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Measurements of Peroxides and What They Tell Us

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Contents

1. Introduction

The chemical composition of the atmosphere at the trace gas level is largely controlled by the presence of various oxidants in the troposphere, which effectively determine the lifetime of many natural and anthropogenic pollutants (e.g., methane (CH_4), carbon monoxide (CO), nonmethane hydrocarbons, nitrogen oxides (NO_X), and sulfur dioxide (SO_2)). In turn, these pollutants can affect the level of oxidants and thus impact the atmosphere's response to future perturbations. Peroxides can be important oxidants in their own right,[1−3] and as reservoirs of other oxidant species they can be indicators of the chemical processing that has taken place in the troposphere. Since peroxides are formed as a result of free radical chemistry involving hydroxyl radicals (OH), the presence of large amounts of hydrogen peroxide (H_2O_2) in the atmosphere is indicative of the presence and importance of this key oxidant in the chemistry of the Earth's atmosphere.

H_2O_2 has been known to be a component of rainwater for at least a century.[4] The presence of peroxides and ozone (O_3) in the lower atmosphere was previously ascribed to electrical activity,[4] but both, as is now well-known, are formed photochemically. The chemical route to the production of OH in the troposphere, and the subsequent production of peroxides, was first proposed by Levy in 1971.[5] This was not done in isolation, however, since Weinstock and Niki[6,7] had stipulated the need for OH in the troposphere based on their studies of the behavior of carbon monoxide, which had a stable concentration despite massive emissions. The solution was provided by measurements of the O_3 absorption spectrum in the critical region of 290−320 nm where its photolysis gives rise to the production of singlet oxygen atoms ($O(^1D)$) that react with water vapor to form OH, which produces peroxy radicals by reaction with CO and other gases.[8] The combining of peroxy radicals then produces peroxides.

Thus, the formation of H_2O_2 is a direct consequence of sunlight shining on an atmosphere containing O_3 and water vapor together with gases such as CO and hydrocarbons, some of which are provided naturally and some of which result from human activities. The peroxy radicals have other fates and are ultimately involved in both the destruction and the production of O_3 in the atmosphere. Thus, peroxide formation or lack of formation is intimately linked to the extent of OH radical chemistry taking place in the atmosphere and with the cycle of O_3 in the troposphere. These are the main themes that will be dealt with in this review, and as such, it will be significantly different to previous reviews,[9,10] which have tended to present large surveys of atmospheric measurement methods and data sets along with detailed aspects of the chemistry of peroxides.

Another of the major roles of H_2O_2 in the atmosphere is the efficient oxidation of sulfur dioxide to sulfuric acid (H_2SO_4) in cloud droplets. The first paper describing this process in atmospheric terms was published by Penkett et al. in 1979,[1] and it stimulated a search for sensitive and specific methods of peroxide measurements. This became of major importance because of the concern in the 1970s and early 1980s over the effects of acid deposition on sensitive ecosystems in Europe and North America. An excellent review of the level of understanding of this problem was published as a US National Academy of Sciences report in 1983 chaired by J. G. Calvert.[11] Extensive measurements of peroxides in the atmosphere became available from about 1985 onward, and papers describing atmospheric peroxides are still being produced currently at a substantial rate. The database is still inadequate, unfortunately, due to deficiencies in the measurement techniques

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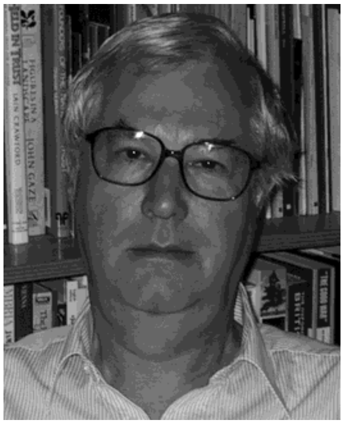
Claire Reeves graduated from the School of Environmental Sciences, University of East Anglia (UEA) in 1986 with a BSc in Environmental Sciences, having specialized in atmospheric and aquatic sciences. She stayed on at UEA to do a Ph.D. in atmospheric sciences under the supervision of Prof. Stuart Penkett, with one year at the University of Oslo with Prof. Ivar Isaksen, graduating in 1989. Since then, Claire has continued to work as a post-doc at UEA with Stuart Penkett. During this time, she was the Data Manager for the NERC Thematic Program Atmospheric Chemistry Studies of the Oceanic Environment and is currently funded as a PDRA for the NERC Centres for Atmospheric Sciences Distributed Institute for Atmospheric Composition. Her interest in atmospheric chemistry not only includes fast photochemistry but also long-range transport of pollution and the budgets of ozone depleting and long-lived greenhouse gases.



Stuart Penkett began his career in atmospheric chemistry in 1968. From 1968 to 1985, he worked at the Atomic Energy Research Establishment (AERE) in Harwell, England. After leaving Harwell in May he was briefly a visiting scientist at the National Center for Atmospheric Research (NCAR). Returning to England, he took up a NERC (Natural Environment Research Council) Readership in the Schools of Chemical and Environmental Sciences at the University of East Anglia in Norwich in September of 1985. He was made a professor in the School of Environmental Sciences in 1990. His research interests include the trace gas composition of the stratosphere and troposphere and the reactive chemistry of the troposphere. His publications are concerned with measurements of many trace gases, such as hydrocarbons, halocarbons, and sulfur compounds; oxidation of sulfur dioxide in both gas and liquid-phase reactions; and measurements of peroxy radicals, peroxides, PAN, and ozone in both polluted and clean atmospheres. He is an external member of the Max Planck Institute for Chemistry in Mainz and was an Affiliate Scientist at NCAR from 1997 to 2000.

and also to a lack of comeasurement of vital parameters such as the O_3 concentration, the water vapor concentration, and the photolysis rate coefficients for O_3 and peroxides. Ideally, a global database should be generated from satellite measurements, but this is not very likely soon and possibly never.

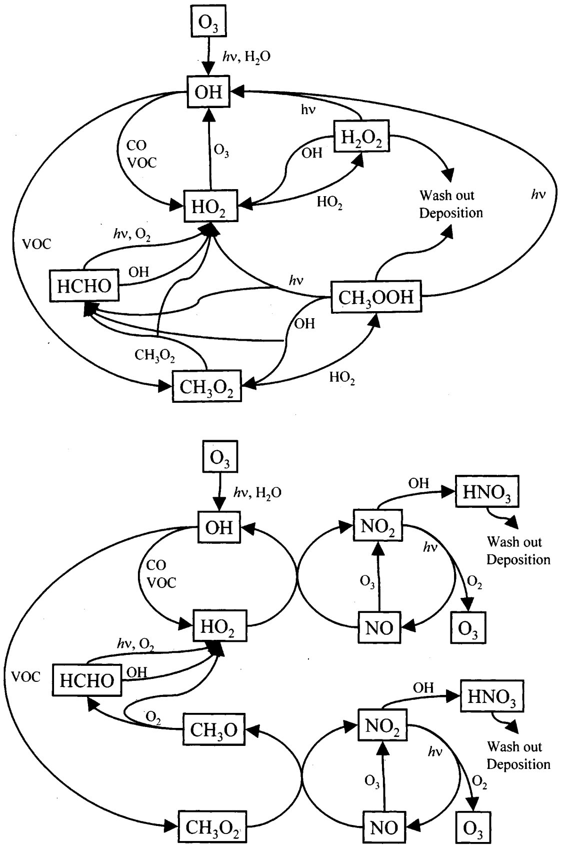


Figure 1. Tropospheric peroxy radical chemistry (a) NO_X poor and (b) NO_X rich.

This review is not intended to be an exhaustive examination of peroxide measurements or laboratory studies but is rather an assessment of the nature and extent of global tropospheric gas-phase chemistry as elucidated by atmospheric measurements of peroxides. It will therefore present material on the photochemical theory of atmospheric peroxides in section 2, an overview of the peroxide measurement techniques in section 3, and available global data sets in section 4. Section 5 then relates what these measurements of peroxides tell us about the atmospheric photochemistry leading to the production of hydroxyl radicals and the destruction and production of O_3. Because of the predominance of data on H_2O_2, this review has consequently tended to focus on inorganic peroxide rather than the organic peroxides. Newer aspects of the role of peroxides in the creation of free radical species in the upper troposphere will also be reviewed.

2. Photochemical Theory

In the troposphere, the primary oxidant is the OH radical, the main source of which is the photolysis of O_3 in the presence of water vapor (H_2O) (Figure 1).

$$O_3 + h\nu \rightarrow O(^1D) + O_2 \tag{1}$$

$$O(^1D) + H_2O \rightarrow 2OH \tag{2}$$

The excited $O(^1D)$ atom can also be quenched to $O(^3P)$ by reaction with N_2 or O_2.

$$O(^1D) + M \rightarrow O(^3P) \tag{3}$$

where M is either N_2 or O_2. The value of k_3 is approximately an order of magnitude less than k_2,[12] so the reaction of $O(^1D)$ with H_2O to produce OH is quite competitive with its quenching to $O(^3P)$ but is highly dependent on the water vapor concentration. For typical water vapor concentrations of 10 000 ppmv in the marine boundary layer (MBL), about 10% of the $O(^1D)$ production from O_3 photolysis leads to the production of OH, and the effective production ratio is 20%. The tropospheric water vapor concentration ranges approximately from 100 to 20 000 ppmv, so there is a large variation in OH production efficiency from O_3 photolysis, and in the upper troposphere (UT) it is very low, creating opportunities for other OH sources to play a role (see section 5.4). Recently, there have been a number of very detailed examinations of the production of $O(^1D)$ from O_3 at wavelengths up to 340 nm, and this suggests that the limiting wavelength of 310 nm is incorrect and also that OH production will occur efficiently at quite high latitudes where radiation of less than 310 nm in wavelength is almost absent (see review by Matsumi et al.[13] and references therein).

The OH radicals can oxidize many species, with most of the OH reacting with CO and CH_4, particularly in the remote atmosphere, to produce peroxy radicals (HO_2, CH_3O_2).

$$OH + CO \rightarrow HO_2 + CO_2 \tag{4}$$

$$OH + CH_4 \rightarrow CH_3O_2 + H_2O \tag{5}$$

The fate of the peroxy radicals is critical in determining the oxidant levels in the troposphere. In a low NO_X atmosphere, the HO_2 reacts with itself to form H_2O_2 or with the methyl peroxy radical (CH_3O_2) to form methyl hydrogen peroxide (CH_3OOH) (MHP) (Figure 1a).

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2 \tag{6}$$

$$HO_2 + CH_3O_2 \rightarrow CH_3OOH + O_2 \tag{7}$$

The relative rate of formation of H_2O_2 and MHP is dependent on the rate coefficients k_6 and k_7 and the concentrations of HO_2 and CH_3O_2, which themselves are dependent on their rate of formation via the reactions of OH with CO (k_4) and with CH_4 (k_5). The rate coefficient k_5 is slower than k_4, particularly in the UT, where k_5 is reduced due to the lower temperatures.[12] However, this is compensated for by higher concentrations of CH_4 than CO and the rate coefficient for the reaction of HO_2 with CH_3O_2 (k_7) generally being faster than that of the HO_2 self-reaction (k_6), particularly in the upper troposphere. In the moist MBL, the pressure dependence and, in particular, the water vapor dependence of the HO_2 self-reaction increases k_6 considerably[14] making it comparable to that of k_7. Overall, this tends to lead to similar concentrations of H_2O_2 and MHP in many parts of the atmosphere.

The peroxides are reservoirs for radicals. If the peroxides are photolyzed, then radicals are released, but if they react with OH or are washed out or deposited to the surface, the peroxides essentially become a sink for the radicals.

$$H_2O_2 + h\nu \rightarrow 2OH \tag{8}$$

$$CH_3OOH + h\nu \rightarrow HO_2 + OH + HCHO \tag{9}$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O \tag{10}$$

$$CH_3OOH + OH \rightarrow 0.7CH_3O_2 + 0.3OH + 0.3HCHO \tag{11}$$

Note that in dry air (e.g., the upper troposphere), the source of HO_X ($OH + HO_2$) via the photolysis of O_3 may be considerably reduced, and other sources, such as the photolysis of peroxides, may become relatively more important.

