other fog waters, higher or lower oxalate and DOC concentrations can occur, and the photochemical formation rate of H_2O_2 varies correspondingly.

A significant amount of H_2O_2 is photochemically formed, and dissolved SO_2 is oxidized in real fog water. With consideration of previous studies, one may suggest that the photochemical cycling of Fe(III)-Fe(II) complexes is involved in this process. The Fe(II) that is formed simultaneously with H_2O_2 can further produce OH radicals by a photo-Fenton reaction (*10–12, 27, 28*).

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Aqueous-Phase Photochemical Formation of Peroxides in Authentic Cloud and Fog Waters

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Gas-to-drop partitioning of hydrogen peroxide and its precursor, the hydroperoxyl radical ($HO_2^{\cdot}$), has been considered the predominant or sole source of hydrogen peroxide in atmospheric water drops. However, atmospheric water can absorb solar ultraviolet radiation, which initiates the photoformation of peroxides (primarily hydrogen peroxide). Measurements of peroxide photoformation rates in authentic atmospheric water samples demonstrate that aqueous-phase photochemical reactions are a significant, and in some cases dominant, source of hydrogen peroxide to cloud and fog drops. This additional source could significantly change the current understanding, and hence, the models, of sulfuric acid deposition because hydrogen peroxide is the limiting reagent in the dominant pathway for the oxidation of sulfur dioxide to sulfuric acid in the troposphere over eastern North America.

Interest in the sources and reactions of peroxides and other oxidants in atmospheric water drops has been motivated by questions that are related to chemical transformations in the troposphere (*1–4*), such as the (i) formation of sulfuric acid, (ii) destruction of ozone, (iii) redox cycling of iron, and (iv) oxidation of organic compounds. The two main sources of hydrogen peroxide (H_2O_2) to cloud and fog drops are aqueous-phase photoformation, which has received little attention, and gas-to-drop partitioning of gas-phase H_2O_2 and its precursor, $HO_2^{\cdot}$, which has been extensively studied. This report focuses on aqueous-phase photochemical sources.

Cloud and fog water samples were obtained from researchers at different sites in the United States and from aircraft flights over Ontario, Canada. Samples were stored in the dark at 2° to 10°C and were untreated except for filtration (0.5-μm Teflon) immediately upon receipt. Peroxides were quantified by the methods of Kok and coworkers (*5*).

Atmospheric waters contain constituents that absorb solar ultraviolet light (*6, 7*). This absorption initiates aqueous-phase photochemical reactions that form peroxides. The peroxide photoformation, and its approach to a photostationary state, that was typically observed is shown in Fig. 1. Speciation studies of the peroxides that were formed showed that in all of the eight cloud and fog waters studied, at least 97% of the detectable peroxides were H_2O_2.

Typical equinox-normalized photoformation rates of H_2O_2 in 44 cloud and fog water samples from six different locations in North America ranged from 0.4 to 3.5 μM $hour^{-1}$, with rates as high as 5.8 μM $hour^{-1}$ (Table 1) (*8*). By comparison, field studies of clouds over the eastern United States and Canada have shown that all (~100%) winter cloud water samples, most (58 to 100%) spring and fall samples, and few (3 to 7%) summer samples had H_2O_2 concentrations <5 μM (*9, 10*). Moreover, H_2O_2 concentrations in all of the winter cloud water samples were <1 μM (*9*). Thus, the photoformation rates reported in Table 1 demonstrate that the aqueous-phase photochemical formation of H_2O_2 is a significant, and in some cases dominant, source of H_2O_2 to atmospheric water drops. Quantum yields for H_2O_2 formation on exposure to 313-nm light were typically 6×10^{-4} to 5×10^{-3} (Table 1) (*8*).

