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An investigation of the relationship between gas-phase and aerosol-borne hydroperoxides in urban air

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Abstract

Simultaneous measurements of hydroperoxides in both the gas- and the aerosol-phase have been made for the first time. In addition, hydroperoxide levels in the ‘coarse’ ($> \text{PM}_{2.5}$) and ‘fine’ ($\text{PM}_{2.5}$) aerosol modes have been characterized. Hydrogen peroxide (H_2O_2) was found to be the major hydroperoxide present, with trace amounts of methyl hydroperoxide (CH_3OOH , MHP) occasionally being observed. Between May and August 2001, ambient gas- and aerosol-phase hydroperoxide levels were in the range 0.5–3.5 ppbv, and 0–13 ng m^{-3} , respectively. On average, about 40% of aerosol-phase H_2O_2 was associated with fine particles. The observed aerosol mass loadings correspond to aqueous concentrations of 10^{-4} – 10^{-3} M, above the levels necessary to induce lung epithelial cell damage in laboratory studies. The measured H_2O_2 mass loadings were found to be several times larger than could be explained by the solubility of gaseous H_2O_2 in liquid water. Potential reasons for this discrepancy are briefly discussed.

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1. Introduction

Aerosols have long been known to obscure visibility, damage materials, and adversely affect human health. During recent years, research in this area has escalated due to recognition of the role of aerosols, particularly those smaller than $2.5 \mu\text{m}$ ($\text{PM}_{2.5}$), in delivering potentially toxic compounds deep into the lungs. Recent epidemiological studies (Pope, Thun, & Namboodiri, 1995) indicate that increases in human mortality are associated with significantly lower concentrations of sulfates and fine particles ($\text{PM}_{2.5}$) than those previously thought to affect human health. The origins of this toxicity

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are not well established. Physical properties such as size or total mass, bulk chemical properties such as acidity, and specific chemical compounds have all been proposed as the ‘causative agent’.

Due to ppbv-levels of hydrogen peroxide (H_2O_2) and organic hydroperoxides (ROOH) in ambient air (Gunz & Hoffmann, 1990; Jackson & Hewitt, 1999), their high solubility in water, and the presence of a large mass fraction of water in submicron aerosol (Seinfeld & Pandis, 1997), hydroperoxides are expected to be present in fine particles at concentrations of the order of 0.1 mM (Friedlander & Yeh, 1998). It has been demonstrated that the exposure of respiratory tract cells to H_2O_2 solutions at concentrations ranging from 20 pM to 1 mM results in significant amounts of cell damage (Gurtner et al., 1987; Hyslop et al., 1988; Simon, Edwards, Reza, & Kunkel, 1991). The effects of the hydrogen peroxide solutions include inhibition of the conversion of ADP to ATP (Crim & Longmore, 1995), and the destruction of the alveolar epithelium including DNA strand breaking and decrease in lung surfactant biosynthesis (Oosting, Bree, Iwaarden, Golde, & Verhoef, 1990; Sporn, Marshall, & Peters-Golden, 1992).

Gas-phase hydroperoxides are formed in the atmosphere via three routes: (1) Gas-phase reactions of HO_2 with HO_2 and RO_2 (e.g., Atkinson, 1997), (2) water reacting with the ‘Criegee intermediate’ product of alkene ozonolysis (e.g., Hasson, Ho, Kuwata, & Paulson, 2001a, Hasson, Orzechowska, & Paulson, 2001b), (3) photochemical reactions of trace species in ambient liquid water (Faust, Anastasio, Allen, & Arakaki, 1993). Hydroperoxides are believed to partition between the gas-phase and liquid water according to their Henry’s law constants:



$$H_{\text{A}} \times P_{\text{A}} = [\text{A}] \quad (\text{E1})$$

where H_{A} is the Henry’s law constant (M atm^{-1}), $[\text{A}]$ is the liquid-phase concentration of A (M), and P_{A} is the gas-phase partial pressure of A (atm).