The overall process of conversion of O_3 to peroxides is essentially a large sink for O_3 since peroxides are very soluble and can be removed efficiently in rain and by deposition to the surface. The recombination reactions to form peroxides are in direct competition with other possible reactions. For instance, HO_2 can also react with O_3 and thus remove it directly; at an O_3 concentration of about 20 ppbv, typical of the MBL, this reaction is competitive with the recombination reaction to form H_2O_2.

$$HO_2 + O_3 \rightarrow OH + 2O_2 \tag{12}$$

The previous reaction is part of an efficient catalytic removal cycle for O_3, which is closed by

$$OH + O_3 \rightarrow HO_2 + O_2 \tag{13}$$

However, if nitric oxide (NO) is present, the peroxy radicals will react with it forming nitrogen dioxide (NO_2), which photolyses giving $O(^3P)$ that then readily reacts with oxygen (O_2) to reform O_3 (Figure 1b).

$$HO_2 + NO \rightarrow NO_2 + OH \tag{14}$$

$$CH_3O_2 + NO \rightarrow NO_2 + HCHO + HO_2 \tag{15}$$

$$NO_2 + h\nu \rightarrow NO + O(^3P) \tag{16}$$

$$O(^3P) + O_2 \rightarrow O_3 \tag{17}$$

This O_3 formation process is terminated by the reaction of OH with NO_2 to form nitric acid (HNO_3), whereby HNO_3, as opposed to H_2O_2, becomes the major sink for odd hydrogen.

$$OH + NO_2 \rightarrow HNO_3 \tag{18}$$

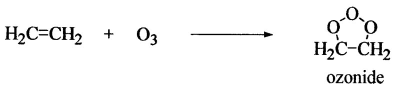
HO_2 also reacts with NO_2 to make peroxy nitric acid (HNO_4)

$$HO_2 + NO_2 \rightarrow HNO_4 \tag{19}$$

HNO_4 is quite stable in the UT, but its lifetime in the lower troposphere is considerably less than 1 min. For HO_2, the rate coefficient (k_{14}) for reaction with NO is nearly 2 times greater than the recombination rate (k_6),[12] implying that O_3 production is favored over H_2O_2 production at NO concentrations exceeding about 10 pptv. Above a certain NO concentration, a cycle of reactions involving free radicals and NO_X (NO + NO_2) can occur in which the amount of O_3 produced exceeds that destroyed, giving net photochemical production of O_3. As the NO_X concentration becomes larger (~2 ppbv), the termination reactions dominate, and O_3 production is suppressed.

Peroxides can still be formed in polluted air. The peroxy radical reactions shown in Figure 1a,b show the dominant reactions in a NO_X poor and NO_X rich atmosphere, respectively, but in reality, these reactions are in competition with each other. Although an increase in NO_X will convert HO_2 into OH via reaction with NO_2, polluted air may also contain significant concentrations of nonmethane hydrocarbons, in particular, longer chain molecules that will lead to larger hydroperoxides (e.g., ethyl hydroperoxide (CH_3CH_2OOH)) being formed, as well as H_2O_2 and MHP through the production of HO_2 and CH_3O_2 in the breakdown of the nonmethane hydrocarbon. These larger alkyl hydroperoxides are formed in an analogous way to the MHP (reaction 7).[15,16] For marine situations, the suite of atmospheric peroxides is almost entirely made up of H_2O_2 and MHP because of the low abundance of nonmethane hydrocarbons. On the continents, it is a different matter, although the two simpler peroxides usually still dominate. There are, however, a dearth of measurements of the higher homologous species. These would be useful in connection with quantifying the role of individual peroxy radicals in creating O_3 in episodes of photochemical air pollution.

The atmosphere is also known to contain more complex peroxides, such as hydroxymethyl hydroperoxide ($CH_2(OH)OOH$) (HMHP), which are formed in the course of the ozonolysis of alkenes in the presence of water vapor,[17] for example:



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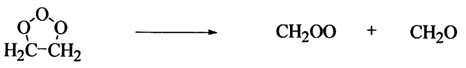

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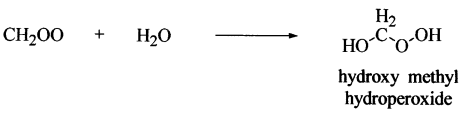

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The ozonolysis of isoprene and some other biogenic hydrocarbons (e.g., terpene and isobutene) can produce various peroxides, including H_2O_2, without involving HO_2.[18,19] The formation of peroxides can be strongly influenced by the presence of water vapor, with yields of H_2O_2 increasing from 1% in dry air to 9% in moist air; the yield of HMHP is increased substantially by water vapor, but the yield of MHP is unaffected.[17]

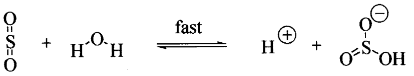
The formation of another organic hydroperoxide, peroxy acetic acid (PAA), involves the $CH_3C(O)OO$ radical that is mainly produced by photooxidation of acetone and peroxy acetyl nitrate (PAN).

$$CH_3C(O)CH_3 + h\nu\ (+\ O_2) \rightarrow CH_3C(O)OO + CH_3O_2 \quad (23)$$

$$CH_3C(O)OO + HO_2 \rightarrow CH_3C(O)OOH + O_2 \quad (24)$$

H_2O_2 and MHP have also been observed to be produced directly by biomass fires.[20] An aqueous phase route to the formation of peroxides in cloudwater has been proposed;[21,22] it has not been quantified, however, and its relevance to the main theme of this review is probably very limited.

In addition to the gas-phase loss of peroxides discussed previously (reactions 8−11), H_2O_2 can be lost via reaction with SO_2 in the aqueous phase. H_2O_2 in particular is very soluble in cloud droplets with a Henry's Law coefficient (K_H) of approximately 3.09 $\times 10^5$ M atm^{-1} at 10 °C and 1.07 $\times 10^5$ M atm^{-1} at 22 °C.[23] The concentration in solution in equilibrium with 1 ppb H_2O_2 is thus 30 μM at 10 °C and 10 μM at 22 °C. These concentrations and higher are commonly observed in cloud droplets over Europe and the US in summer.[9] They will provide enough oxidant to oxidize a large fraction of the SO_2 present at cloud height. The oxidation of SO_2 in solution proceeds mainly through the bisulfite ion that dominates the hydrolysis products of SO_2 over the pH range 2−5, which is the range experienced in most cloud and fog droplets. The mechanism proposed for the reaction of H_2O_2 with HSO_3^- by Hoffmann and Edwards in 1975[24] is



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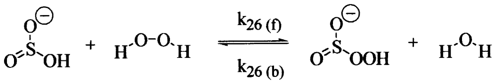

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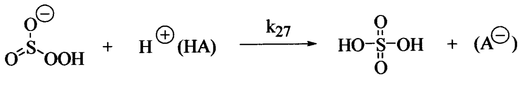


(27)

For [H^+] < 0.1 M, which is the usual situation in cloud droplets, the rate of removal of SO_2 is independent of pH and dependent only on the amount of H_2O_2 present.[2] This means that it is the most efficient method of droplet phase oxidation SO_2 (all other mechanisms becoming slower with increasing H^+) and that in circumstances with high SO_2 levels, it becomes an important sink for H_2O_2. The high solubility of H_2O_2 also means that it is efficiently removed from the atmosphere by rain and by deposition to the surface, at least in the boundary layer (BL). It has also been proposed that aqueous phase

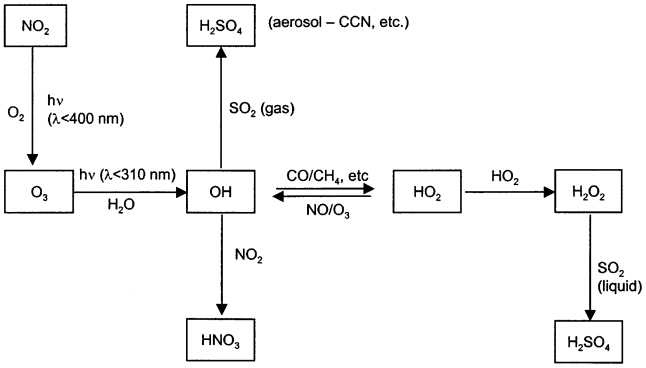


Figure 2. Links between free radicals, oxidants, and acids in the lower atmosphere. Reprinted with permission from ref 29. Copyright 1994 Blackwell Scientific Publications.

loss of H_2O_2 via reaction with OH is another important sink of HO_X.[25,26]

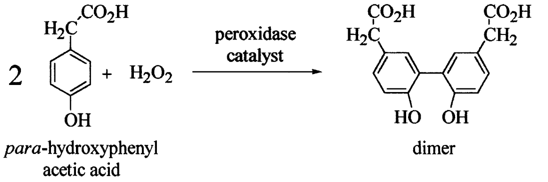
The solubility of organic peroxides is significantly less than H_2O_2, for instance, at 10 °C. O'Sullivan et al.[23] quote K_H, respectively, for H_2O_2 and MHP of 3.09×10^5 and 7.88×10^2 M atm^{-1}, so these types of molecules will be much less subject to physical removal. Multifunctional peroxides such as HMHP are even more soluble than H_2O_2 with a K_H of 9.32×10^6 M atm^{-1} being quoted by O'Sullivan et al.[23]

The main oxidation processes for SO_2 in the atmosphere are reaction with OH in the gas phase and H_2O_2 in the aqueous phase with the aqueous phase process accounting for up to 60−80% of the total.[27,28] The chemistry responsible for production of free radicals and peroxides is thus closely linked with the chemistry responsible for producing strong acids in the atmosphere particularly for H_2SO_4 and HNO_3. This is illustrated graphically in Figure 2.[29]

3. Measurement of Peroxides in the Atmosphere

There are several well-established methods for the measurement of peroxides in the atmosphere, which are discussed in some detail in the reviews by Gunz and Hoffmann[9] and Lee et al.[10] A short summary listing various methods is shown in Table 1, which is largely taken from Lee et al.[10] It is not comprehensive and focuses on systems that have produced most of the data in the literature and those in current use. No attempt is made to compare the quality of data produced by the various techniques, including sampling methods, since to our knowledge no comprehensive intercomparison for all peroxides has ever been carried out.[10]

The early methods using colorimetric and chemiluminescence with luminol were insufficiently sensitive for gas-phase H_2O_2, although the luminol chemiluminescence method was used successfully to make measurements of H_2O_2 in cloudwater at concentrations below 1 μM.[30,31] Gas-phase H_2O_2 was measured successfully down to concentrations below 100 pptv by the peroxylate chemiluminescence,[32] but it was not until the mid 1980s that gas-phase measurements of both H_2O_2 and organic peroxides were made with high time resolution and with the necessary specificity. In 1985, a sensitive method was devised to measure both H_2O_2 and organic peroxides that was both sensitive and free from major interferences. This was the peroxide catalyzed reduction of H_2O_2 and other peroxides by para hydroxy phenyl acetic acid (POPHA).[33]



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Above is the reaction for H_2O_2. A similar reaction occurs for organic peroxides, and in both reactions a stable dimer is formed that fluoresces with a peak absorption at 320 nm and a peak emission at 400 nm. This therefore provides a measure of total peroxide.

Separate measurements of H_2O_2 and organic peroxides are made with the use of the enzyme catalase, which selectively removes H_2O_2 prior to measurement. This requires the use of a second channel in the fluorometer.[34] However, its use is not simple, and the measurements are subject to error. A much more specific measurement method of the different peroxides involves separation by high performance liquid-phase chromatography (HPLC) followed by detection by the POPHA method.[35,36] This method has identified many peroxides, but the time response is limited by the time taken for them to elute through the GC column. The low time response (one measurement takes approximately 2 min) makes this technique less suitable for aircraft measurements, although it has been used for this purpose.[37] Another separation method makes use of the fact that H_2O_2 is many times more soluble than most organic peroxides (HMHP being an exception) and using two collectors in series. The first collector collects H_2O_2 with close to 100% efficiency and MHP with 50−75% efficiency.[37−39] The second collector collects 50−75% of the residual organic peroxide. The method is only suitable for marine conditions when MHP exceeds 0.1 ppbv. It is not capable of separating H_2O_2 from HMHP and thus is not suitable for measurements made over continents such as North America. It should be noted that in clean air over the oceans, the organic peroxides make only about a 20% contribution to the signal of the first collector. This is within the precision of the measurement for H_2O_2, and it has therefore been assumed that this measurement is suitable for comparison with a calculated H_2O_2 (see sections 5.1 and 5.2). We have referred to this as a measure of peroxide since it is neither H_2O_2 nor total peroxide.

The Lazrus group also made substantial improvements to the method of collection of gas-phase H_2O_2.[34] The two main techniques are cryogenic collection that has been used in conjunction with the peroxylate[32] and with the HPLC method[36] and the use of collection coils where the air flows counter current through the coil to the collection fluid (usually water buffered to pH 1).[34] This allows for near continuous measurements of peroxide with a time delay imposed by the chemistry that has to take place before detection in the fluorimeter (up to 2 min).

Table 1. Analytical Methods for Measurement of Hydroperoxides

method	species measured	ref
colorimetry	H_2O_2	*a* and *b*
chemiluminescence with luminol and peroxidase	H_2O_2	*b*−*d*
chemiluminescence with peroxylate	H_2O_2	52
dual enzyme fluorescence with peroxidase + catalase	total peroxide and total organic peroxide	33
enzyme fluorescence with peroxidase	total peroxide and total organic peroxide	*e*
nonenzyme fluorescence with Fenton reagent	H_2O_2	*f* and *g*
HPLC with postcolumn enzyme derivatization	H_2O_2 + individual organic peroxides	35 and 36
TDLAS	H_2O_2	40 and 41

[a] Bufalini, J. J., Jr.; Gay, B. W.; Brubaker, K. L. *Environ. Sci. Technol.* **1972**, *6*, 816. [b] Kok, G. L.; Darnall, K. R.; Winer, A. M., Jr.; Pitts, J. N.; Gay, B. W. *Environ. Sci. Technol.* **1978**, *12*, 1077. [c] Kok, G. L.; Holler, T. P.; Lopez, M. B.; Nachtrieb, H. A.; Yuan, M. *Environ. Sci. Technol.* **1978**, *12*, 1072. [d] Ames, D. L. *General Electricity Generating Board Report No. TPRD/L/2552/N83*; Leatherhead: Surrey, UK, 1983. [e] Hwang, H.; Dasgupta, P. K. *Environ. Sci. Technol.* **1985**, *19*, 255. [f] Lee, J. H.; Tang, I. N.; Weinstein-Lloyd, J. B. *Anal. Chem.* **1990**, *62*, 2381. [g] Lee, J. H.; Tang, I. N.; Weinstein-Lloyd, J. B.; Halper, E. B. *Environ. Sci. Technol.* **1994**, *28*, 1180.