The aqueous-phase H_2O_2 photoformation rate was linearly dependent on the irradiance of the simulated sunlight for all seven of the atmospheric waters samples that were studied (Fig. 2). This is consistent with our theoretical predictions that the rate of aqueous-phase H_2O_2 photoformation from reactions of $HO_2^{\cdot}$ or $O_2^{\cdot -}$ with itself or with reductants [such as Fe(II) and

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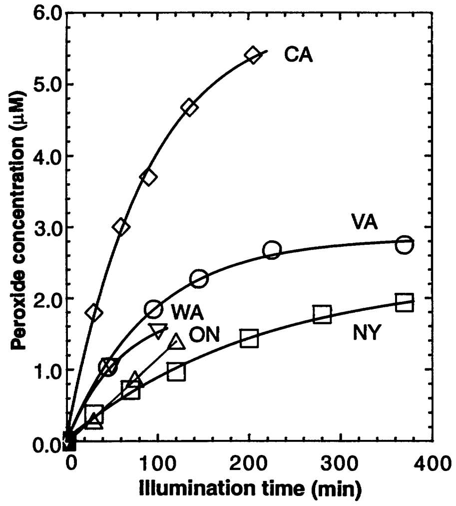

Fig. 1. Examples of the aqueous-phase photochemical formation of peroxides in samples of cloud water (VA, WA, ON, and NY) and fog water (CA) that were illuminated with simulated or real sunlight. Sampling locations: VA = Virginia, WA = Washington, ON = Ontario, NY = New York, and CA = California. Solid lines represent least squares fits of linear or exponential functions to the data.

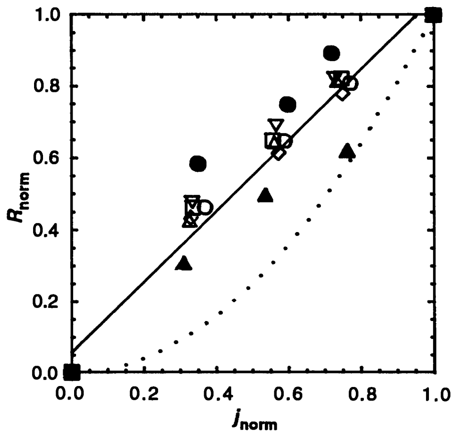

Fig. 2. Normalized initial rate of aqueous-phase peroxide photoformation, R_{norm} (*15*), measured in an atmospheric water sample that was illuminated with simulated sunlight, versus the normalized actinometer rate constant, j_{norm} (*16*), under the same conditions of irradiation. The actinometer's photolysis rate constant, j_A, and therefore j_{norm}, is directly proportional to the irradiance of the simulated sunlight (*6*). Note that R_{norm} and j_{norm} are normalized, and therefore dimensionless, parameters. The solid line represents the linear dependence of the photoformation rate on irradiance and is a least squares fit of the data ($R^2 = 0.96$): $R_{norm} = (0.985 \pm 0.036)j_{norm} + (0.055 \pm 0.073)$, where the uncertainties are standard errors. The slope (0.985 ± 0.036) agrees well with the theoretical slope of 1 expected for a linear relation. For comparison, the dotted line represents a squared dependence of the rate on irradiance and is given by $R_{norm} = (j_{norm})^2$. Data for seven cloud and fog water samples shown.

Cu(I)] is linearly dependent on solar irradiance for conditions typical of atmospheric waters. In contrast, the gas-phase photoformation rate of H_2O_2 in the troposphere has been implicitly assumed to exhibit a squared dependence on solar irradiance. The implicit assumption of this squared dependence, from the current understanding of H_2O_2 chemistry, is based on the gas-phase reaction $2\ HO_2^{\cdot} \rightarrow H_2O_2 + O_2$, which is the only known gas-phase source of tropospheric H_2O_2 (*1–4*). The rate of H_2O_2 formation from this reaction is proportional to $[HO_2^{\cdot}]^2$ and hence proportional to the square of the irradiance.

This large difference in the functional dependence of the H_2O_2 photoformation rate on solar irradiance, a linear dependence for the aqueous phase and a squared dependence for the gas phase, suggests that the seasonal variability in solar irradiance would cause the relative contributions of water drop sources to be even larger in fall, winter, and spring, compared with summer. The aqueous-phase photoformation and its associated linear dependence on solar irradiance are not currently incorporated into any model of sulfuric acid deposition. Their incorporation could have a profound effect on the predictions of such models.