Only one previous study of aerosol-phase hydroperoxides has been carried out. In their paper, Hewitt and Kok (1991) briefly mention measurements of aerosol phase hydroperoxides. In this work, H_2O_2 mass loadings as high as 10 ng m^{-3} were reported at Niwot Ridge, Colorado. It is important to note, however, that the authors do not report sampling and analysis method validation, and so this data may not be reliable. Although gas-phase hydroperoxide levels were not simultaneously measured, ambient concentrations of H_2O_2 rarely exceed a few ppbv.

A study of ‘reactive oxygen species’ (ROS) (oxygen centered free radicals and their metabolites) as equivalent H_2O_2 in size-segregated aerosols has also been made (Hung & Wang, 2001) in urban air. In this study, the equivalent H_2O_2 concentrations were significantly higher than the Hewitt and Kok study (1991), falling in the range of $0\text{--}50 \text{ ng/m}^{-3}$. As discussed below, at least some of this measurement may be due to an artifact produced by the extraction process. Given that typical aerosol mass loadings are of the order of $100 \text{ } \mu\text{g m}^{-3}$, these two studies suggest that hydroperoxide levels within the aerosol may be higher than concentrations predicted by Henry’s law (E1) by a factor of 10 or more.

The chemical composition of submicron aerosol is extremely complex; in addition to water, these particles contain elemental carbon, organic compounds (such as carboxylic acids), metals, and inorganic ions such as NH_4^+ , SO_4^{2-} and NO_3^- (Seinfeld & Pandis, 1997). The presence of these species is likely to perturb $[\text{H}_2\text{O}_2]_{\text{aq}}$ from its H_{A} equilibrium concentration. Whether this perturbation is positive or negative, however, is not clear. In clouds and fogs, the reaction of H_2O_2 with dissolved

S(IV) compounds tends to lower $[\text{H}_2\text{O}_2]_{\text{aq}}$ from its H_A value e.g., (Heikes, Kok, Walega, & Lazrus, 1987; Noone et al., 1991; Sauer, Schuster, Schafer, & Moortgat, 1996). On the other hand, a laboratory investigation indicated that ammonium sulfate might enhance the effective solubility of hydrogen peroxide in aerosols by around 70% (Lind & Kok, 1986).

In this preliminary study we report ambient measurements of gas- and aerosol-phase hydroperoxides at an urban site (West Los Angeles). Simultaneous measurements of hydroperoxides in both phases have been made for the first time. In addition, hydroperoxide levels in the ‘coarse’ ($> \text{PM}_2$) and ‘fine’ (PM_2) aerosol modes have been characterized, also for the first time. The results of this investigation provide information on both the fundamental interactions of hydroperoxides with ambient aerosols, and the potential environmental and health effects of these species.

2. Experimental

2.1. Sampling

Samples were collected periodically between April and August 2001 on the roof of the Math Sciences Building at UCLA in West Los Angeles (WLA), 36 m above ground level. Sampling times varied slightly from day to day, but measurements were typically conducted between 9 AM and 6 PM. Meteorological data were acquired using instruments located at the hydroperoxide sampling site. Ozone and NO_x measurements were taken from the South Coast Air Quality Management District (SCAQMD) monitoring station in WLA, about 1 km SW of the UCLA site. A comparison of O_3 and NO_x measurements taken at the UCLA site and the SCAQMD station were previously found to be well correlated between about 9 : 30 AM and 6 PM when prevailing winds deliver air directly from WLA to UCLA (this lab, unpublished work).