Other collection methods include impingers and a reflux concentrator;[10] however, the collection coils are simple and allow for continuous collection and measurements of H_2O_2 down to concentrations below 10 pptv.

A more direct method of measurement, which is exclusive to H_2O_2, is to use a tunable diode laser (TDLAS).[40,41] This is highly specific and is quite sensitive, being able to measure H_2O_2 to a level significantly below 100 pptv. It is not as sensitive as the POPHA method, though, which can detect peroxides down to concentrations of the order of 10 pptv, and it cannot be used for organic peroxides. The advantages of the TDLAS over the POPHA system is that it is highly specific and is not subject to interferences. SO_2 interferes significantly with the POPHA method, but it can be removed by adding HCHO to the collection solution;[33] in the marine atmosphere, where many measurements have been made, it is virtually nonexistent. Both the TDLAS and the POPHA method can suffer from losses during sampling, and care should be taken to minimize the length of sampling lines.

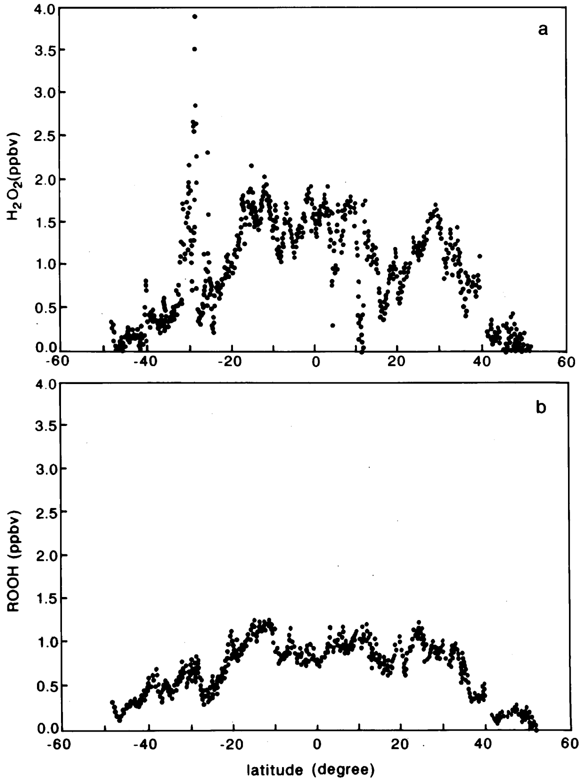

Figure 3. Latitudinal distribution of peroxides observed in the marine boundary layer of the Atlantic Ocean during October and November 1990: (a) hydrogen peroxide and (b) total organic hydroperoxide. Reprinted with permission from ref 50. Copyright 1994 Kluwer Academic Publishers.

4. Atmospheric Peroxide Measurement Database

The measurement database for atmospheric peroxides was tabulated in some detail in the main reviews by Gunz and Hoffmann in 1990[9] and by Lee et al. in 2000,[10] both of which were published in *Atmospheric Environment*. Gunz and Hoffman[9] reviewed both aqueous and gaseous phase peroxide data. The earliest data came from a paper in Japanese in 1949 by Matsui[42] entitled “On the content of hydrogen peroxide in atmospheric precipitation”, which showed concentrations between 10 and 25 μM. The range of rainwater concentrations is from 0.1 to 300 μM;[43] in cloudwater, the maximum observed was 247 μM on Whiteface Mountain in New Hampshire.[44] Higher concentrations were observed in summer, and organic peroxides were observed in only a minority of cloud samples up to a concentration of 40 μM.[45] Concentrations of H_2O_2 in cloudwater were strongly anticorrelated with S(IV).[46,47] Gas-phase measurements ranged from 0.1 to 8 ppbv,[48] although typical levels were close to 1 ppbv. Daum[48] observed “strong daily variations related to different air masses sampled with different water vapor concentrations; H_2O_2 is significantly present over a wide range of altitudes; SO_2 is largely confined to the boundary layer; insufficient H_2O_2 is present in the boundary layer on occasion for complete SO_2 oxidation.” Mohnen and Kadlecek[31] also noted that there was a sharp drop in [H_2O_2] during cloud formation, and it remained low until SO_2 reached very low concentrations after which [H_2O_2] recovered quickly. All these observations and many others confirm that H_2O_2 plays a major role in SO_2 oxidation throughout the atmosphere. This affects acidity in rain over wide areas, and it creates most of the sulfate aerosol that is present in the atmosphere where it can strongly influence climate.[27]

Lee et al.[10] reviewed only the gas phase measurements, but they also included measurements of organic peroxides in papers published up to 1999. On

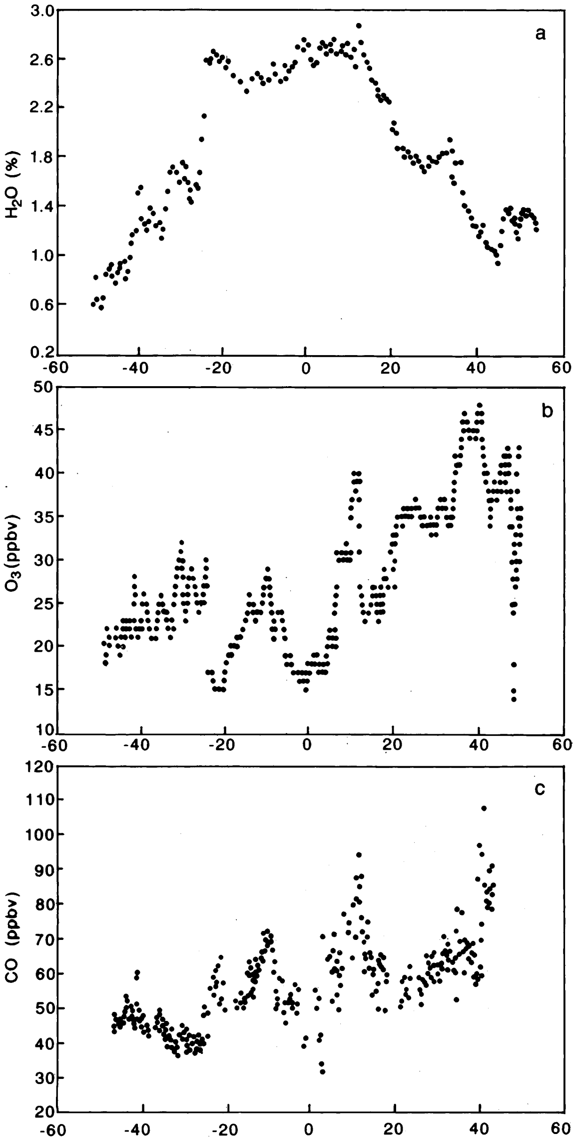

Figure 4. Latitudinal distribution of trace gases observed in the marine boundary layer of the Atlantic Ocean during October and November 1990: (a) water vapor, (b) ozone, and (c) CO. Reprinted with permission from ref 50. Copyright 1994 Kluwer Academic Publishers.

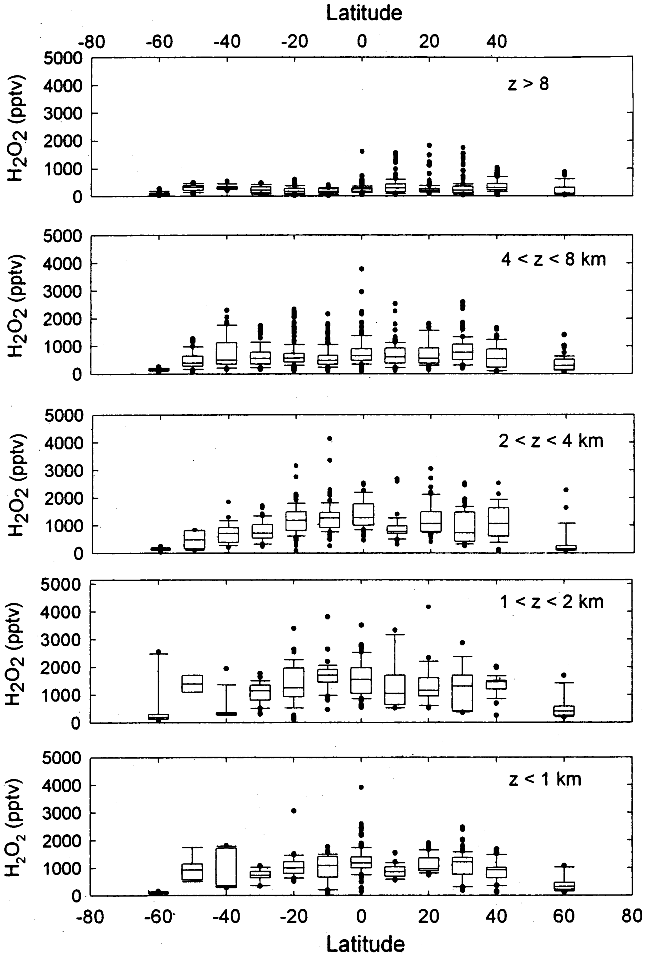

Figure 5. Latitudinal distribution of hydrogen peroxide as a function of altitude for longitudes >155 °E and <245 °E as observed over the Pacific and South Atlantic Oceans during NASA's Global Tropospheric Experiment program. In the box and whisker plots, the center line is the median; the box represents the 25th and 75th percentile, and the whiskers are the 10th and 90th percentile. The solid symbols are the data points outside the 10th and 90th percentile. Reprinted with permission from ref 39. Copyright 1999 American Geophysical Union.

average, the ratio of inorganic to organic peroxides is approximately 2:1. The maximum concentration of H_2O_2 recorded was in excess of 10 ppbv,[39] but the means were much lower ($H_2O_2 = 0.63$ ppbv, MHP = 0.28 ppbv for the Northwest Pacific and $H_2O_2 = 0.8$ ppbv, MHP = 0.48 ppbv for the Central Tropical Pacific). Several important papers were published in the 1990s drawing attention to the anticorrelation between H_2O_2 and O_3 in clean marine air.[49−51]

The most extensive data sets on the global distribution of peroxides have been provided by measurements on the German ship *RV Polarstern*, which makes annual visits to Antarctica from Germany, and by the NASA PEM Experiment (Pacific Exploratory Mission).

Figure 3 shows the latitudinal transects of H_2O_2 and MHP from approximately 50 °N to 50 °S collected on the *RV Polarstern* by Slemr and Tremmel in October and November of 1990.[50] Also published in the same paper were the latitudinal transects of O_3, CO, and water vapor (Figure 4), and it is obvious that the distribution of the peroxides bears a strong resemblance to the water vapor distribution with much more being present in the tropics. Jacob and Klockow[52] had previously observed a similar latitudinal distribution for H_2O_2 during a similar cruise on the *RV Polarstern* in 1988 with positive relationships between H_2O_2 and both $J(O(^1D))$ and H_2O.

Two more independent data sets on the latitudinal transects for H_2O_2 and MHP in the MBL were published by Weller et al.[53] In this case, two independent techniques were used to produce the speciated data (POPHA and HPLC); the agreement between them was of the order of 25%, and the concentrations reported were very similar to those found by Slemr and Tremmel[50] taking into account the different seasons. The average ratio of H_2O_2 to MHP was about 2:1 with relatively more organic peroxide to H_2O_2 in the Southern Hemisphere. An interesting feature of the Slemr and Tremmel[50] data that was not shown by Weller et al.[53] is the large excursion in H_2O_2 at latitude 30 °S (Figure 3). This

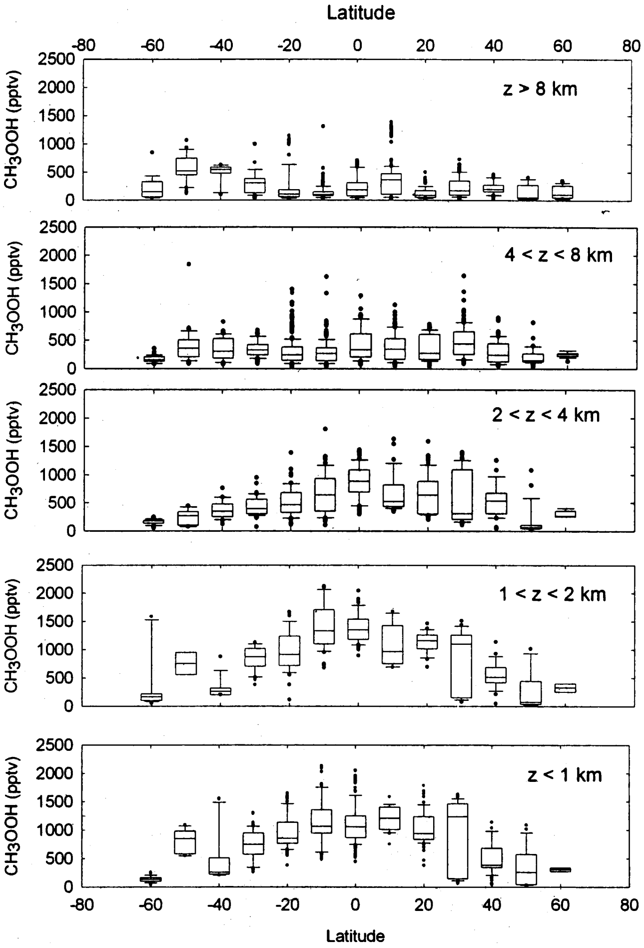

Figure 6. Latitudinal distribution of methylhydroperoxide as a function of altitude for longitudes >155 °E and <245 E as observed over the Pacific and South Atlantic Oceans during NASA's Global Tropospheric Experiment program. See Figure 5 for an explanation of the box and whisker plots. Reprinted with permission from ref 39. Copyright 1999 American Geophysical Union.

was not shown in the organic peroxide data (Figure 3) and was ascribed to H_2O_2 production by reactions taking place in cloudwater. Such phenomena have also been observed from time to time in aircraft profiles, but they are uncommon (Penkett and Bandy, unpublished data).

