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Measurement and interpretation of cloud effects on the concentrations of hydrogen peroxide and organoperoxides over Ontario, Canada

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Abstract

Measurements of gaseous hydrogen peroxide (H_2O_2) and organoperoxides (ROOH) in clear air and cloudy air were made from a Twin Otter aircraft over central Ontario, Canada, during March and April of 1990 as part of the Eulerian Model Evaluation Field Study (EMEFS). In clear boundary layer air (altitude 500 m to 1750 m), unperturbed by the presence of cloud, the ratio $[\text{H}_2\text{O}_2]/[\text{ROOH}]$ depends on NO_2 mixing ratios, while in the presence of cloud perturbing H_2O_2 , the ratio $[\text{H}_2\text{O}_2]/[\text{ROOH}]$ was significantly decreased compared with those in clear air mainly due to the high solubility of H_2O_2 . In order to examine the effects of cloud processing on air that was detrained from cloud, we selected measurements made in cloud-free air located between two passes made in air with high liquid water content. Gaseous H_2O_2 concentrations in these detrained air masses were often higher than those in the cloudy air, and sometimes higher than those in the clear air for high NO_2 conditions (>500 ppt) but lower than clear-sky levels for low NO_2 (<500 ppt) conditions. This result is in general agreement with that from photochemical modeling, namely, for chemical regimes typical of high- NO_2 (more polluted) conditions, where aqueous-phase reactions of dissolved HO_2 lead to net production of $\text{H}_2\text{O}_2(\text{aq})$ that can subsequently be detrained from the cloud.

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1. Introduction

Clouds play an important role in some aspects of tropospheric chemistry. Clouds represent a highly complex environment where both the gas phase and aqueous phase coexist. Homogeneous gas-phase and aqueous-phase, as well as heterogeneous, reactions can occur simultaneously, and chemical reaction chains are drastically altered once an air parcel is cooled, condensation occurs, and a cloud develops (Graedel and Weschler, 1981; Chameides and Davis, 1982; Chameides, 1984). Research has pointed to the noticeable effect of cloud chemical processes on tropospheric photochemistry in the background atmosphere. Lelieveld and Crutzen (1991) pointed out that hydrogen peroxide (H_2O_2) concentrations in the background troposphere are significantly decreased by the presence of clouds.

Hydrogen peroxide and methylhydroperoxide (CH_3OOH) are often contrasted with respect to their behavior in cloudy environments due to their different solubilities. Their ratio, $[\text{H}_2\text{O}_2]/[\text{CH}_3\text{OOH}]$, is a strong indicator of recent cloud contact in precipitating deep convective clouds (Cohan et al., 1999) and under certain conditions in nonprecipitating boundary layer clouds (Kim et al., 2002). In some previous studies of cloud chemistry, it has been assumed that the H_2O_2 in cloud water is exclusively due to the direct dissolution of gaseous H_2O_2 into droplets and this assumption is not inconsistent with observed $[\text{H}_2\text{O}_2]$ in rainwater of $0.1\sim 7 \times 10^{-5}$ M (Zika et al., 1982; Kok, 1980). However, another important effect of clouds on $\text{H}_2\text{O}_2(\text{aq})$ is related to free radicals. Previous studies have pointed out that free-radical reactions in the aqueous phase may have a significant impact on the chemistry of precipitation (Chameides and Davis, 1982; McElory, 1986; Graedel and Goldberg, 1983; Seigneur et al., 1984). Chameides and Davis (1982) found that aqueous-phase reactions involving HO_2 could represent a major sink of gas-phase free radicals as well as an important source of H_2O_2 in cloud water. HO_2 is formed by gas-phase photochemical reactions and, due to its high solubility, is rapidly dissolved into cloud water. Because of this link to gas-phase photochemistry, gas-phase concentrations of HO_2 are also linked to atmospheric NO_x concentrations.

In light of this, a modeling study of how H_2O_2 , CH_3OOH , and the ratio $[\text{H}_2\text{O}_2]/[\text{CH}_3\text{OOH}]$ behave in non-precipitating clouds in the remote troposphere was undertaken and the rate of reestablishment of these species to clear-sky levels was simulated (Kim et al., 2002). This study indicates that cloud interactions may deplete or enhance H_2O_2 but have a minor effect on CH_3OOH . The rate of recovery of the ratio $[\text{H}_2\text{O}_2]/[\text{CH}_3\text{OOH}]$ after perturbation by cloud interactions depends on $[\text{NO}_x]$ ($=[\text{NO}]+[\text{NO}_2]$) mixing ratios, cloudwater pH, and the time of day that cloud is encountered. In particular, significant quantities of $\text{H}_2\text{O}_2(\text{aq})$ may be generated within cloud droplets for daytime, high- NO_x , and low-pH ambient conditions.