Gas-phase hydroperoxides were extracted into the aqueous phase using a helical coil collector of the design of Hartkamp and Bachhausen (1987), as used in previous laboratory studies by this group (Hasson et al., 2001a,b). Ambient air was drawn through the stripping coil at 4.5 l min^{-1} , while 10 ml of stripping solution ($10^{-4} \text{ M Na}_2\text{EDTA}$ adjusted to pH 3.5 with sulfuric acid) was simultaneously circulated through the coil at a flow rate of 1 ml min^{-1} . This sampling technique strips both gas- and aerosol-phase hydroperoxides from the air sample. Since aerosol-phase hydroperoxide concentrations are typically 10^3 times smaller than gas-phase levels, however, the systematic errors introduced into the measured gas-phase concentrations are negligible. Following sampling, the stripping solution contains both hydrogen peroxide and carbonyl compounds. These species are known to react with each other in solution to form hydroxyalkyl hydroperoxides and dihydroxyperoxides. We find no evidence for these reactions, however, under our sampling conditions (below). Samples were collected for 30 min. On several occasions, two or more gas-phase samples were collected to investigate fluctuations in gas-phase hydroperoxide concentrations over the course of the aerosol-phase sampling period.

Aerosol samples were collected on 47 mm, $2 \mu\text{m}$ pore-size Teflon filters (Pall Corporation). Total suspended particulate (TSP) samples were collected by drawing 110 l min^{-1} of ambient air through the filters (supported on stainless steel filter holders) for 6 h. Size segregation of the coarse and fine aerosol was achieved using a virtual impactor, with flow rates of 105 l min^{-1} for the fine mode and 5 l min^{-1} for the coarse mode. At these flow rates, the size cut was at PM_2 . The aerosol-phase

hydroperoxides were extracted into the aqueous phase by wetting the filters with 0.2 ml of ethanol, and then adding 3 ml of stripping solution. It was initially hoped that the hydroperoxides could be rapidly extracted from the filters using a sonic bath. It was found, however, that after 15 min of sonication, pure, deionized water contained hydrogen peroxide at concentrations an order of magnitude larger than the levels expected in the sample solutions. The samples were, therefore, gently agitated every few minutes, and complete extraction of the aerosol-phase hydroperoxides from the filters took several hours.

2.2. Hydroperoxide analysis

Quantification of the hydroperoxides present in aqueous solution was achieved using the HPLC-fluorescence technique first reported by [Hellpointner and Gäb \(1989\)](#), and which has been described in detail previously ([Hasson et al., 2001a,b](#)). In brief, hydroperoxides are first separated on a reversed-phase C18 analytical column. At the end of the column, a mixture of the reagents horseradish peroxidase and *para*-hydroxyphenyl acetic acid (POHPAA) are added. The horseradish peroxidase enzyme catalyses the stoichiometric reaction between hydroperoxides and POHPAA resulting in the formation of one POHPAA dimer for every hydroperoxide molecule present. This dimer is detected by fluorescence, with excitation and emission wavelengths of 320 and 400 nm, respectively. The hydroperoxides are identified by comparison of their retention times with those of hydroperoxide samples synthesized in the laboratory. The concentrations of hydroperoxides are determined by comparison of the integrated fluorescence peak areas with those of standardized hydrogen peroxide solutions.

2.3. Validation of aerosol sampling method

Two tests were performed to validate the aerosol-phase hydroperoxide collection method. First, ‘standardized’ aqueous hydrogen peroxide aerosols were generated in the laboratory by flowing 1.5 l min^{-1} of dry nitrogen through a Collison nebulizer containing $3 \times 10^{-4} \text{ M H}_2\text{O}_2$. The resultant aerosol was diluted with $2\text{--}10 \text{ l min}^{-1}$ air before being collected on Teflon filters for 15 min and then extracted as described above. Total aerosol mass loadings were estimated from particle counter measurements and the aerosol-volume characteristics reported for the Collison nebulizer ([May, 1973](#)). The H_2O_2 signals were found to increase for 2–3 h, with final concentrations within 20% of the expected values. This indicates that hydrogen peroxide solutions do not decompose appreciably on Teflon filters. Second, ambient aerosol samples were collected and extracted as described above, but with two filters in series. H_2O_2 was only observed on the front filter showing that essentially all aerosol is collected on the first filter, and that deposition of gas-phase hydrogen peroxide to Teflon filters is negligible.