Extensive distributions of both H_2O_2 and MHP have been published by Heikes and co-workers[39] that include variation in altitude and longitude as well as variation in latitude. These show that H_2O_2 is more abundant than MHP throughout the altitude range above the BL (1 km) up to more than 8 km. The longitudinal data also show evidence for the production of peroxides in association with biomass plumes or pollution plumes over the South Atlantic Ocean close to Africa, over the Pacific Ocean west of northern South America, and adjacent to Southeast Asia. Latitude plots at various altitudes for H_2O_2 and MHP are shown in Figures 5 and 6, respectively, from these NASA measurements. The lowest altitude values (<1 km) are somewhat similar to the ship transects for H_2O_2 with higher values in the tropics. The highest concentrations of the peroxides occur between 1 and 4 km; above 4 km, the concentrations decline as a result of the lower production rates due to the lower water vapor concentrations, while the loss rates are reasonably invariant. This sort of vertical profile is typical and has been observed by many workers in several locations in a variety of meteorological conditions (e.g., refs 54−56); above the BL, H_2O_2 exhibits a strong positive relationship with water vapor (e.g., refs 55 and 56).

A set of H_2O_2 profiles was determined over Arkansas in the US as a function of season (Figure 7).[57] All profiles showed a maximum at about 2 km. In the winter, concentrations were approximately 0.2 ppbv at 2 km altitude. This increased to 1 ppbv H_2O_2 in the spring months and to over 3 ppbv in the summer before dropping to about 1 ppbv in the autumn. Finally, in this overview, it is worth noting that profiles of HMHP have also been reported over the US coincident with profiles of H_2O_2 and MHP with concentrations up to 2 ppbv in the boundary layer.[58,59]

5. What Peroxide Measurements Tell Us about Atmospheric Chemistry

As described previously in section 2, peroxides can play a key role in many aspects of tropospheric photochemistry. Their measurement can therefore be an important diagnostic tool for testing photochemical theory and determining the extent of chemical processing that has taken place in a given air mass. Photochemical theory suggests that in a low NO_X atmosphere, typical of large parts of the background troposphere (Figure 1a), peroxides provide a measure of the O_3 that has been photochemically destroyed in the presence of water vapor. While in NO_X rich atmospheres, O_3 and peroxides are both produced (Figure 1b); thus, the concentrations of peroxides indicate the amount of O_3 that has been photochemically produced. These phenomena have been assessed by examining observed relationships, in both space and time, between peroxides and O_3, water vapor and photon flux, and by comparing observed concentrations of peroxides with those calculated using various chemical models. Similarly, the HO_X budget has been assessed using measurements of peroxides with a focus on the peroxides as a sink of HO_X in the MBL and a source of HO_X in the UT. Also, measured H_2O_2 concentrations have been used in the determination of the sensitivity of O_3 production to NO_X and hydrocarbons.

5.1. Diurnal and Seasonal Cycles of Peroxide and Ozone in the Marine Boundary Layer: Evidence for Substantial Photochemical Destruction of Ozone in the Troposphere and an Examination of the HO_X Budget

Various authors have studied the diurnal variation of peroxides and their relationship with ozone in clean air. Ayers et al.[49] identified an anti-correlation between the diurnal cycles of peroxide and O_3 observed at Cape Grim, with the peroxide concentrations increasing during the daylight hours while the O_3 concentrations decreased. Similar diurnal cycles have been observed by Jacob and Klockow[52] and Slemr and Tremmel[50] in the Atlantic MBL and by

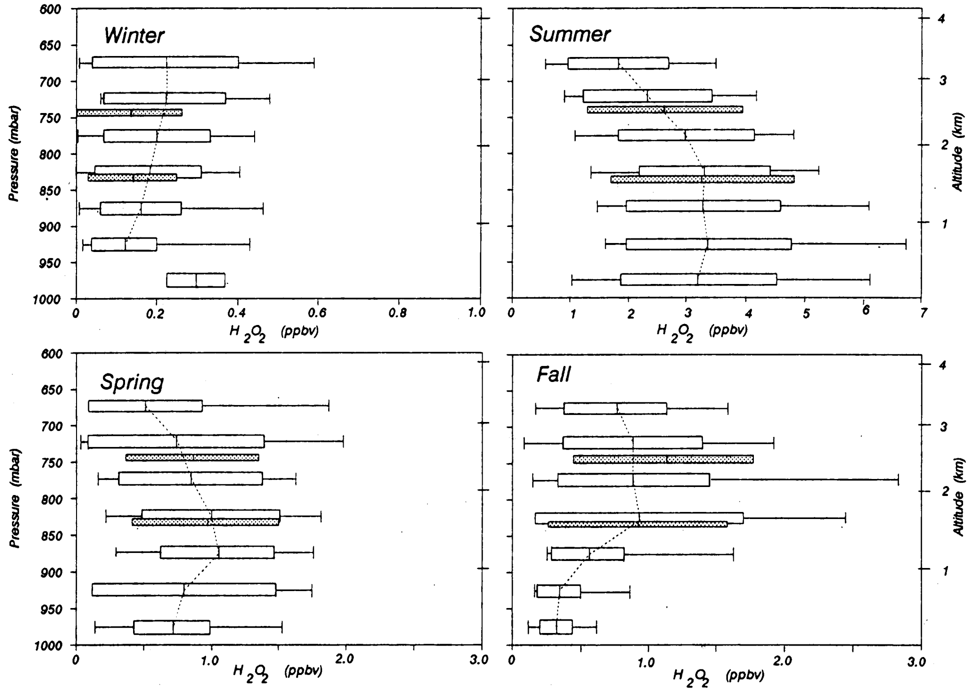

Figure 7. H_2O_2 mixing ratio distributions at 50 mbar intervals for each season from a site in central Arkansas during 1988. Central lines are mean values, and the box spans ±1 standard deviation. The lines connect the minimum and maximum mixing ratios. The stippled boxes are for the level flight segments. Reprinted with permission from ref 57. Copyright 1992 American Geophysical Union.

Chen et al.[60] in the MBL in the Pacific near Christmas Island.

The work at Cape Grim involved making very careful measurements of peroxide and O_3 over a period of 13 months from February 1991 to March 1992. The instrument used was a dual channel fluorometer detecting peroxide by the POPHA method but with data only from the first collector being used. It therefore represents mostly H_2O_2 as discussed previously in section 3. The advantage of the large ground-based data sets collected continuously over many 24 h cycles is that average diurnal behavior can be studied in some detail with the confidence that it does indeed represent average conditions. This is especially true of the Cape Grim data set for baseline conditions where air reaches the measurement site after traversing the Southern Ocean for thousands of miles without passing over land. The range of concentration measured at Cape Grim is very similar to that shown in the shipboard and aircraft measurements in Figures 3, 5, and 6.

Two papers by the CSIRO and UEA groups[49,61] have studied the covariance of peroxide and O_3 at Cape Grim and have shown that the behavior of O_3 in the remote MBL is dominated by in situ photochemical loss balanced by input from the free troposphere above; loss to the ocean surface is a relatively minor term. Figure 8 shows the monthly mean diurnal cycles for O_3 and peroxide in January and October. The diurnal cycles at Cape Grim were evident in all the summer months but with the amplitude declining with reduced solar intensity toward the austral midwinter, at which point no diurnal cycle was discernible. The associated O_3 loss in January from reaction of $O(^1D)$ with water vapor (reaction 2), reaction of HO_2 with O_3 (reaction 12), and reaction of OH with O_3 (reaction 13) is calculated to be 1.23, 0.2, and 0.13 ppbv per day, respectively, giving a total loss of 1.6 ppbv per day, which is identical to the observed value. The average January data for peroxide is similar to another set of measurements of H_2O_2 in clean air over the North Atlantic and over the Pacific Ocean close to Tasma-

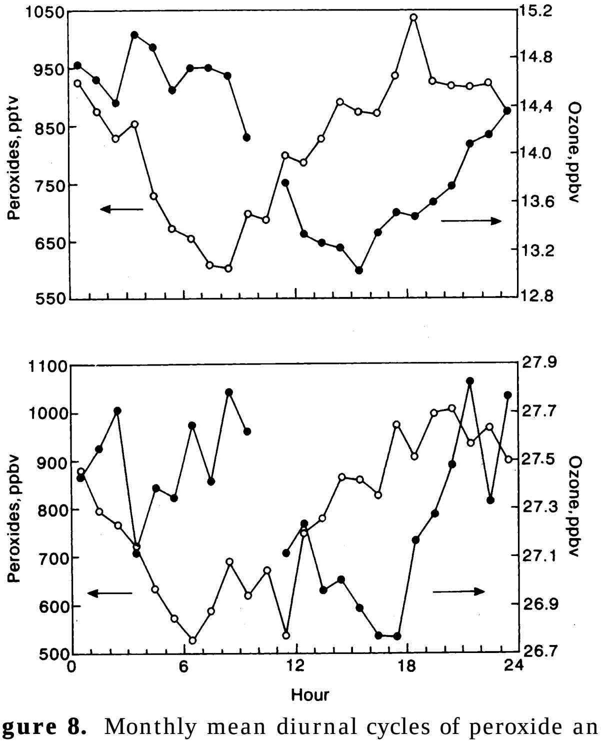

Figure 8. Monthly mean diurnal cycles of peroxide and ozone for baseline conditions at Cape Grim, Tasmania: (upper panel) January 1992 and (lower panel) October 1991. Reprinted with permission from ref 61. Copyright 1996 Kluwer Academic Publishers.

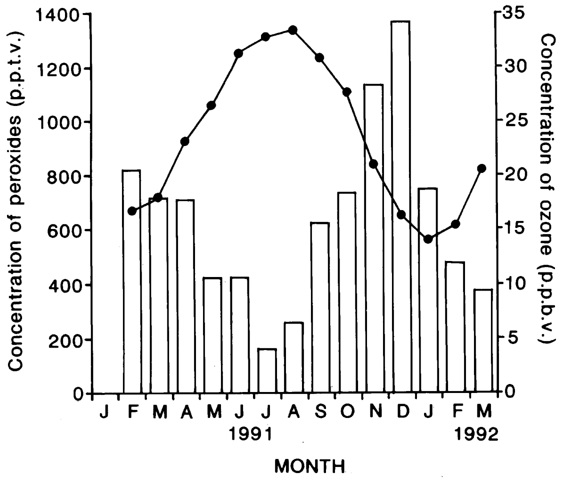

Figure 9. Comparison of peroxide (open histogram) and ozone (filled squares) seasonal cycles in baseline air at Cape Grim, Tasmania. Reprinted with permission from ref 49. Copyright 1992 Macmillan Magazines Limited (http://www.nature.com).

nia,[62] so the conclusions drawn would appear to be applicable to the world oceans. In October, the calculated loss at Cape Grim is 0.9 ppbv per day as compared to a measured loss of approximately 1 ppbv per day.[61] Loss of O_3 in winter is much more difficult to measure; however, the photochemistry can still be observed in November, at least in terms of peroxide production.[61] The nighttime O_3 appears to be replenished by transport of O_3 rich air from above the MBL, while the peroxide is lost through dry deposition to the ocean.

Slemr and Tremmel[50] also made a detailed study of the diurnal behavior of both peroxides and O_3, and they clearly observed O_3 loss over the Atlantic during October and November at all latitudes between 20 and 50 °S. The amplitude of the H_2O_2 cycle is almost identical to that observed by Ayers et al.[49] (50 vs 40%). In the latitude band between 20 and 50 °S, the average O_3 loss is about 1.8 ppbv per day, which is again very similar to that measured by Ayers et al.[49] Slemr and Tremmel[50] observed an O_3 loss rate of 262 pptv h^{-1} similar to the H_2O_2 production rate of 250 pptv h^{-1} calculated from a photochemical model. Comparing this to the observed H_2O_2 production rate of 67 pptv h^{-1} leaves a deficit of 195 pptv h^{-1}, which they attributed to by a high deposition rate of H_2O_2 of 4×10^{-5} s^{-1}.

