Reports

Photochemical Formation of Hydrogen Peroxide in Surface and Ground Waters Exposed to Sunlight

Abstract. *A rapid increase in the concentration of hydrogen peroxide was observed when samples of natural surface and ground water from various locations in the United States were exposed to sunlight. The hydrogen peroxide is photochemically generated from organic constituents present in the water; humic materials are believed to be the primary agent producing the peroxide. Studies with superoxide dismutase suggest that the superoxide anion is the precursor of the peroxide.*

Hydrogen peroxide (H_2O_2) appears to be ubiquitous in the hydrosphere; it has been measured in rainwater (*1*), seawater (*2, 3*), and freshwater (*4*). Its presence in rainwater is believed to be the result of either rainout or washout from the gas phase or from chemical reactions with O_3 or other reactive gas-phase constituents in cloud aerosols (*5*). Although the H_2O_2 in surface waters may be derived in part from rainfall or from direct deposition from the atmosphere, it is likely that other sources are required to maintain the concentrations observed (Table 1).

It has been proposed that natural humic materials in waters might photochemically reduce oxygen to give the superoxide anion, $O_2\cdot^-$, and that subsequent disproportionation of this free radical could lead to the formation of H_2O_2 (*3*). If this hypothesis is correct, then the concentration of H_2O_2 in surfaced ground waters and surface waters, which may contain high concentrations of dissolved humic materials, should be correlated to the amount of dissolved humic material when the waters are exposed to sunlight. To explore this possibility, we collected surface waters in the southeastern United States and filtered them through 0.22-μm washed Nuclepore filters [filtration was shown not to affect the total organic carbon (TOC) content of the samples]. Ground water samples, not previously exposed to light, were collected from several locations in the United States and were used without filtering. The water samples were transferred into 300-ml quartz round-bottom flasks and exposed to sunlight. The H_2O_2 was determined (*6*) as a function of incident near-ultraviolet (290 to 385 nm) radiation as measured (in watt-hours per square meter) with an Eppley ultraviolet radiometer located immediately adjacent to the reaction site (the total analytical error of the H_2O_2 measurement in sunlight-irradiated samples was ±2 percent).

Figure 1 summarizes the accumulation rate of H_2O_2 as a function of TOC. The accumulation rate is the net rate of formation of H_2O_2, that is, the sum of the production and decomposition reactions maintaining the solution concentration of H_2O_2. The accumulation rate increased with TOC in both surface and ground waters. The apparent difference in the H_2O_2 concentration of the ground water and surface water samples is due to the initially low values of H_2O_2 in the ground waters.

The absolute concentration of H_2O_2 is related to TOC, insofar as the TOC is representative of natural aquatic humic materials. For example, the Sodus water did not have an absorption spectrum typical of the other waters investigated, a possible indication of the absence of natural aquatic humic materials (*7*). The highest concentration of H_2O_2 observed was $1 \times 10^{-5}M$.

A precursor of H_2O_2 could be $O_2\cdot^-$, according to the equation

$$2O_2\cdot^- + 2H^+ \rightarrow H_2O_2 + O_2$$

Superoxide dismutase (SOD) catalyzes this reaction and has been used as a specific probe for the presence of $O_2\cdot^-$

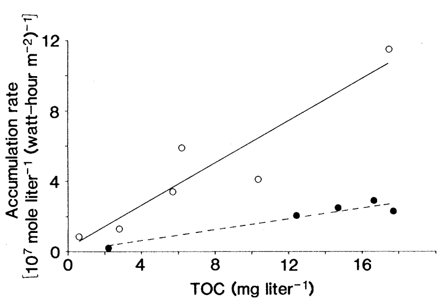

Fig. 1. Accumulation rate of H_2O_2 as a function of total organic carbon (TOC). The accumulation rate was determined as the initial rate of increase in the H_2O_2 concentration (in moles per liter) as a function of the cumulative solar energy (in watt-hours per square meter); TOC was determined by ultraviolet persulfate digestion of the organic matter (in milligrams per liter) as carbon; ground water samples (○) were unfiltered, and surface water samples (●) were filtered through a 0.22-μm polycarbonate membrane filter prior to TOC analysis.