The coupling between the gas and aqueous phases occurs primarily through the free radical species HO_2 . This species is quite soluble, with a Henry's Law equilibrium constant of 4.3×10^3 M atm⁻¹ at 298 K. Its solubility is further enhanced by acid–base dissociation:



The generation of $\text{H}_2\text{O}_2(\text{aq})$ can occur in the aqueous phase via:



The relative concentrations of $\text{HO}_2(\text{aq})$ and O_2^- are strongly dependent on pH ($[\text{O}_2^-]/[\text{HO}_2(\text{aq})]=K_2/[\text{H}^+]$). Thus reaction (2), and the in-cloud production of H_2O_2 , is most rapid at pH ~ 4.5 , where $[\text{O}_2^-] \approx [\text{HO}_2(\text{aq})]$.

Since HO_2 is effectively partitioned to the aqueous phase during cloud contact, the gas-phase production rate of H_2O_2 via $\text{HO}_2 + \text{HO}_2$ is slowed, thereby reducing the total H_2O_2 (i.e. g+aq) concentrations in the cloud. Further, H_2O_2 can also be destroyed by other reactions in the aqueous phase. If the aqueous-phase generation of H_2O_2 is insufficient to overcome these reductions, cloud contact will serve as a net sink of H_2O_2 , and concentrations in air detrained from cloud will remain depleted until gas-phase photochemical reactions can re-establish the clear-sky chemical environment. Methylhydroperoxide levels can also be affected by cloud contact, although the effects are not as pronounced as for H_2O_2 (Kim et al., 2002).

In this work, measurements of peroxides are analyzed to examine the effect of cloud encounter on concentrations of H_2O_2 and organoperoxide (ROOH), and their ratio, $[\text{H}_2\text{O}_2]/[\text{ROOH}]$. The observed effects of clouds, along with comparisons to the modeled recovery rate to clear sky-levels after cloud evaporation, are discussed. Results are then compared with those from model simulations, and similarities and differences between observations and model results are discussed.

2. Experimental description

The observations reported here were made in Ontario, Canada, during the March–April 1990 intensive measuring periods of the Eulerian Model Evaluation Field Study (EMEFS). Airborne measurements were made from the National Council of Canada DHC-6 Twin Otter aircraft. The flights were of about 1.5–3.5 h in duration and generally consisted of vertical profiles over two surface chemistry sites, located approximately 240 km apart at Egbert and Lake Traverse (45.93°N, 78.91°W), with constant-altitude transects between the sites. The flight plans centered on collecting data for evaluation of the Canadian and US regional Eulerian models (ADOM and RADM, respectively), and typically consisted of collecting vertical profile data over each ground site, and filter and instrumental data at multiple levels during the transects. Clouds were sampled whenever present during either profiles or level flight. Ideally, on cloudy days, vertical profile data were collected at Egbert and Lake Traverse, cloudwater was sampled at one or more levels between the surface sites, and filter samples were collected at one or more altitudes below cloud. For additional flight descriptions, see Isaac et al. (1991) and Macdonald et al. (1995).

Gas-phase NO_2 was measured using a Unisearch LMA-3 Luminol detector. Details of the application of this technique and calibrations are described by Leaitch et al. (1994). The detection limit is 100 pptv and the uncertainty is ± 100 pptv. Under the conditions encountered during EMEFS, concentrations of NO were much less than NO_2 , so NO_2 is used here as approximately equivalent to NO_x when reporting these measurements. There is an unquantifiable error associated with the NO_2 measurements because the instrument was also sensitive to PAN. Specifically, the presence of about 1 ppb PAN produces an interference signal of about 0.25 ppb NO_2 . Surface level PAN concentrations ranged from <0.100 ppb to 1.800 ppb during EMEFS.