The seasonal cycles of peroxide and O_3 at Cape Grim were also found to be anti-correlated[49] (Figure 9), suggesting that the photochemistry responsible for the diurnal pattern in peroxide and O_3 is almost certainly responsible for the annual cycle of O_3 observed at Cape Grim and at other maritime sites in both hemispheres.[63] The O_3 maximizes in August (i.e., late winter) and then declines through the spring and summer to produce a minimum in January. The peroxide cycle shows a minimum in July. It is therefore slightly out of phase with the O_3 cycle but clearly suggests that the O_3 loss and the peroxide gain are related by photochemistry. Occasionally, peroxide concentrations up to 1 ppbv were observed in the winter, but this was shown to be associated with transport from lower latitudes.

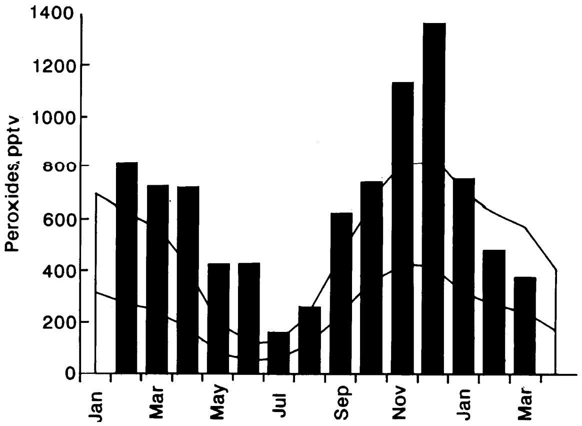

Figure 10. Monthly mean measured peroxide values (histogram) plotted with the model-predicted annual cycle (lines) for Cape Grim, Tasmania. The lower line depicts the model prediction for H_2O_2, and the upper line shows the model prediction for H_2O_2 plus CH_3OOH. Reprinted with permission from ref 61. Copyright 1996 Kluwer Academic Publishers.

This simultaneous analysis of peroxide and O_3 data illustrated that the O_3 concentration at sites such as Cape Grim can be explained by vertical mixing in the lower few kilometers, slow dry deposition to the surface, and daytime photochemistry that simultaneously destroys O_3 and produces HO_X. Also, higher water vapor concentrations in summer lead to enhanced photochemical destruction of O_3, suggesting that this, rather than transport, is likely to be the major cause of the O_3 seasonal cycle. The source of the O_3 in the Southern Hemisphere at Cape Grim appears to be a mixture of the stratosphere and in situ production according to calculations by Lelieveld and Dentener.[64] In summary, the study of the behavior of peroxides and O_3 in the remote marine atmosphere has confirmed the importance of O_3 photolytic loss in the troposphere. The study is sufficiently quantitative to account for all of the O_3 loss observed; other O_3 loss processes involving halogen radicals may therefore be of limited importance. This comment is supported by the correspondence of measured and calculated concentrations of peroxides at Cape Grim (Figure 10). The peroxide levels calculated show a tendency to be below those measured, suggesting that if anything, the model underestimates the rate of conversion of O_3 to peroxides and thus could account for more O_3 loss than observed. However, the discrepancy between measured and calculated peroxides could be improved by making the assumption that some peroxide is transferred from the free troposphere where it is present at concentrations approximately 30% higher. This situation is very likely as shown in the aircraft measurements (Figure 7).

The budget of O_3 and peroxides in the clean MBL was also a subject of study in TRACE-A (Transport and Atmospheric Chemistry near the Equator−Atlantic) by Heikes et al.,[51] in which they calculated that the loss of O_3 in the remote MBL proceeded primarily through the formation and surface deposition of the hydroperoxides, with a direct loss of O_3 to the surface being of secondary importance. They showed that O_3 loss and production of peroxides

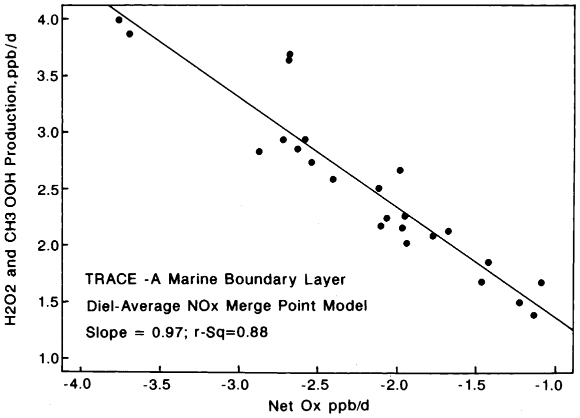

Figure 11. Relationship between H_2O_2 and CH_3OOH gross production and the net O_3 destruction expressed, as negative units of production, calculated for the MBL over the South Atlantic during September and October 1992. The solid line shows the least squares linear fit through the data. The slope of the line is -1.0, and the coefficient of determination is 0.83. The photochemical destruction of O_3 is balanced by the net production of the hydroperoxides. Reprinted with permission from ref 51. Copyright 1996 American Geophysical Union.

balance in a 1:1 relationship (see Figure 11), agreeing with a previous analysis by Ayers et al.[49] and Thompson et al.[65] The mean loss of O_3 was calculated to be 2.2 ppbv per day (25% deposition, 75% photochemical), giving a mean lifetime for O_3 in the MBL of 12 days. The corresponding peroxide lifetime was approximately 1.5 days (1.9 days for H_2O_2 and 1.1 days for MHP). They also showed that O_3 destruction in the MBL was significantly larger than the O_3 flux from the stratosphere, which was comparable to the surface loss only. The extra O_3 required to balance the budget came from production in the upper troposphere. In a closely related paper, Jacob et al.[66] proposed that most of the O_3 formation was occurring in association with the Pacific Walker Circulation, whereby NO_X ascending from the continents over South America, Africa, and Oceania was supplemented by lightning produced in the ascending components of the Walker cells. Transfer of NO_X from the stratosphere was shown to be insignificant by comparison with Walker cell activity.[67-69]

An O_3 loss of 2 ppbv per day in the global MBL constitutes a total O_3 loss by photochemistry in the troposphere of the order of 2×10^9 tons year^{-1}. This confirms global model predictions of large O_3 losses from photochemistry, which need to be balanced by large O_3 gains from photochemistry in the troposphere;[64] the amount of O_3 transferred from the stratosphere to the troposphere is not sufficient for this purpose since it is unlikely to exceed 1×10^9 tons year^{-1}.[63] The amount of peroxide made from O_3 destruction in the troposphere is of course of a very similar magnitude, making peroxides some of the predominant trace gases produced in the troposphere. Their production rate is at least as large as the amount of CO emitted directly to the atmosphere (i.e., in excess of 2×10^9 year^{-1}). Measurements of peroxides are thus a vital component of the study of tropospheric O_3. They confirm the predominance of photochemistry in the O_3 budget over purely meteorological processes of input from above and deposition to the surface.

Table 2. Summary of Diel Average HO_X Sources and Sinks for the Tropical Pacific Boundary Layer[60]

sources	flux divergence (10^5 molecules cm^{-3} s^{-1})	percent contribution (%)
	Photochemical Sources	
$O(^1D) + H_2O$	16.0	80
	Transport Processes	
$F(H_2O_2)^a$	1.9	10
$F(MHP)^a$	1.9	10
total sources	19.8	100
sinks	**flux divergence (10^5 molecules cm^{-3} s^{-1})**	**percent contribution (%)**
$OH + HO_2$	1.6	8
$H_2O_2 + OH$	1.9	10
H_2O_2 physical removal	5.7	29
MHP + OH	4.6	23
MHP physical removal	6.0	30
total sinks	19.8	100

[a] Transport of peroxide from the buffer layer above to the boundary layer, which is then photolyzed.

As well as using measured peroxide data to examine the O_3 budget in the MBL, the HO_X budget can also be evaluated. Using a time-dependent photochemical box model constrained by measured concentrations of H_2O_2 and MHP, Chen et al.[60] (Table 2) calculated the HO_X budgets for the MBL near Christmas Island. They found that the reaction of $O(^1D)$ with H_2O (reaction 2) contributed 81% of the OH, while the photolysis of H_2O_2 and MHP (reactions 7 and 8) contributed 8 and 2%, respectively. For HO_X, reaction 2 was again the most dominant (80%) in the tropical MBL, with most of the remaining source attributed to transport of H_2O_2 and MHP from the buffer layer immediately above the boundary layer. About 90% of the HO_X loss is via the peroxides. Loss via H_2O_2 was calculated to account for 39% of the total, of which 75% is via physical removal (rainout, dry and wet aerosol scavenging, and dry deposition to the ocean surface), and 25% is due to reaction with OH (reaction 10). Loss via MHP was calculated to account for 53% of the total, with physical and chemical (reaction 11) both making significant contributions (43 and 57%, respectively). It was also found that dry deposition was most likely to be the dominant physical loss process. Chen et al.[60] concluded that overall these results suggest that to accurately assess the tropical MBL HO_X budget, it is critical to have reliable measurements of peroxides.

Within the MBL, vertical profiles of peroxides, in particular H_2O_2, and water vapor are found to be negatively correlated, with H_2O increasing toward the ocean surface, which is its source, and the peroxide concentration declining due to deposition.[70] Further, the H_2O_2 calculated using photochemical theory (i.e., ignoring dry deposition) overpredicts that observed substantially,[71] which illustrates the importance of the H_2O_2 as a sink of odd oxygen, as discussed previously. Similarly, Jacob et al.[66] used H_2O_2 and MHP measurements to validate their photochemical model. Above the boundary layer, calculated concentrations compared well with those observed indicating that, within the stated measurement and kinetic uncertainties, the model captured odd hydrogen and odd oxygen chemistry of the free troposphere rather well. However, near the Earth's surface, the model overpredicted the observed peroxides, again illustrating the importance of dry deposition for odd oxygen. Heikes et al.[51] calculated that the surface loss rate of H_2O_2 was approximately twice its diel-average photochemical loss, while for MHP, surface deposition was about $^1/_2$ its diel-average photochemical loss, in agreement with Chen et al.[60] Including the surface deposition, the model of Jacob et al.[66] reduced the concentrations of H_2O_2 and CH_3OOH by about 50 and 33%, respectively, resolving the modeled and measured concentrations.[51]

Slemr and Tremmel[50] found that concentrations of H_2O_2 calculated using expression I (see next) compared better with the concentrations they had observed in the Atlantic MBL when the dry deposition rate (k_{dep}) was set as a linear function of wind speed. Ayers et al.[61] also noted a dependence of peroxide concentrations on wind speed at Cape Grim. Both these studies illustrate that the loss of odd oxygen and odd hydrogen through H_2O_2 surface deposition is likely to increase with increasing wind speed. Ayers et al.[61] also found a systematic decrease in measured peroxide with rainfall events as would be expected from the high solubility of peroxides.[72] Slemr and Tremmel[50] attributed the relatively low concentrations of H_2O_2 as compared to the less soluble ROOH measured in the region of the ITCZ to rainout. Ground-based data sets are heavily influenced by physical removal processes such as deposition, which is almost continuous, and washout, which is spasmodic. In the continental BL, there is the additional effect of the variability in NO concentrations on the radical consumption processes that leads to greater variability in the concentrations of peroxides in the BL as compared to the free troposphere.[55] This makes interpretation of the instantaneous BL data sets difficult, although as seen previously, average data sets are capable of useful interpretation.

Slemr and Tremmel[50] derived an expression to calculate H_2O_2 concentrations in the MBL

$$[H_2O_2] = \frac{k_2 j_1 [O_3][H_2O]}{k_3[M](k_{10}[OH] + k_{dep})} \qquad (I)$$

where k_{10} is the rate coefficient for the reaction of H_2O_2 with OH, k_{dep} is its dry deposition rate, j_1 is the photolysis rate of O_3 to form $O(^1D)$, and k_2 and k_3 are the rate coefficients for reaction of $O(^1D)$ with H_2O and with O_2 and N_2 molecules (M), respectively. Slemr and Tremmel[50] substituted [OH] with a term for $[HO_2]$ and assumed a constant value of 84 for the ratio $[HO_2]/[OH]$ based on typical concentrations of CO, O_3, and NO in the MBL. Note that, since this simple expression for H_2O_2 is based on the assumption that the photolysis of O_3 in the presence of water vapor is the only source of HO_X, Slemr and Tremmel[50] chose not to include the photolytic loss term for H_2O_2 on the basis that it simply cycles HO_X rather than removes it.

Slemr and Tremmel[50] applied equation I to data that had been collected in the Atlantic MBL between 54 °N and 51 °S on board the *RV Polarstern* and found that it reproduced the coarse shape of the latitudinal variation in the observed H_2O_2, which exhibited higher concentrations toward the equatorial region. This distribution is mainly driven by the H_2O concentrations and photon flux that also increase toward low latitudes, once again illustrating the dependence of HO_X radical chemistry on water vapor and the HO_2 self-reaction on water vapor.[14] Using a deposition rate (k_{dep}) of 4×10^{-5} s^{-1}, the expression fitted their data over the whole latitudinal range. However, this deposition rate is substantially larger than values for k_{dep} used by others (e.g., refs 56 and 73).