3. Results

In both the gas- and the aerosol-phase, H_2O_2 accounts for the majority of the total of hydroperoxides present. On several occasions, trace quantities (5–20 ppbv) of methyl hydroperoxide (CH_3OOH , MHP) were observed in the gas-phase, but no other organic hydroperoxides were

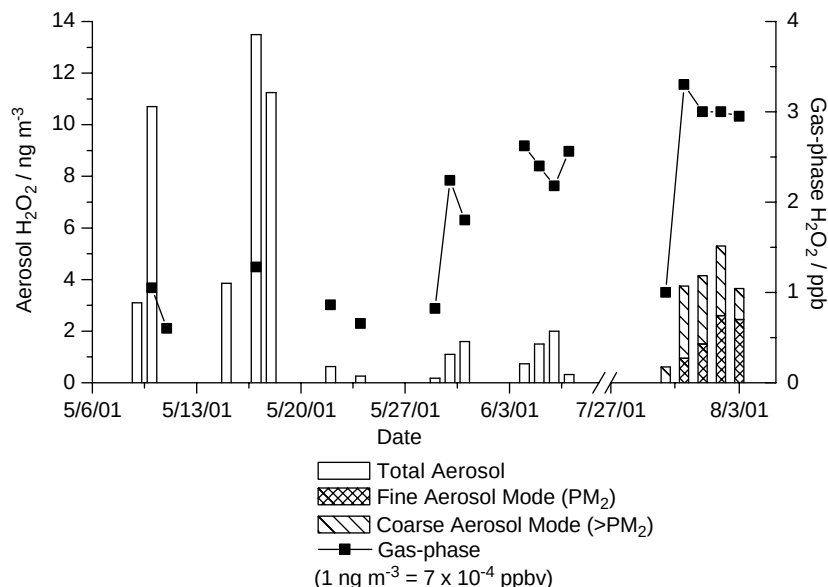


Fig. 1. Ambient H_2O_2 measurements May–August 2001.

detected. MHP was only observed in two aerosol samples, with mass loadings of 0.1 and 0.4 ng m^{-3} on May 9 and 10, respectively.

3.1. Gas-phase H_2O_2

Measured gas- and aerosol-phase concentrations of hydrogen peroxide are shown in Fig. 1. In all cases, more than 99.9% of total ambient H_2O_2 was found to be in the gas-phase ($1 \text{ ng m}^{-3} \equiv 0.7 \text{ pptv}$). Gas-phase measurements, made with half-hour time resolution, are averaged to daily values. Hourly fluctuations in gas-phase hydroperoxide concentrations were found to be relatively small ($< 30\%$), but had a much larger day-to-day variability. This implies that the measured gas-phase hydroperoxide concentrations are representative of the average exposure of aerosols to gas-phase peroxides over the 6-h aerosol-sampling period. H_2O_2 concentrations were found to be in the range 0.6–3.3 ppbv. H_2O_2 levels increased from an average of around 1 ppbv in early May to 3 ppbv in early August (although day-to-day fluctuations of 100% or more were observed). This seasonal increase in H_2O_2 is in agreement with previously observed trends (Gunz & Hoffmann, 1990; Jackson & Hewitt, 1999). A strong negative correlation between NO_x and H_2O_2 was observed ($R^2 = 0.42$, $P = 0.008$ for a linear fit to a plot of $[\text{H}_2\text{O}_2]$ versus $1/[\text{NO}_x]$), as has been reported previously (e.g., Sauer, Limbach, & Moortgat, 1997). Ambient H_2O_2 was uncorrelated with O_3 , which ranged from 30 to 70 ppbv ($R^2 = 0.02$), and possibly weakly correlated with relative humidity ($R^2 = 0.12$, $P = 0.19$) over a limited range (65–85% RH). In contrast, Hung and Wang (2001) and Olszyna, Bailey, Simonaitis and Meagher (1998) observed strong correlations between ambient O_3 levels and aerosol and gas phase ROS, respectively.