Gas-phase peroxide was measured with the enzyme fluorometric method described by Lazrus et al. (1986). Calibrations were usually carried out with liquid standards; however, the system was also verified with gaseous standards from a permeation system. One channel of the instrument was used to measure total peroxide, whereas the second channel measured only the organic peroxide component. Thus, the H_2O_2 concentration was determined as the difference between the two signals. Contributions of organic peroxides to total peroxides ranged from 18% to 42% (median of 23%). The uncertainty in the gaseous measurements is expected to be 10%–15% (Macdonald et al., 1995).

Liquid water content (LWC) was measured with a King probe. The King probe was calibrated in the National Research Council of Canada icing wind tunnel and the uncertainty in the LWC is estimated at $\pm(0.02+0.15 \times \text{LWC}) \text{ g m}^{-3}$. Further details on the experimental configurations can be found in the work of Macdonald et al. (1995) and Isaac et al. (1991).

3. Method

In exploring the behavior of peroxides and the impact of clouds, it was necessary at first to isolate the cloud effect. We examined data collected between the altitudes of 500 m and 1750 m. Each measurement was classified as either clear air, cloudy air, or detrained air. Clear air was defined as air with zero liquid water content (LWC), and air was considered cloudy when the observed LWC was $>0.1 \text{ g m}^{-3}$. Detrained air was defined as any air located between two cloudy passes that was cloud-free (zero LWC) with a potential temperature within 10% of that of the neighboring cloudy air. An example from April 10, 1992 is shown in Fig. 1. Detrained air with zero-LWC is assumed for about 15 min between two passes through cloud. In this illustration, all of the observations were at an altitude of 1200 m, and the potential temperature in the cloud-free air was within 10% of that in the cloudy air. For the entire data set, the average time between two cloud passes was 700~800 s.

We employ the coupled gas and aqueous-phase chemical/microphysical Lagrangian parcel model. The model includes a gas-phase photochemical reaction mechanism that considers

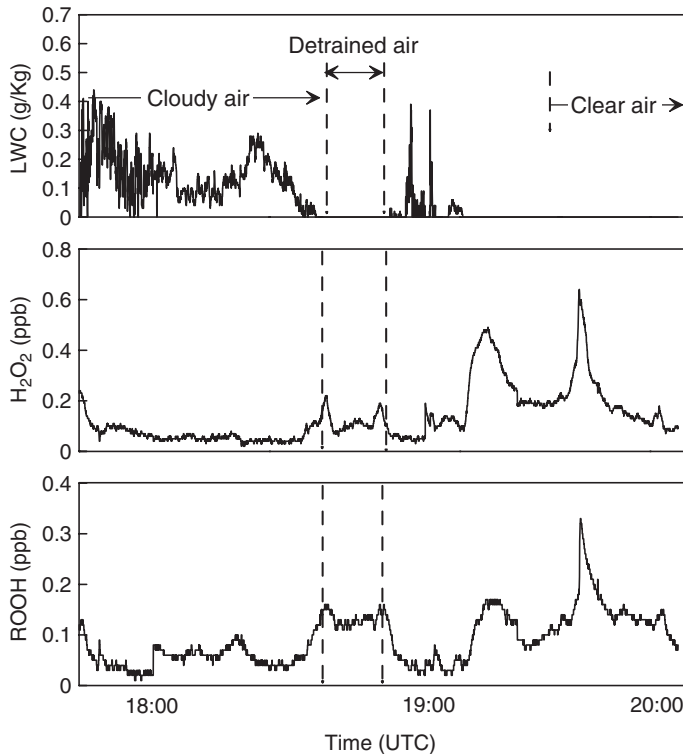


Fig. 1. Time series of altitude (m), liquid water content ($\text{g} \cdot \text{kg}^{-1}$), H_2O_2 concentrations (ppb), and ROOH concentrations (ppb) for a selected time segment of the research flight on April 10, 1990.

reactions involving 14 gas-phase species, with methane being the highest hydrocarbon initialized. The aqueous-phase chemical mechanism treats 49 aqueous-phase species, and does not include sulfur compounds. Equilibrium between the phases is not assumed, but rather the rates of mass transfer for the various species are computed. The gas- and aqueous-phase reactions and their rate constants used are summarized in Kim et al. (2002).

The parcel is driven along the path of a kinematic trajectory through a stratocumulus capped boundary layer; parameters such as cloud liquid water content, drop size, and contact time are prescribed (Feingold et al., 1998). A large eddy simulation (LES) of a cloudy boundary layer was used to obtain representative trajectories of cloud contact and LWC history. We stress that these LES simulations were not performed for the exact conditions of the EMEFS boundary layers. Thus, our simulations offer a basis for a qualitative, and not quantitative, comparison between observations and modeling.