The reaction of H_2O_2 with HSO_3^- (an aqueous anion formed from SO_2) in atmospheric water drops is the dominant source of H_2SO_4 in the troposphere over eastern North America and other regions (*2–4*). Furthermore, in these regions, H_2O_2 is very often the limiting reagent (relative to SO_2) in this reaction (*3, 4*). Consequently, an accurate assessment of all sources of H_2O_2 in clouds is of critical importance to the definition of the spatial and temporal patterns of H_2SO_4 formation and regional acid deposition (*3, 4*). The work presented here requires a reassessment of acid deposition models with respect to the mechanisms of H_2O_2 formation and the subsequent predictions of H_2SO_4 deposition.

Table 1. Photoformation rates of peroxides (primarily H_2O_2) in equinox-normalized sunlight (*17*) and quantum yields at 313 nm for peroxide formation in authentic cloud and fog waters. The results represent aqueous-phase photochemical sources of H_2O_2 in an atmospheric water drop (that is, they do not include any contributions from gas-to-drop partitioning of H_2O_2 or $HO_2^{\cdot}$). A blank entry in the table indicates that the quantity is not available. ND, not detectable.

Location*	Type of event	Photoformation rate			Quantum yield		
		Mean (μM hour^{-1})	Range (μM hour^{-1})	Samples (no.)	Mean	Range	Samples (no.)
California	Fog	3.5	0.8 to 5.8	8	6.0×10^{-4}	$(3.4 \text{ to } 9.8) \times 10^{-4}$	8
New York	Cloud	1.9	0.4 to 3.4	7	5.4×10^{-3}	$(2.7 \text{ to } 10) \times 10^{-3}$	6
Ontario	Cloud	0.74	0.07 to 2.1	17			
Virginia and N. Carolina	Cloud	0.40	0.04 to 1.4	6	1.4×10^{-3}	ND to 3.0×10^{-3}	8
Washington	Cloud	1.1	ND to 3.0	5	9.7×10^{-4}	ND to 2.0×10^{-3}	7

*Samples were collected between 1990 and 1992. Locations: Davis, California; Whiteface Mountain, New York; Ontario, Canada; Shenandoah Park, Virginia, and Mount Mitchell, North Carolina; and Stampede Pass, Washington.

The H_2O_2-mediated production of H_2SO_4 in atmospheric water drops also affects the formation of acidic and light-scattering sulfate aerosols, which form when the water drops evaporate. This will, in turn, affect the magnitude and spatial distribution of the cooling effect that the aerosols exert on the global climate (*11*). It has been proposed that, under some conditions, the aqueous-phase oxidation of SO_2 by ozone contributes to H_2SO_4 formation (*12*), but the assumptions and conditions in these studies are probably not applicable to the continental regions discussed here.

The chromophores that are responsible for aqueous-phase H_2O_2 photoformation have not been identified. The photoformation rate is correlated with the relative fluorescence of the atmospheric water, and the relative fluorescence is correlated with the concentration of dissolved organic carbon (DOC) in the sample (1.9 to 31 mg of carbon per liter, 31 samples). However, the correlation between H_2O_2 photoformation rate and DOC concentration was not strong. This is probably because not all organic compounds are chromophores for H_2O_2 photoformation and the relative concentrations of the different H_2O_2-forming organic chromophores undoubtedly vary from sample to sample. We conclude that fluorescent organic chromophores might be responsible for the H_2O_2 photoformation.

The aqueous-phase photochemical formation of H_2O_2 in clouds and fogs is a widespread and significant phenomenon in the terrestrial troposphere of the Northern Hemisphere. Because anthropogenic SO_2 emissions in the Northern Hemisphere are estimated to represent ~65% of all sulfur emissions to the global troposphere (*13*), it is especially important to understand aqueous-phase oxidation processes in the Northern Hemisphere. It is likely, however, that the aqueous-phase photoformation is also significant in the Southern Hemisphere.

