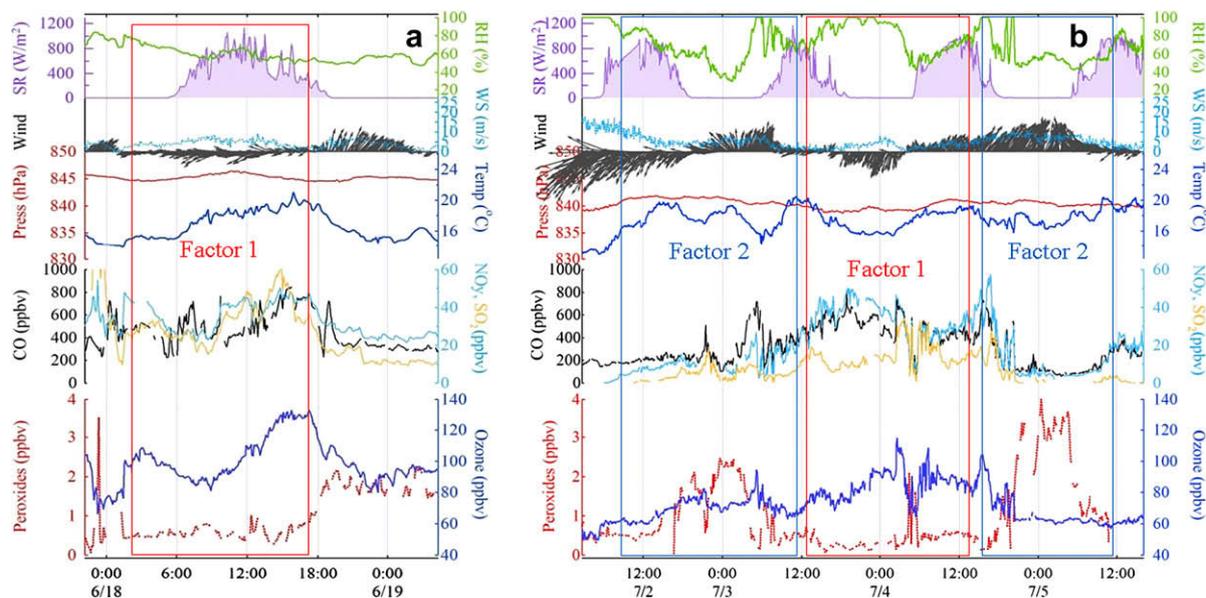


Fig. 7. Time series of trace gases and meteorological parameters for (a) June 18–19 and (b) July 2–5.

abundant SO₂ concentrations (often 10 ppbv or higher) make cloud scavenging followed by reaction with dissolved SO₂ a rapid and important sink for atmospheric peroxides in the region. Higher concentrations of peroxides were often observed at night in descending air masses with relatively low concentrations of NO_x and lower water vapor concentrations. The peroxide observations reported here are useful for the assessment of photochemical activity in eastern China and its role in the formation of sulfate and associated acid deposition.

Acknowledgments

The authors would like to acknowledge Mr. Steven Poon, Dr. Wang Jin, Mr. Sun Tingli, Mr. Li Penghui, Mr. Nie Wei, and Mr. Xue Likun for their help in organizing the field study and in setting up the instruments. Dr. Taehyoung Lee is gratefully acknowledged for assistance with preparation of the peroxide analyzer in advance of field deployment. We thank Professor Wang Wenxing and Zhang Qingzhu for their support for this study. We are grateful to the Mt. Tai Meteorological Observatory for its support of the field study and for providing meteorological data. The HYSPLIT model was provided by the NOAA Air Resources Laboratory (ARL). This research was funded by the National Basic Research Program of China ('973 Project No. 2005CB422203) and the Niche Area Development Scheme of the Hong Kong Polytechnic University (Project 1-BB94). Additional support for CSU's participation in the study was provided by the U.S. National Science Foundation (ATM-0711102).

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