Slemr and Tremmel[50] also found MHP, calculated by equation II, to agree well with the observed latitudinal distribution of ROOH.

$$[CH_3OOH] = \frac{k_5[CH_4][OH]}{(k_{11}[OH] + k_{depR})} \qquad (II)$$

where k_5 and k_{11} are the rate coefficients for the reactions of OH with CH_4 and MHP, respectively, and k_{depR} is the deposition rate for ROOH. Again, Slemr and Tremmel[50] substituted for OH based on a constant $[HO_2]/[OH]$ ratio, and since their expression for $[HO_2]$ involved j_1 and $[H_2O]$, this indicates the dependence of ROOH on photon flux and water vapor, but to a lesser degree than for H_2O_2, which, along with the almost even distribution of CH_4, explains the less pronounced latitudinal variation in ROOH and the increasing ROOH/(ROOH + H_2O_2) ratio with increasing latitude.

5.2. Calculated and Measured Peroxide Vertical Profiles: Evidence for Substantial Photochemical Destruction and Production of Ozone in the Free Troposphere

Physical removal is much less of a problem above the boundary layer and may be near zero in clean air conditions that have not been subject to recent precipitation events. This does certainly allow a much more detailed analysis of the peroxide data record and has been used by various groups to validate models of tropospheric chemistry and to examine the tropospheric O_3 budget.[66,74]

As described previously in section 4, several free tropospheric data sets exhibited a strong correlation between peroxide and water vapor. Daum et al.[55] showed that the relationship for H_2O_2 observed over Ohio in summer was consistent with a photochemical theory based on a simple relationship (see next). Tremmel et al.[56] also showed that in the free troposphere over the Northeastern United States, the observed correlation of the H_2O_2 mixing ratio with water vapor, ranging from 1.4 to 5.1 ppbv H_2O_2/%H_2O, was in reasonable agreement with calculations using a zero-dimensional time-dependent photochemical model with CH_4 as the sole hydrocarbon. Also, Weinstein-Lloyd et al.[58,59] published data col-

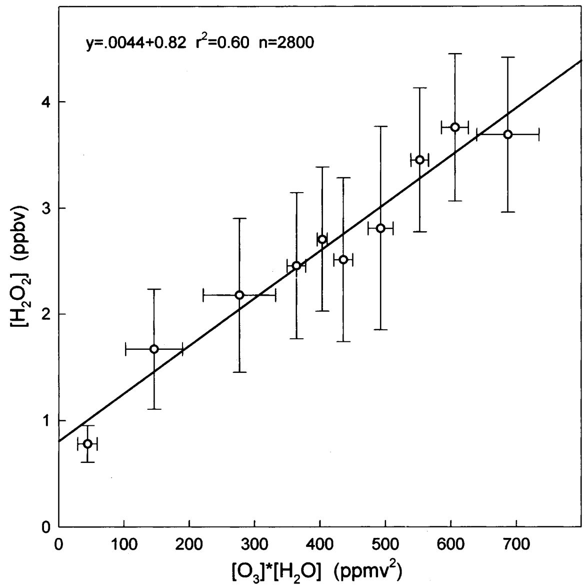

Figure 12. Production of H_2O_2 from precursors in the free troposphere based on data from the Southern Oxidants/Middle Tennessee study during the summer of 1995. Data collected for altitude >1500 were aggregated into 10 bins in order of increasing values of $O_3 \cdot H_2O$, each containing 10% of the data. Symbols represent mean of each population; standard deviation is shown by horizontal and vertical bars. Reprinted with permission from ref 59. Copyright 1998 American Geophysical Union.

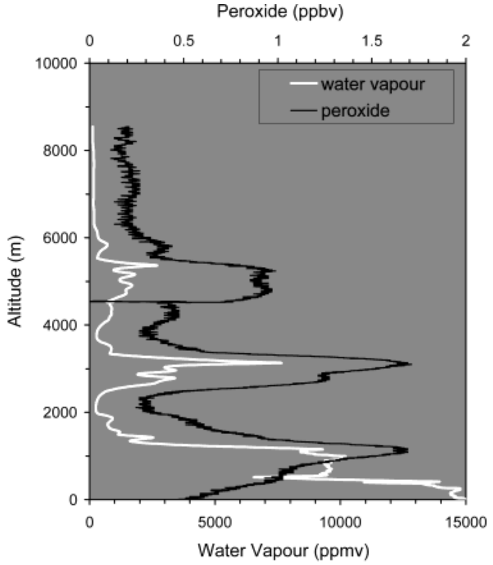

Figure 13. Measured peroxide (black) and measured H_2O (white) concentrations (ppb) for Flight A267 over the North Atlantic off Sable Island in August 1993.

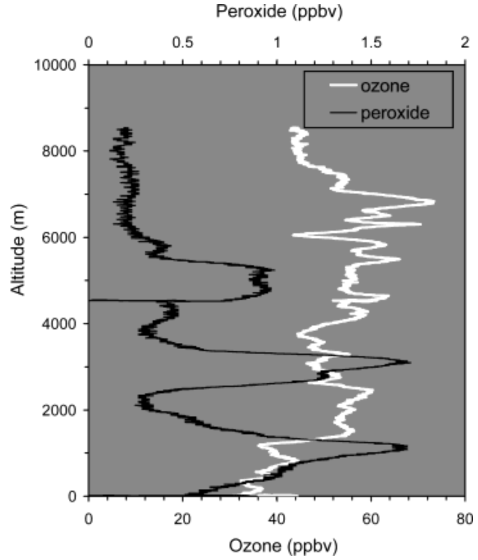

Figure 14. Measured peroxide (black) and measured ozone (white) concentrations (ppb) for Flight A267 over the North Atlantic off Sable Island in August 1993. Reprinted with permission from ref 71. Copyright 1998 American Geophysical Union.

lected over the southern US (1998) and in outflow from the US in NARE (North Atlantic Regional Experiment) campaigns (1996) that clearly showed a strong relationship between H_2O_2 concentrations and the product of O_3 and water vapor (see Figure 12).

Penkett et al.[70] used the different relationships between observed peroxide, water vapor, and O_3 concentrations as markers for net O_3 production or destruction. Using vertical profiles of data obtained by the first collector of a dual channel fluorometer over the North Atlantic and Western Pacific oceans during the OCTA (Oxidizing Capacity of the Tropospheric Atmosphere) and TOGA–COARE (Tropical Ocean Global Atmosphere–Coupled Ocean Atmosphere Response Experiment) projects, respectively, they demonstrated that peroxide was often positively correlated with water vapor in the layered structures above the boundary layer and that this relationship suggested that the maximum amount of peroxide formation, and therefore HO_X free radical chemistry, in the free troposphere is limited by the water vapor content. Further, coincident with this positive relationship between peroxide and water vapor, a negative relationship between peroxide and O_3 was often observed (mostly over the equatorial Pacific), providing evidence for the simultaneous production of peroxide and destruction of O_3. In these conditions, the measured peroxide concentrations compared well with H_2O_2 calculated as some factor of the O_3 and water vapor concentrations, as predicted by Kleinman[75,76] and Daum et al.[55] and also observed by Weinstein-Lloyd et al.[58,59]

The close relationship between peroxide and water vapor is clearly demonstrated in the vertical profile shown in Figure 13 over the North Atlantic. Above the MBL, which is easily detected by the large increase in water vapor concentration and the rapid fall-away of peroxide due to deposition at altitudes below 1 km, the water vapor concentration ranges from about 10 000 ppmv to a few hundred ppmv. The O_3 concentration, however, is much less variable, possibly a factor of 2 up to 8 km (Figure 14). Since peroxides are an integrator of the extent of OH chemistry, this implies that water vapor is the species that has the largest influence on the standing concentration of the OH radicals and the extent of their chemical processing. This is a profound statement, and it indicates succinctly why peroxide measurements in the atmosphere are so important. It also suggests that the observed layered structures in O_3 and its anti-correlation with water vapor commonly

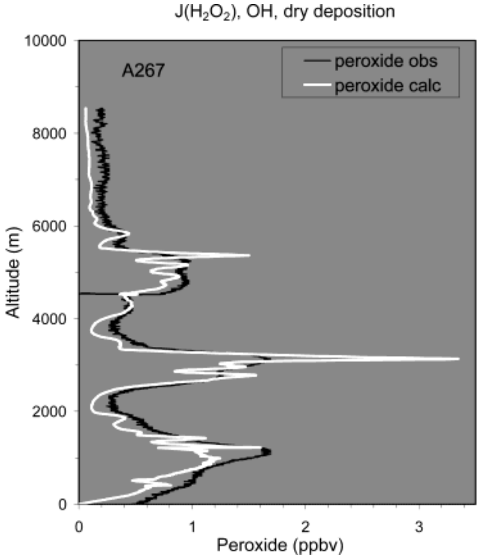

Figure 15. Measured peroxide (black) and calculated H_2O_2 (white) concentrations (ppb) for Flight A267 over the North Atlantic off Sable Island in August 1993. Reprinted with permission from ref 71. Copyright 1998 American Geophysical Union.

observed over the world oceans[77] may not be due to transport of dry O_3 rich air from the stratosphere but rather the photochemical destruction of O_3 in the moist tropospheric air.[70]

Assuming H_2O_2 to be in steady state and that photolysis of O_3 in the presence of water vapor is the only source of OH, and reaction of these radicals with CO is their only sink and the only source of HO_2, then

$$[H_2O_2] = \frac{k_2 j_1 [O_3][H_2O]}{k_3[M](j_8 + k_{10}[OH] + k_{dep})} \quad \text{(III)}$$

where j_8 is the photolysis rate for H_2O_2.[71] This expression is very similar to that derived by Slemr and Tremmel[50] (equation I), except that the photolytic loss of H_2O_2 is included. Penkett et al.[71] also used OH concentrations taken from a 2-D global model rather than substitute with calculated HO_2 concentrations.

When the observed peroxide and O_3 concentrations were negatively correlated in profiles, the H_2O_2 calculated using equation III was often found to agree well with the observed peroxide.[71] This suggested that the few reactions assumed in deriving equation III were dominating and that net photochemical destruction of O_3 was occurring. Figure 15 shows such a comparison for flight A267. The agreement is quite remarkable considering that the 24 h average *j* values used were taken from a global 2-D model with respect only for time of year, altitude, and latitude; the model also provided the 24 h average OH fields. Diel average values are thought to be applicable for use in equation III since there is no evidence of any large diurnal cycle in free tropospheric H_2O_2, rather the concentrations are probably average values arrived at after several days processing, without removal by washout.

The influence of different removal processes on the calculated H_2O_2 concentration is illustrated in Figure 16. In Figure 16a, the only removal process is photolysis of H_2O_2; the fit is quite good except below 1 km. The fit improves when OH removal is also considered (Figure 16b), particularly in the regions between 2 and 6 km where peroxide increases. The large overshoots in calculated H_2O_2 that do not show in the measured data are due to the presence of layers of enhanced water vapor in the profiles, which the peroxide instrument cannot respond to because of its relatively large response time (~20 s). The agreement in the boundary layer becomes much better when surface removal is also added to the part of the profile in the boundary layer (Figure 16c). This does suggest that the H_2O_2 in the free troposphere is largely isolated from surface removal, at least for a period of time that is sufficiently long for the concentration to come to photochemical equilibrium (2−3 days). The good agreement throughout most of the profile also suggests that washout is not a major factor, at least in flight A267.

Further, the large amount of calculated H_2O_2 in the boundary layer that is rarely seen indicates the real importance of H_2O_2 as an atmospheric species and that surface measurements are often difficult to

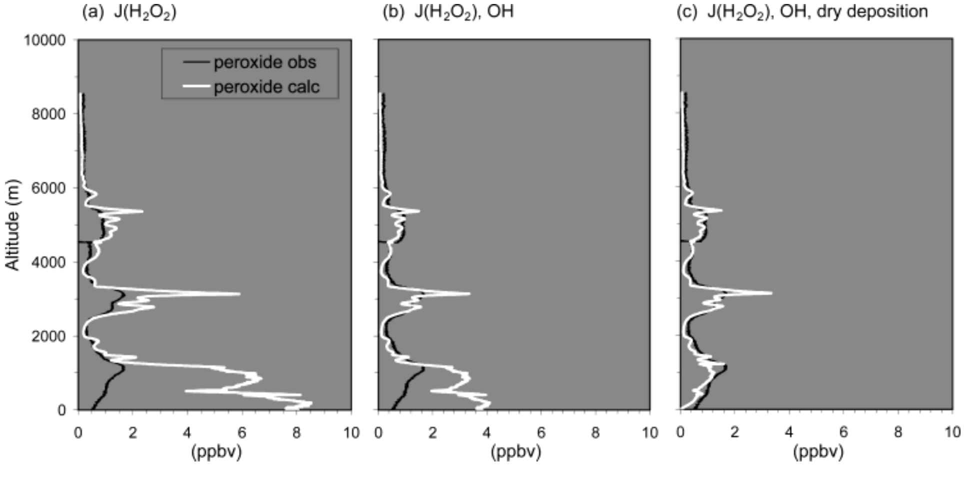

Figure 16. Measured peroxide (black) and calculated H_2O_2 (white) (ppb) for Flight A267 over the North Atlantic off Sable Island in August 1993. H_2O_2 is calculated considering the following loss processes: (a) photolysis only loss, (b) photolysis and reaction with OH, and (c) photolysis reaction with OH and dry deposition in the boundary layer. Reprinted with permission from ref 71. Copyright 1998 American Geophysical Union.