Sakugawa and Kaplan (1990) measured gaseous H_2O_2 at UCLA in August 1986 and reported maximum concentrations of around 0.3 ppbv, an order of magnitude lower than the levels reported here. The average NO_x concentration during their sampling period was about 40 ppbv, whereas during this campaign, the corresponding value was about 20 ppbv. Thus, given the strong anti-correlation between $[\text{NO}_x]$ and $[\text{H}_2\text{O}_2]$, it is likely that $[\text{H}_2\text{O}_2]$ was lower during their field campaign. Sakugawa and Kaplan (1990) proposed that their cryogenic sampling method might collect less H_2O_2 relative to the stripping coil method employed in this study, possibly due to the reaction of O_3 with water in the stripping coil. This hypothesis is not borne out either by the lack of a correlation between gas-phase H_2O_2 and O_3 in ambient air or with our laboratory measurements in chambers (Hasson et al., 2001a).

3.2. Aerosol-phase H_2O_2

In the period between May and August, H_2O_2 mass loadings ranged from < 0.1 to 13 ng m^{-3} (Fig. 1). Several aerosol samples were collected during April, but no H_2O_2 was observed (the detection limit is 0.1 ng m^{-3}). This range of values is in broad agreement with the only previous measurements of this quantity (< 0.01 – 10 ng m^{-3} , Hewitt & Kok, 1991). The ROS measured by Hung and Wang (2001) are significantly higher than ours, despite the fact that the aerosol masses they measured (10 – $200 \text{ } \mu\text{g/m}^{-3}$) are similar to those typical for Los Angeles (Air Resources Board, 1993, 1994). There are several possible explanations for this, including real differences in the samples, and a systematic error in one of the methods. In their study of ROS in aerosols, Hung and Wang (2001) used 10 min of ultrasonication to extract their samples, which may explain both their very high blank levels and the high aerosol mass loadings reported.

Virtual impactor samples collected in July and August demonstrate that a significant fraction (25–70%) of the total H_2O_2 mass loading is in the fine aerosol ($\text{PM}_{2.5}$) mode (Fig. 1). Comparison of chromatograms from coarse and fine aerosol samples suggests that the coarse mode aerosol contains an additional hydroperoxide species that elutes just before H_2O_2 . Because the peaks nearly co-elute, it was not possible to quantify the contribution from this second species, but a visual inspection of the chromatograms suggests that it comprises around 30% of the total coarse mode signal and 20% of the TSP signal.

4. Discussion

If the amount of aerosol-phase H_2O_2 is determined by its solubility in water, then the mass loading should be correlated with the gas-phase concentration of H_2O_2 and the volume of liquid water present. The latter quantity is determined by the total aerosol mass loading, the hygroscopicity of the aerosol (determined by its chemical composition), and the relative humidity. If the gross assumption is made that both the aerosol mass loading and chemical composition are invariant over the sampling period, the fraction of ambient H_2O_2 in the aerosol-phase (i.e. $[\text{H}_2\text{O}_2]_{\text{aerosol}}/[\text{H}_2\text{O}_2]_{\text{gas}}$) should be positively correlated with the relative humidity. Within the limited data set, this was found to be the case (not shown, $R^2 = 0.32$, $P = 0.03$).

To establish whether or not the H_2O_2 mass loading is in line with Henry's law predictions, it is necessary to know the aerosol mass loading of water. Unfortunately, this parameter could not be