Another important difference between the model results and the observations is that the measurements were of total organoperoxides (ROOH), whereas the model includes only the single species methylhydroperoxide (CH_3OOH). Recent ground- and aircraft-based peroxide measurements have demonstrated that CH_3OOH and hydroxymethyl hydroperoxide (HOCH_2OOH) are the major hydroperoxides so far identified in significant concentrations in the atmosphere (Hellpointner and Gab, 1989; Hewitt and Kok, 1991; Weinstein-Lloyd et al., 1998). Our comparisons assume that CH_3OOH is the dominant contributor to [ROOH], although this assumption will introduce some additional uncertainty.

As in Kim et al. (2002), gas-phase only simulations were run to a diurnal steady state for fixed concentrations of O_3 and NO_x , chosen for this study to be consistent with the reported observations. The species concentrations predicted by the steady-state simulations were then used as initial conditions for time-dependent simulations along LES trajectories that included six 12-min cycles through cloud; each cloud contact was followed by 48 min in cloud-free air. For comparison with the observations, modeled species concentrations were taken from specific segments of the time-dependent simulations. The initial conditions along the trajectory were assumed to represent clear-air concentrations; concentrations during the simulated cloud cycles were used to define modeled cloudy-air conditions; and the species concentrations in the clear-air conditions after completion of the six cloud passes were used to represent detrained-air species concentrations. We used output from daytime cloud simulations as the observations occurred from 17 to 22 UTC.

4. Results and discussion

Clear air, cloudy air, and detrained air respectively comprise about 71%, 21% and 8% of the observations used here. Some characteristics of this data set are shown in Table 1. The mean LWC in the cloudy air was $0.42 \pm 0.51 \text{ g m}^{-3}$ with a peak of 3.1 g m^{-3} . The mean clear-air H_2O_2 concentration was 0.57 ppb with a standard deviation of 0.55 ppb and a maximum of 2.0 ppbv. In cloudy air, H_2O_2 is significantly depleted and the mean concentration is below detection limit (BDL; <0.1 ppbv), which is expected due to the high solubility of H_2O_2 . The mean clear-air concentration of ROOH is 0.21 ± 0.17 ppbv, and the mean ROOH in the cloudy air is <0.1 ppbv. Note that in calculating the means of all the gas-phase species, values that were BDL were included in the statistics as their actual determined value (e.g. a value of H_2O_2 determined to be 0.05 ppbv would be BDL, but included in the mean as 0.05). In determining the values of the ratio of $[\text{H}_2\text{O}_2]$ to $[\text{ROOH}]$, only values for both species that were above the detection limit were included. In both the clear and detrained air, the mean

Table 1

Summary of mixing ratios of peroxides and relevant chemical species measured over Ontario, Canada during the March–April 1990 intensive measuring periods of the Eulerian Model Evaluation Field Study (EMEFS)

	Mean	σ	Range	Number of observations
<i>1) Clear air</i>				
Altitude	1110	420	500–1750	19565
H ₂ O ₂ (ppb)	0.57	0.55	<0.1–2.0	19565
ROOH (ppb)	0.21	0.17	<0.1–0.7	19565
Ratio	2.5	1.0	0.6–5.1	19565
Liquid water content (g m ⁻³)	0	–	–	19565
NO ₂ (ppb)	0.63	0.34	bdl–1.4	19565
O ₃ (ppb)	42	9	29–81	7353
SO ₂ (ppb)	1.6	1.8	bdl–12.52	9605
Temperature (K)	279	9	267–297	19565
<i>2) Cloudy air</i>				
Altitude	1072	282	790–1750	6062
H ₂ O ₂ (ppb)	<0.1	<0.1	<0.1–0.7	6062
ROOH (ppb)	<0.1	<0.1	<0.1–0.4	6062
Ratio	1.8	0.8	0.7–3.8	307
Liquid water content (g m ⁻³)	0.42	0.51	<0.1–3.1	6062
NO ₂ (ppb)	0.79	0.33	bdl–1.4	6062
O ₃ (ppb)	35	7	21–53	2214
SO ₂ (ppb)	3.1	1.9	<0.2–7.7	3642
Temperature (K)	272	1.8	268–276	6062
<i>3) Detrained air</i>				
Altitude	1070	180	830–1530	2166
H ₂ O ₂ (ppb)	0.36	0.19	<0.1–0.9	2166
ROOH (ppb)	0.15	0.04	<0.1–0.36	2166
Ratio	2.5	1.2	0.6–4.4	2166
Liquid water content (g m ⁻³)	0	–	–	2166
NO ₂ (ppb)	0.45	0.19	<0.1–1.3	2166
O ₃ (ppb)	43	3	22–51	730
SO ₂ (ppb)	4.1	2.9	0.3–8.9	1004
Temperature (K)	274	1.0	269–275	2166