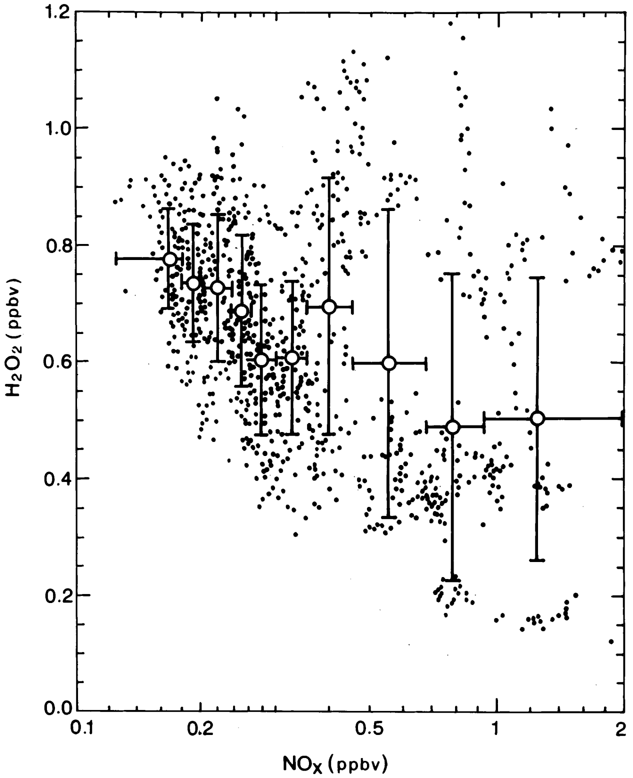

Figure 17. Correlation between H_2O_2 and NO_X for dry periods, 1000−1700 LST and $j_{(NO_2)} \geq 0.006\ s^{-1}$ during the summer at Niwot Ridge, CO. The individual 1 min averages are shown by the data points. Each symbol shows the average of 10% of the data set. The vertical and horizontal bars give the ±standard deviation and the range, respectively, of the points included in the average. Reprinted with permission from ref 78. Copyright 1995 American Geophysical Union.

interpret because of the predominance of physical removal. Moreover, the excess of measured over calculated peroxide at higher altitudes in Figure 16, panels b and c may mean that vertical transport from below is an important factor in the peroxide budget at altitudes where concentrations would otherwise be low; it may also reflect sources of hydroxyl radicals other than O_3 photolysis.

Penkett et al.[70,71] also observed occasions where the peroxide−O_3 relationship in several vertical profiles over the North Atlantic was positive, suggesting that the continental emissions from both North America and Europe had perturbed the natural oxidant budget with coproduction of peroxide and O_3. In these cases, the calculated H_2O_2 tended to greatly exceed the observed peroxide suggesting that the tropospheric processes operating could not be satisfactorily represented by the limited number of reactions assumed in equation III.[71] In such cases, NO_X chemistry was expected to be important with reaction of NO with peroxy radicals leading to net photochemical O_3 production.

Daum et al.[55] derived a similar expression to that of Slemr and Tremmel[50] but also included a term for the emission of NO_X. They found that the relationship between H_2O_2 and dew point calculated for NO_X ranging from 20 to 200 ppt was consistent with the observed relationship in the free troposphere over the Upper Midwest of the US in summer. Concentrations of H_2O_2 calculated with NO_X concentrations of 200 pptv were 1−3 ppb lower than those for NO_X of 20 pptv.

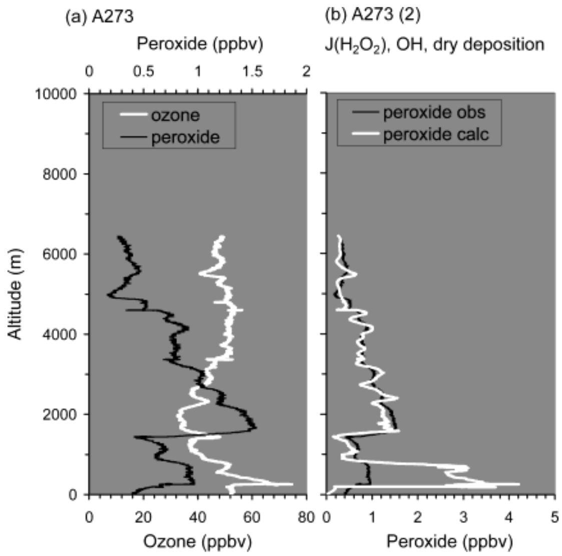

Figure 18. Ozone and peroxide concentrations (ppbv) for the second profile on Flight A273 over the North Atlantic off Spain in September 1993: (a) measured peroxide (black) and measured ozone (white) and (b) measured peroxide (black) and calculated H_2O_2 (white). Reprinted with permission from ref 71. Copyright 1998 American Geophysical Union.

The overall impact of this chemistry involving nitrogen oxides is that peroxide concentrations are suppressed when O_3 formation is occurring. The relationship between H_2O_2 and NO_X is shown graphically in Figure 17 from data collected at Niwot Ridge (CO).[78] An increase of NO_X to about 0.5 ppbv suppresses the H_2O_2 observed by about a factor of 2. In the presence of NO_X, peroxides and O_3 are formed simultaneously. This has also been observed at Cape Grim when the direction of the wind changes from baseline to nonbaseline (i.e., from clean to polluted air) and in many vertical profiles of peroxide and O_3 published by various authors (see, e.g., Weinstein-Lloyd et al.,[58,59] Tremmel et al.,[56] and Penkett et al.[70]).

Figure 18 illustrates one example over the North Atlantic,[71] others over the Pacific are shown in Penkett et al.[70] Figure 18 is a particularly good example since it illustrates the change over from peroxide production associated with O_3 loss above 1 km to coproduction of both O_3 and peroxide at altitudes below. Above this altitude, O_3 and peroxide are anticorrelated (Figure 18a), and below this they are positively correlated, at least until the sudden drop in peroxide at very low altitudes, which is where surface removal is active according to the water vapor record. The measured peroxide concentration below 1 km in Figure 18b is about a factor of 3 less than the H_2O_2 calculated. This would occur in the presence of approximately 1 ppbv of NO_X (Figure 17), which is entirely to be expected for a profile taken offshore of Portugal with an easterly wind. Unfortunately, NO_X was not measured in this plume, but subsequent measurements in many European plumes moving out over the Atlantic have confirmed that concentrations of NO_X between 0.2 and 2 ppbv are common.[79]

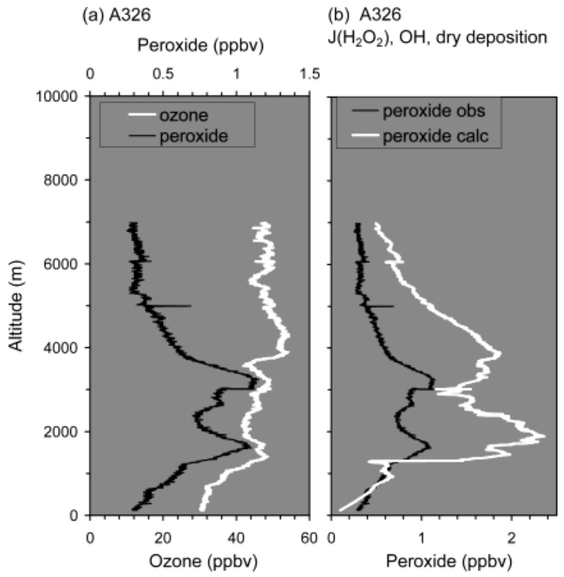

Figure 19. Ozone and peroxide concentrations (ppb) for Flight A326 over the North Atlantic off the Azores in April 1994: (a) measured peroxide (black) and measured ozone (white) and (b) measured peroxide (black) and calculated H_2O_2 (white). Reprinted with permission from ref 71. Copyright 1998 American Geophysical Union.

The peroxide:O_3 production ratio has been observed to vary from 1:5 in Tasmania to 1:60 in air over the United States[80] and is a function of the NO_X present since it reflects the competition between the peroxy radical reactions with NO (reactions 14 and 15) and their self-reaction (reactions 6 and 7). On the basis of the ratio between peroxide and O_3 and their observed concentrations over the North Atlantic, it can be conservatively estimated that at least about 40% of the observed O_3 is formed by in situ photochemistry.[70] In reality, the percentage of O_3 made by in situ photochemistry over the North Atlantic is more likely to be on the order of 80% according to some recent analyses by Li et al.[81]

While this positive correlation between peroxide and O_3 and over-prediction of measured peroxide by equation III appeared to be mostly confined to polluted layers in summer (Figure 18), it was more prevalent throughout the whole profile up to 7 km in spring (Figure 19).[71] On April 26, 1993, a profile was collected in the region of the Azores in an air mass with a westerly origin (i.e., it originated over the American continent). On this occasion, the calculated H_2O_2 was a factor of 1.5−2.5 greater than the measured peroxide in air where peroxide and O_3 were positively correlated up to 7 km. It was argued that this provided experimental evidence of the extensive production of O_3 in spring in the Northern Hemisphere that could account for the observed spring maximum in O_3 at clean air ground based sites (e.g., Mace Head). Approximately 500 pptv of NO_X would be required to give rise to the difference between the measured and the calculated profiles shown in Figure 19; this is certainly possible, at least in air masses leaving the coast of North America.

Monks[82] has debated the whole subject of the ozone spring maximum recently. He refers to the various theories that have been proposed suggesting stratospheric[83−85] and tropospheric sources.[86−88] Evidence for a tropospheric photochemistry origin for the build-up in O_3 in spring as originally proposed by Penkett and Brice[88] has been produced very recently by the TOPSE (Tropospheric Ozone Production about the Spring Equinox) experiment, which collected data on O_3 and many other species including tracers of the stratosphere (Be^7 and PV) and of the troposphere (particularly PAN) in flights made from about 40 °N to about 80 °N over the period of February to May 2000. TOPSE clearly showed a high correlation of PAN with O_3 from 40 to 100 ppbv and no correlation of O_3 with PV or Be^7.[89] Some of the O_3 present before the spring build-up could well have come from the stratosphere.[89]

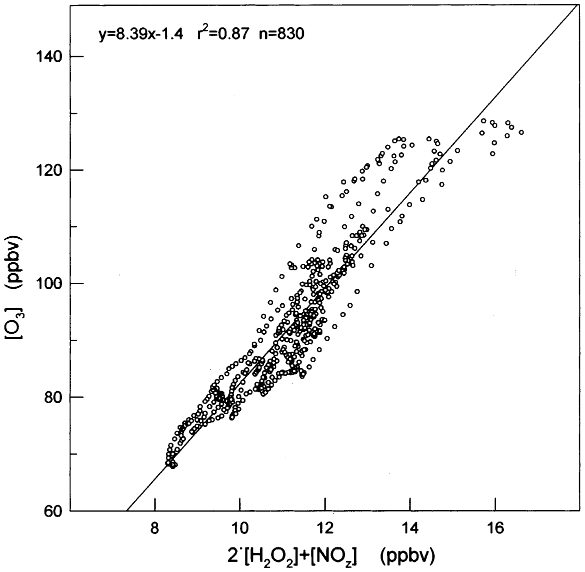

Figure 20. Correlation between O_3 and $2H_2O + NO_Z$ on July 11, 1995 during the Southern Oxidants/Middle Tennessee study. Reprinted with permission from ref 59. Copyright 1998 American Geophysical Union.