The aqueous-phase photoformation of another oxidant, the hydroxyl radical ($\cdot$OH), was also observed in authentic cloud and fog waters. The measured $\cdot$OH photoformation rates ranged from 0.44 to 5.3 μM hour^{-1} in the four cloud and fog waters that were studied (*7, 14*). These rates are similar to the calculated fluxes of $\cdot$OH to atmospheric water drops from all other known sources (*2, 3*). Aqueous-phase photoformation of singlet molecular oxygen and unspeciated peroxyl radicals have been reported previously (*6*), but the previous work did not demonstrate the formation of H_2O_2 or any other peroxide.

In view of this additional source of H_2O_2 and other oxidants to atmospheric water drops, tropospheric aqueous-phase oxidations must exert even more influence than has previously been recognized on the atmospheric chemical cycles of peroxides, ozone, sulfur, iron, and carbon. These oxidations will also influence the formation of H_2SO_4, which affects the magnitude of acid deposition and the postcloud aerosol characteristics and optical properties of the atmosphere. Photoreactions such as those reported here for clouds and fogs are also likely to be important sources of oxidants in other atmospheric hydrometeors, such as hydrated aerosols, rain, and dew, and also on wetted foliage.

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14. We quantified the $\cdot$OH photoformation rate by monitoring the appearance of phenol from the $\cdot$OH-mediated oxidation of benzene, which was added to the atmospheric water as a probe for $\cdot$OH.
15. For a given atmospheric water,

$$R_{\text{norm}} = \frac{\dfrac{d[\text{peroxide}]}{dt}}{\max \dfrac{d[\text{peroxide}]}{dt}}$$

where $d[\text{peroxide}]/dt$ is the rate of peroxide photoformation for a series of experiments on one atmospheric water with different irradiances.
16. For the actinometer, $j_{\text{norm}} = (j_A)/(\max j_A)$, where j_A is the corresponding first-order rate constant for direct photolysis of the actinometer (2-nitrobenzaldehyde in distilled water) for the same series of experiments with the atmospheric water.
17. Measurements were normalized with a chemical actinometer to conditions of an isolated spherical water drop in a 100% clear sky at solar noon on 24 September 1990 in Durham, NC (solar zenith angle, 36°; elevation, 121 m).
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Genetic Conversion of a Fungal Plant Pathogen to a Nonpathogenic, Endophytic Mutualist

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The filamentous fungal ascomycete *Colletotrichum magna* causes anthracnose in cucurbit plants. Isolation of a nonpathogenic mutant of this species (path-1) resulted in maintained wild-type levels of in vitro sporulation, spore adhesion, appressorial formation, and infection. Path-1 grew throughout host tissues as an endophyte and retained the wild-type host range, which indicates that the genetics involved in pathogenicity and host specificity are distinct. Prior infection with path-1 protected plants from disease caused by *Colletotrichum* and *Fusarium*. Genetic analysis of a cross between path-1 and wild-type strains indicated mutation of a single locus.

Filamentous fungal plant pathogens cause worldwide losses of billions of dollars and of millions of tons of agricultural produce annually (*1*). Use of chemical fungicides has led to the evolution of fungal resistance and to concern over the potential effects of these chemicals on other eukaryotes. Definition of the genetic and biochemical bases of fungal pathogenesis may lead to the development of more effective, long-term, and ecologically safe fungal control strategies.

Fungal pathogenesis of host plants involves penetration of host tissue, host pathogen compatibility, dissemination through host tissue, induction of disease symptoms, and amplification of the pathogen by sporulation (*2*). The biochemical and genetic bases of host tissue penetration (*3, 4*), host compatibility (*5, 6*), and sporulation (*7, 8*) of fungal pathogens have been extensively studied. Here, we analyze a mutation in the process that allows pathogenic fungi to dis-

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