The data described here are a subset of the field data, restricted to boundary layer observations (500–1750 m).

value of this ratio was 2.5 with standard deviations of 1.0 and 1.2 for clear and detrained air respectively, while its value was 1.8 ± 0.8 in the cloudy air. Note that due to the detection limit restriction placed on the values used in determining the ratio, the population number for this quantity is only 307 for the cloudy air. Most of the values were BDL and the true ratio in cloud is likely to be much lower than 1.8.

It is interesting that ROOH is depleted in the cloudy air, despite the low solubility of CH₃OOH. Some of the other compounds comprising ROOH are likely to have similar solubilities to H₂O₂ and must be responsible for this observed depletion in ROOH. Nevertheless, the strong response of the ratio, [H₂O₂]/[ROOH], to cloud contact demonstrates that H₂O₂ dissolves more readily than the sum of species represented in ROOH.

The ratios in clear and detrained air masses are plotted as a function of [NO₂] in Fig. 2. The cloud-perturbed gaseous ratios [H₂O₂]/[ROOH] tend to be higher than those in clear air under high-[NO₂] conditions, but, under low-[NO₂] condition, ratios for clear-sky tend to be higher than those in cloud-perturbed air, although the values of clear air mass show rather scattered and dispersed (Fig. 2). This implies that the effect of clouds is linked to the photochemical processes governing free radicals in the atmosphere, which are influenced by [NO_x] (Kim et al., 2002).

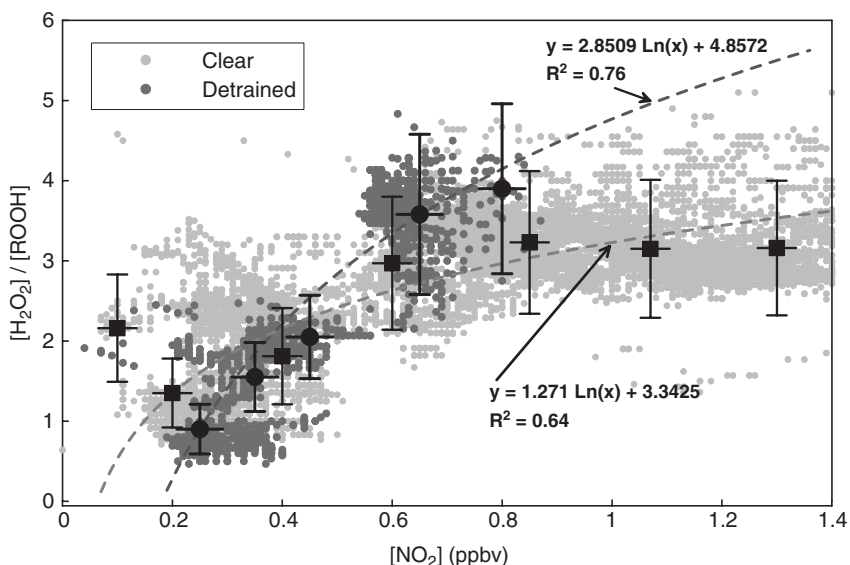


Fig. 2. The variation of the ratio $[H_2O_2]/[CH_3OOH]$ with $[NO_2]$ (ppb) in clear (gray symbols), cloudy (open symbols) and detained air (black symbols). Best-fit lines for each set of data are shown.

Sorting observations by $[O_3]$ showed only a slight trend toward increased ratios at higher $[O_3]$; the dependence upon $[NO_2]$ was much stronger.