5.3. Use of H_2O_2 in the Determination of the Sensitivity of Ozone to NO_X or Hydrocarbons

Studies have also been made of the use of H_2O_2 measurements for indicating whether O_3 production is either NO_X limited or hydrocarbon limited.[90] As discussed previously in section 2, the formation of H_2O_2 (reaction 6) and HNO_3 (reaction 18) are sinks for HO_X, and reaction 6 dominates in an NO_X poor (limited) atmosphere, while reaction 18 will dominate in an NO_X rich (hydrocarbon limited) atmosphere. Sillman[90] showed that the ratio of H_2O_2/HNO_3 is an excellent indicator of the sensitivity of O_3 to NO_X or hydrocarbons and that the transition between these two regimes occurred when this ratio was at a value of about 0.4. Updates to reaction rates have led to a revision of this value to 0.20−0.30.[91] Ratios of H_2O_2/NO_Y and H_2O_2/NO_Z with values of 0.13−0.17 and 0.15−0.20, respectively, can also be used to indicate this transition when observations of HNO_3 are unavailable ($NO_Y = NO_X + HNO_3 +$ PAN + alkyl nitrates, $NO_Z = NO_Y - NO_X$). Sillman and co-workers[90−93] have used H_2O_2/NO_Z and O_3/NO_Z as indicators to show that while air sampled in Los

Angeles was hydrocarbon limited, air sampled at other locations in the US can be close to the NO_X–hydrocarbon transition (e.g., Nashville) or NO_X limited (e.g., Atlanta). Similarly, observations of the H_2O_2/HNO_3 ratio at Niwot Ridge, CO and Kinterbish, AL have also indicated that the O_3 production is NO_X limited.[78,94] This situation is probably true for large parts of the boundary layer over the US because of the large emissions of natural hydrocarbons, particularly isoprene. The importance of isoprene is illustrated by the comparison between the observations at Niwot Ridge and Kinterbish. At both sites, a positive relationship between H_2O_2 and temperature were found, similar to the dependence of isoprene concentrations on temperature, and concentrations of H_2O_2 were 3 times higher at Kinterbish, consistent with the higher temperatures and isoprene concentrations.[78,94] Further, at Kinterbish the diurnal patterns of H_2O_2 and the ratio of isoprene/NO_X matched remarkably closely. It should be noted here that while the O_3 production is found to be NO_X limited, peroxides and O_3 can still be produced concurrently at substantial rates. Frost et al.[95] calculated the midday rate of production of O_3, H_2O_2, and organic peroxides to be around 4–7, 0.5, and 1 ppb h^{-1}, respectively, at Kinterbish. The loss of radicals to produce peroxides was thus around 3 ppb h^{-1}, while the loss to HNO_3 was less than 0.1 ppb h^{-1}, clearly indicating NO_X limitation. The large emissions of isoprene in the US could also account for the very high concentrations of peroxides including HMHP as compared to Europe. Even so, H_2O_2/HNO_3 ratios observed in Switzerland also indicate NO_X limitation.[96]

Sillman[90] also identified the linear relationship between O_3 and $2H_2O_2 + NO_Z \cdot H_2O_2$ and NO_Z represent the cumulative sink for odd hydrogen, with the H_2O_2 concentrations being multiplied by 2 to account for the two radicals being consumed in the formation of each molecule of H_2O_2. The relationship of this radical sink term with O_3 assumes that O_3 is the dominant radical source through reactions 1 and 2. In some situations where HCHO, for example, might be a nonnegligible source, this assumption may not be true. Since both H_2O_2 and HNO_3 are considered here, this relationship should apply in both NO_X limited and hydrocarbon limited atmospheres. This relationship has been tested by data from a number of field experiments. Weinstein-Lloyd et al.[58] found the NARE data set to exhibit a linear correlation ($r^2 = 0.73$), and Daum et al.[55] concluded that this strong relationship indicated that the sampled air masses had not been in contact with source regions for several days, that the radical sinks (H_2O_2 and HNO_3) had not been lost via wet or dry deposition, and that the air mass had not aged to the point where the formation of H_2O_2 involved the consumption of O_3. The observed relationship also emphasizes that O_3 is the principal source of the radicals. Similarly, Weinstein-Lloyd et al.[59] observed a strong relationship ($r^2 = 0.87$) in data collected at Nashville, TN (Figure 20), which supports the use of H_2O_2/HNO_3 ratios as indicators of NO_X or hydrocarbon limitation.[91]

5.4. Peroxides as a Source of Hydroxyl Radicals in the Upper Troposphere

Chatfield and Crutzen[97] first suggested that convective transport of H_2O_2 might represent a source of HO_X in the UT and that production or consumption of H_2O_2 in clouds was an important area for further study. Subsequently, measurements of HO_2 in the UT during STRAT (Stratospheric Tracers and Atmospheric Transport) were found to be underpredicted by model calculations in some situations, usually when a few days downstream of deep convection or midlatitude cyclonic storms.[98] This air was identified as being of recent boundary layer origin by its high concentrations of condensation nuclei (CN) and methyl iodide (CH_3I) and low concentrations of O_3. Including elevated concentrations of peroxides, in particular MHP (assuming H_2O_2 to have been scavenged), in the model resulted in better agreement between calculated and measured HO_2. Further, Jaeglé et al.[98] calculated the lifetime of the perturbed HO_Y ($= HO_X + HNO_4 + HNO_2$ and peroxides) to be about 6 days and suggested that convection could be globally important as a source of HO_X in the UT (8–12 km). Prather and Jacob[99] reached a similar conclusion using a model of convective transport and average concentrations observed during the TRACE-A and PEM-West experiments.

Cohan et al.[100] identified marine convective outflow in the PEM-Tropics A data by elevated concentrations of CH_3I in conjunction with high humidity and elevated bromoform concentrations and low concentrations of O_3 and acetylene (C_2H_2). In this air, MHP was found to be enhanced by a factor of 6 and H_2O_2 by a factor 2. Cohan et al.[100] estimated the scavenging of the H_2O_2 in the convective cloud to be 55–70% and negligible for MHP and calculated the perturbed HO_Y in PEM-Tropics A to decay on a time scale of 2–3 days. The perturbed MHP was calculated to decay on a time scale of 1–2 days, while the cycling within the HO_Y family led to the perturbed H_2O_2 decaying on a time scale of 5 days. Similarly, Crawford et al.[101] suggested that observations of elevated H_2O_2 in the UT during PEM-West may have been due to the increased photochemical production due to the transported water vapor from the MBL rather than the convective transport of the H_2O_2 itself. Further, in a low water environment, perturbations to MHP can lead to elevated H_2O_2, which can remain above the expected steady-state level for several days after MHP has dissipated. This, they suggested, could explain why H_2O_2 can be observed at concentrations above steady state when MHP concentrations are below. Ravetta et al.[102] observed concentrations of MHP in aged convective outflow during PEM-Tropics B to be enhanced by 350% relative to background air, while H_2O_2 concentrations were not enhanced. The MHP enhancement was attributed to convective uplift from the MBL, while the lack of enhancement in H_2O_2 was attributed to its higher solubility and thus washout in the convective updraft.

Steady-state models constrained by observations have been shown to reproduce the concentration of H_2O_2 with varying degrees of accuracy. Schultz et al.[103] found that steady-state model calculations

Table 3. Summary of Diel Average HO_X Sources and Sinks for the Tropical Pacific at 8−12 km[99]

	fresh convective outflow		background	
	10^4 molecules cm^{-3} s^{-1}	%	10^4 molecules cm^{-3} s^{-1}	%
Sources				
$O(^1D) + H_2O$	4.9	35	2.1	28
$H_2O_2 + h\nu$	3.1	22	1.7	23
MHP + $h\nu$	2.5	18	0.9	12
HCHO + $h\nu$	2.9	21	2.3	30
acetone + $h\nu$	0.5	4	0.5	7
total sources	13.9	100	7.5	100
Sinks				
$HO_2 + HO_2$	5.1	37	2.3	31
$HO_2 + CH_3O_2$	4.4	32	1.5	20
$OH + HO_2$	3.4	24	2.5	33
other	1.0	7	1.2	16
total sinks	13.9	100	7.5	100

underestimated H_2O_2 observed above 8 km during PEM-Tropics A by 30%. Jaeglé et al.[104] were able to reproduce H_2O_2 concentrations observed during SONEX to within 50% if HO_2 to H_2O_2 heterogeneous conversion on aerosols was considered. This source was estimated to be almost as important as the gas-phase production via reaction 6. Further, Jaeglé et al.[104] successfully simulated the OH and HO_2 to within 40% with the model constrained by observed H_2O_2 and MHP. However, steady-state models often appear to substantially underpredict observed concentrations of MHP. Schultz et al.[103] and Jaeglé et al.[104] both found model calculations to underestimate, by a factor of 2, the MHP concentrations observed in PEM-Tropics A and SONEX (Subsonic Assessment Ozone and Nitrogen Oxide Experiment), respectively. Schultz et al.[103] concluded that deep convection did not seem to be able to account for all of it and suggested that some of the discrepancy in the MHP concentrations could be accounted for by the large uncertainty of a factor of 3 at 235 K[12,105] in the rate of the reaction of CH_3O_2 with HO_2 (reaction 7). Similarly, Ravetta et al.[102] found that a model constrained by observations, including the peroxides, calculated an imbalance between the production and the loss terms of MHP and H_2O_2 for both convected and background UT air; loss exceeded production for MHP, while production exceeded loss for H_2O_2. Given the lifetime of the peroxides, this is not expected for the background air. However, these discrepancies could largely be resolved by using a rate for the reaction between CH_3O_2 and HO_2 (reaction 7) 3 times greater than recommended[12,105] but still within the quoted uncertainty at the low temperatures of the UT. This reaction then became the single most important loss pathway for HO_X in the UT.

Further, Cohan et al.[100] found the HO_X in the convected air during PEM-Tropics A to be increased by 50%, half of which they calculated to be due to the increase in water vapor brought up by the convection and half due to the photolysis of the peroxides (Table 3). Convective enhancements of acetone and formaldehyde (HCHO) were not included in the model due to a lack of observations with which to constrain the calculations. Note also that even in the background UT air, Cohan et al.[100] calculated 35% of the HO_X to come from the photolysis of the peroxides. Ravetta et al.[102] also observed concentrations of HO_2 to be enhanced by 50% in the convective outflow during PEM-Tropics B. This they attributed to the photolysis of the additional MHP (reaction 9), with this source of HO_X being calculated to be 1.7 times greater than the source from reaction of $O(^1D)$ with H_2O (reaction 2). Both Cohan et al.[100] and Ravetta et al.[102] found OH not to be enhanced in the convective outflow, which they ascribed to the increased sink from reaction with transported MHP (reaction 11). During SONEX, Jaeglé et al.[104] found that the HO_X budget was not generally perturbed by convection. Under these conditions, they calculated the peroxides to contribute about half of the primary HO_X source from acetone and water vapor, with H_2O_2 photolysis being more important than MHP photolysis, but that these sources were balanced by a loss of HO_X through the formation of the peroxides (reactions 6 and 7).

Much of the UT data discussed previously has been collected over the ocean, and Folkins et al.[106], who observed enhanced peroxides with elevated concentrations of CH_3I during PEM-West B, also noted that this was accompanied by low concentrations of NO, consistent with convected MBL air. Thus, although HO_X may be enhanced, the low NO concentrations led to a slow production of O_3. The impact of an enhancement of peroxides in the UT on O_3 production is therefore dependent on the origin of the convected air and the associated NO_X concentrations.

To summarize, enhanced concentrations of peroxides, in particular MHP, but on occasion H_2O_2, have been observed in convective outflow in the UT. In general, the models can reproduce the H_2O_2 concentrations observed in the UT reasonably well, but most models tend to substantially underpredict MHP. This, however, is within the large uncertainty in the reaction rate of HO_2 with CH_3O_2. Calculations using observed peroxide concentrations suggest that peroxides are an important source of HO_X in the UT and that HO_2, but not OH, is enhanced, partially by the peroxides, in convective outflow. Further, the impact of this enhanced HO_X on the production of O_3 is also dependent on the NO_X content of the convected air.

6. Summary

Measurements of peroxides in the atmosphere have contributed enormously to the present understanding both of the processes controlling the distribution of hydroxyl radicals and to the main source of O_3 in the troposphere, namely, tropospheric chemistry. Through the comeasurement of peroxides, O_3, and water vapor, it has been demonstrated that the O_3 diurnal and seasonal cycles in the MBL are largely a result of in situ photochemical destruction, with the majority of the O_3 being lost via peroxides and their subsequent deposition. The amount of peroxide made from O_3 destruction is of a very similar magnitude to the amount of O_3 destroyed, making peroxides some of the predominant trace gases produced in the troposphere and their measurement a vital component of the study of tropospheric O_3. Further, these measurements have shown that the layered structure in O_3 and its anti-correlation with water vapor often observed throughout much of the troposphere may not be due to the transport of O_3 rich air from the stratosphere but rather photochemical destruction of O_3 in the moist air. It is the water vapor concentration that appears to be the major controlling factor, and its higher concentrations in the summer and the consequent enhanced photochemical destruction of O_3, rather than transport, which is the major cause of the O_3 cycle in the remote marine atmosphere.

The large amounts of O_3 calculated to be lost by photochemistry need to be balanced by O_3 gains far exceeding those predicted to come from the stratosphere, which indicates that substantial photochemical production of O_3 is also occurring. Extensive O_3 production in the free troposphere has been inferred from positive correlations in observed peroxide and O_3 and the comparison of measured and calculated concentrations of peroxide. O_3 production can be limited by NO_X or hydrocarbons. The ratio of H_2O_2/HNO_3 has been demonstrated to be an excellent indicator of this sensitivity; thus, H_2O_2 measurements can aid the implementation of effective emission controls. Since O_3 photolysis is the primary source of OH, this also implies that water vapor is the species that has the largest influence on the concentration of this key oxidant. In the MBL, the peroxides, predominantly via their deposition, have also been shown to be the major sink for HO_X. In the upper troposphere, where the source of OH from O_3 photolysis is diminished due to the drier conditions, the measurement of peroxides has shown them to be a significant source of HO_X, which is enhanced when additional peroxides are transported by convection to this region. Overall, measurements of peroxides have clearly illustrated the substantial amount of photochemical processing that is occurring in the troposphere.

7. References

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