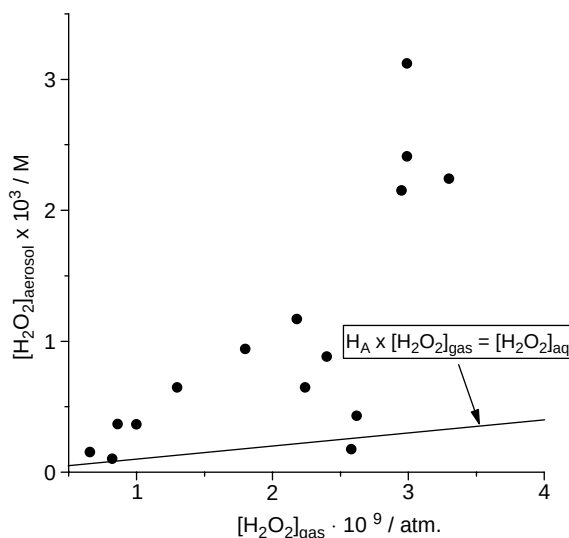


Fig. 2. Henry's law plot (assuming $50 \mu\text{g m}^{-3}$ liquid water).

measured during the study. We can, however, consider Henry's law behaviour using an upper limit of about $50 \mu\text{g m}^{-3}$ aerosol liquid water. This number is based on an upper limit for aerosol mass loadings in West Los Angeles of $100 \mu\text{g m}^{-3}$; this is certainly an upper limit as 24 h average values for TSP in the mid-1990's were typically $60 \mu\text{g m}^{-3}$ (Air Resources Board, 1993, 1994). Further, water comprises less than 50% of the total mass of Los Angeles aerosol at $\text{RH} < 80\%$ (Zhang, McMurry, Hering, & Casuccio, 1993). Fig. 2 shows a Henry's law plot of $[\text{H}_2\text{O}_2]_{\text{aq}}$, calculated from measurement data by assuming $50 \mu\text{g m}^{-3}$ of aerosol liquid water for all sampling days vs. $[\text{H}_2\text{O}_2]_{\text{gas}}$. Also included in Fig. 2 is the expected relationship between gaseous and aqueous H_2O_2 concentrations given that H_A is $1 \times 10^5 \text{ M atm}^{-1}$ (Sander, 1999). The calculated $[\text{H}_2\text{O}_2]_{\text{aq}}$ values are clearly several times larger than their H_A equilibrium values. It is important to note that the unknown aerosol liquid water content translates into a large uncertainty in $[\text{H}_2\text{O}_2]_{\text{aq}}$. The actual liquid water content is almost certainly lower than the assumed $50 \mu\text{g m}^{-3}$, however, and so the calculated $[\text{H}_2\text{O}_2]_{\text{aq}}$ values represent conservative lower limits, and the discrepancy between $[\text{H}_2\text{O}_2]_{\text{aq}}$ and the H_A equilibrium values is significant. Further, the aerosol-phase $[\text{H}_2\text{O}_2]$ (10^{-3} – 10^{-4} M) is high enough to potentially pose a significant health risk.

Here we consider three possible explanations for the elevated aerosol-phase hydrogen peroxide concentrations: (1) hydrolysis of an unidentified compound to produce H_2O_2 during sample extraction; (2) aqueous-phase photochemical production of H_2O_2 in the aerosol; (3) a higher effective Henry's law constant (H_A^*) in the aerosol. Laboratory studies have shown that alkene–ozone reactions under ambient conditions can generate hydroxyalkyl hydroperoxides (e.g., Tobias, Docherty, Beving, & Ziemann, 2000). Hydroperoxides formed from larger alkenes are likely to have low vapor pressures, and may condense on existing particles to produce secondary organic aerosol. By analogy with C_1 and C_2 hydroxyalkyl hydroperoxides (Hasson et al., 2001a), during sample extraction the hydroperoxides present in the aerosol probably hydrolyse to produce H_2O_2 and a carbonyl compound.

Non- and semi-volatile hydroperoxides are unlikely to be very soluble in water, however, and so this mechanism cannot account for the positive correlation between $[\text{H}_2\text{O}_2]_{\text{aerosol}}/[\text{H}_2\text{O}_2]_{\text{gas}}$ and RH.