Fig. 3a summarizes the variation of the observed ratio $[H_2O_2]/[ROOH]$ as a function of $[NO_2]$ for clear, cloudy, and detained air parcels, respectively. Fig. 3b shows, for comparison, the modeled variation in the ratio $[H_2O_2]/[CH_3OOH]$ as a function of $[NO_x]$. The modeled ratio is larger than the observed by about a factor of 2. This discrepancy may be due to the fact that organic peroxides other than CH_3OOH are excluded in the model. For example, measurements by Weinstein-Lloyd et al. (1998) show that the median concentration of total ROOH (excluding H_2O_2) was 2.8 ppbv during the summer 1995 intensive of the Southern Oxidants/Middle Tennessee study, and the contributions of CH_3OOH and $HOCH_2OOH$ to ROOH were 61%, and 35%, respectively. These data imply an expected reduction in the measured ratio of $[H_2O_2]/[ROOH]$, as compared with $[H_2O_2]/[CH_3OOH]$, of a factor of 1.5. Application of this factor brings the observations and model results into closer agreement, although as mentioned earlier there are other reasons for these comparisons to be more qualitative than quantitative.

In qualitative agreement with the observations, the model predicts that the ratio in detained air is higher than that in clear air for high- $[NO_2]$ conditions, whereas the opposite is true in low- $[NO_2]$ environments. The change in the predicted relative ratios in clear and detained air occurs near 0.35 ppb NO_x , very similar to the observed crossover point. Changing the assumed $[O_3]$ had only a minor effect on the results: the vertical bars in Fig. 3a show the range in variation in computed ratio for $15 \text{ ppb} \leq [O_3] \leq 65 \text{ ppb}$, spanning the observed $[O_3]$.

The modeled trends in the ratio arise primarily from the simulated variation in cloud water pH with $[NO_x]$, which switches the chemical regime from net H_2O_2 -consuming to net H_2O_2 -producing. A pH ~ 5.8 was simulated for low- NO_x (5 ppt) conditions, whereas the intermediate (50 ppt) and high (500 ppt) NO_x cases had pH values of ~ 4.8 and 3.5, respectively. The simulated aqueous-phase production of H_2O_2 was most enhanced, over the clear-sky rate, in the more acidic cloudwater in the higher- NO_x cases (Kim et al., 2002).

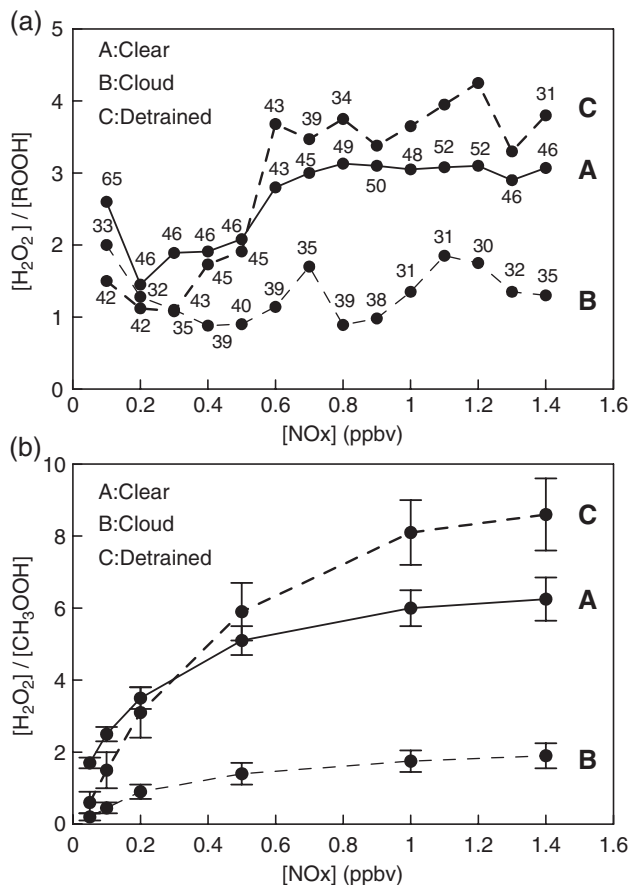


Fig. 3. Comparisons between measured and simulated $[H_2O_2]/[CH_3OOH]$. (a) Observed ratio as a function of $[NO_x]$ (ppb) for clear, cloudy and detrained air parcels. Numbers above symbols represent average ozone concentrations (ppb). (b) Simulated ratio as a function of $[NO_2]$ ($\approx [NO_x]$) (ppb) for clear, cloudy and detrained air parcels. Error bars represent the range of model results for $15 \text{ ppb} \leq [O_3] \leq 65 \text{ ppb}$, spanning the observed $[O_3]$.

For the simulations shown in Fig. 3a, we included reactions of SO_2 in the aqueous phase, as described in Table 7 of Kim et al. (2002), and used measured mean gaseous SO_2 concentrations from Table 1 as initial conditions. The inclusion of reactions of SO_2 acts to deplete $[H_2O_2]$ via the aqueous-phase S(IV)– H_2O_2 reaction, but decreases cloudwater pH by the production of S(VI), enhancing in-cloud H_2O_2 production. Thus the role of reactions involving SO_2 will be to somewhat shift the $[NO_2]$ at which the crossover point between H_2O_2 net in-cloud production and destruction occurs; the model results can be sensitive to the assumptions used to simulate SO_2 chemistry. Nevertheless, neglecting S chemistry completely shifted the crossover point only to about 0.2 ppb NO_2 , still in qualitative agreement with the observations.

Cloud contact could have a pronounced and persistent decreasing effect on the ratio of gaseous $[H_2O_2]$ to $[ROOH]$ in the cloudy air. In clear air and detrained air, however, both observational and numerical study clearly showed that the variation of $[H_2O_2]/[ROOH]$ has an increasing trend according to the $[NO_x]$ mixing ratio; lower ratio of detrained air in low $[NO_x]$ condition and higher in high $[NO_x]$ condition compared with that in clear air. This implies that

aqueous-phase $[H_2O_2]$ and $[ROOH]$ are decreased in the clouds via aqueous chemical reactions in the low $[NO_x]$ condition, but in the high $[NO_x]$ condition, generation of aqueous $[H_2O_2]$ in clouds from the aqueous-phase reaction with free radical exceeds the decreasing rate of ratio during the daytime. This is due to the increased $H_2O_2(aq)$ produced by the chemical reaction from the reaction of $HO_2(aq)$ that was formed by gas-phase photochemical reactions and was rapidly dissolved into cloud due to its high solubility. Because of this relation of gas-phase photochemistry, the generations of $HO_2(aq)$ are directly linked to atmospheric $[NO_x]$ conditions during the daytime, and are thus very sensitive to the time of the cloud encounter. For example, if cloud contact and corresponding reductions in the ratio occur in the late afternoon or at night, photochemistry is inactive regardless of $[NO_x]$ condition and the ratios is likely to remain low until the next diurnal cycle.

5. Summary and conclusion

The effect of clouds on concentrations of peroxides, namely H_2O_2 , $ROOH$ and the ratio $[H_2O_2]/[ROOH]$, were studied using observations from an airborne field study over Ontario, Canada during March and April of 1990. To investigate the effects of cloud contact, species concentrations in the boundary layer were classified as existing in one of three types of air mass: clear air, cloudy air and air detrained from cloud.

The results show that the ratio, $[H_2O_2]/[ROOH]$, was lower in detrained air compared with clear air under low- NO_2 conditions ($[NO_2] < 400$ ppt), but higher than clear-air observations for higher- NO_2 conditions ($[NO_2] > 400$ ppt). The observations are also consistent with current understanding of the photochemical processes involved, which suggests that evaporating clouds are a source of hydrogen peroxide at high- NO_2 (low-pH) conditions, but a net sink at low- NO_2 (high-pH) conditions. We used a coupled gas–aqueous-phase chemistry model to simulate cloud processing of peroxides. The ratio of $[H_2O_2]$ to $[CH_3OOH]$ in clear and detrained air is largely governed by ambient $[NO_2]$ and cloudwater pH. Increases in ambient $[O_3]$ were found to have only a small, positive impact on the ratio in both the modeled and observed cases. The removal of HO_2 radicals from the gas phase by cloud droplets leads to an important daytime source of H_2O_2 in cloud water for low-pH conditions, with about one $H_2O_2(aq)$ molecule being generated by aqueous-phase chemical reactions for each HO_2 radical incorporated into a droplet by heterogeneous scavenging. Modeled and observed trends in the value of $[H_2O_2]/[ROOH]$ as a function of ambient $[NO_2]$ were in generally good qualitative agreement. The results are indicative of the important role that clouds play in perturbing gas-phase species concentrations.

Acknowledgments

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