It has been demonstrated that aqueous-phase photochemical reactions are an important source of H_2O_2 in clouds and fogs (Faust et al., 1993; Faust, Powell, Rao, & Anastasio, 1997). It is possible that similar reactions occur within aqueous aerosols, and may result in the observed H_2O_2 mass loadings. During sampling, however, the filters are not exposed to sunlight. Consequently, once particles have been collected on the filter, they will no longer photochemically generate H_2O_2 . Given that equilibration between the gas- and aerosol-phase is likely to take only a few minutes, and that sample collection took 6 h, aqueous-phase photochemistry cannot be the origin of the high H_2O_2 mass loadings.

As outlined above, the presence of various chemical compounds can affect the steady-state concentration of H_2O_2 in aqueous solution. It is possible that high concentrations of ammonium sulfate (and possibly other salts) enhance the solubility of H_2O_2 (Lind & Kok, 1986), leading to the observed mass loadings. In clouds and fogs, H_2O_2 concentrations tend to be lowered from their H_A equilibrium values due to the reaction of H_2O_2 with dissolved S(IV) compounds e.g., (Sauer et al., 1996) (which originate from aqueous uptake of SO_2). This effect is likely to be much less significant in aerosols due to their lower pH relative to clouds and fogs. H_A^* for SO_2 decreases by a factor of roughly 10^3 as the pH is reduced from five to two, whereas H_A for H_2O_2 is essentially unchanged (Seinfeld & Pandis, 1997). Thus the concentration of S(IV), and the importance of this sink for aqueous H_2O_2 , is probably much less in aerosol than in clouds and fogs. Aerosols also contain significant concentrations of transition metal ions (Seinfeld & Pandis, 1997) that may catalytically consume H_2O_2 (Breytenbach, vanPareen, Pienaar, & vanEldik, 1994). Nonetheless, given the available data, an increase of H_A^* in aerosols relative to liquid water appears to be the most likely explanation for the high mass loading of H_2O_2 .

5. Conclusions

Ambient gas- and aerosol-phase hydroperoxides have been measured together for the first time. H_2O_2 aerosol mass loadings were found to be in the range $< 0.1\text{--}13\text{ ng m}^{-3}$, significantly higher than levels predicted based on the gas-phase concentration and solubility of H_2O_2 in water. Up to two-thirds of the H_2O_2 aerosol mass was found to be in the fine mode. Due to its high solubility, gas-phase H_2O_2 is efficiently removed in the upper respiratory tract when inhaled. On the other hand, fine aerosols, may provide a mechanism by which significant quantities of H_2O_2 can be delivered deep into the lungs. Upon deposition of the particles in the alveoli, the fluid in the lung will dilute the aerosol-phase hydrogen peroxide. Given that the diameter of an alveolus is about $200\text{ }\mu\text{m}$, and that the liquid layer in the alveoli is about $0.2\text{ }\mu\text{m}$ thick (Bastacky et al., 1995), the H_2O_2 in a particle with a diameter of 1 micrometer would be diluted by a factor of about 10^5 . Toxicological studies have shown that H_2O_2 solutions as dilute as $2 \times 10^{-11}\text{ M}$ may cause damage to alveolar cells, thus the observed aerosol-phase $[\text{H}_2\text{O}_2]$ of $10^{-4}\text{--}10^{-3}\text{ M}$, which would be diluted in the alveolus to about $10^{-9}\text{--}10^{-8}\text{ M}$, may represent a serious health risk. As H_2O_2 is stripped from the gas-phase by the respiratory tract, aerosol-phase hydrogen peroxide will desorb from the particles, hence a significant fraction of the aerosol-phase H_2O_2 may not reach the alveolar region of the lung. A recent aerosol exposure study in rats (Morio et al., 2001), however, suggests that a significant amount of H_2O_2

penetrates deep into the lungs, and causes cell damage. Further studies are clearly needed to improve our understanding of (1) the distribution of aerosol-phase H_2O_2 in the boundary layer, (2) factors affecting H_2O_2 mass loadings, and (3) the associated health effects.

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