Table 1. Concentrations and accumulation rates of H_2O_2 in surface and ground waters exposed to sunlight; 1.0 watt-hour m^{-2} is the equivalent of 2.5 hours of full sunlight at midday in June in Miami (latitude, 25°44′N).

Location	TOC (mg liter^{-1})	H_2O_2 (mole liter^{-1}) concentration after sunlight exposure		
		Initial	0.3 watt-hour m^{-2}	1.0 watt-hour m^{-2}
	Surface water			
Chechessee River, S.C.	2.2	8.75×10^{-8}	6.4×10^{-7}	
Combahee River, S.C.	14.7	1.60×10^{-7}	2.30×10^{-6}	
Newman River, Fla.	16.7	1.70×10^{-7}	1.95×10^{-6}	
Peacock River, Ga.	17.8	3.20×10^{-7}	4.62×10^{-6}	
Tamiami Canal, Fla.	12.4	9.00×10^{-8}	2.56×10^{-6}	7.02×10^{-6}
VH Pond, Miami, Fla.		1.4×10^{-7}	1.29×10^{-6}	3.48×10^{-6}
	Ground water			
Tucson, Ariz.	0.2	0	5.75×10^{-8}	6.5×10^{-8}
Spring water, Coudersport, Pa.	0.5	0	3.1×10^{-7}	3.7×10^{-7}
Sodus, N.Y.	0.9	0	0	0
Well 18, Miami, Fla.	2.9	0	6.03×10^{-7}	1.38×10^{-6}
Well 5, Miami, Fla. (6/26/81)	5.7	0	1.60×10^{-6}	3.90×10^{-6}
Well 5, Miami, Fla. (10/15/81)	6.2	0	1.84×10^{-6}	3.30×10^{-6}
Well 23, Miami, Fla.	10.3	0	1.68×10^{-6}	4.45×10^{-6}
Northwest well 1, Miami, Fla.	17.6	0	4.79×10^{-6}	1.00×10^{-5}

(*8*). We added SOD to the ground water sample (13 mg liter^{-1}) and compared the H_2O_2 accumulation rate and the absolute concentration of H_2O_2 to that in a sample to which no SOD had been added. The accumulation rate with SOD was about double the rate in the control. After sunlight irradiation (1.0 watt-hour m $^{-2}$), the H_2O_2 concentrations were $2.8 \times 10^{-6}M$ and $5.4 \times 10^{-6}M$ in the sample without and with SOD, respectively. Thus, we conclude that $O_2\cdot^-$ is a precursor in the sunlight-induced production of H_2O_2 in natural waters.

It is also possible that organoperoxides might be formed. Catalase decomposes H_2O_2 and organic peroxides at different rates (*9*). Therefore, we could distinguish between these two peroxide species on the basis of a comparison of the rate of catalase decomposition of oxidants formed in situ relative to that of added H_2O_2.

Two samples of a ground water were exposed to sunlight for a total irradiation of 1.85 watt-hour m^{-2}, at which time they were brought in out of the sun and the H_2O_2 was measured. In both cases the final H_2O_2 concentration was $1.4 \times 10^{-5}M$ to $1.5 \times 10^{-5}M$. To a third flask of ground water that was not irradiated, stock H_2O_2 was added to give a $1.1 \times 10^{-5}M$ solution. These three solutions were then allowed to stand in the laboratory for 1 hour; no change in H_2O_2 concentration occurred. Catalase (1 mg liter^{-1}) was added to one of the flasks that had been exposed to sunlight and to the one to which H_2O_2 had been added, and the H_2O_2 concentrations were monitored in all flasks for 75 minutes. The H_2O_2 concentration was constant over the period in the control solution (that is, the one to which no catalase had been added). The solutions to which catalase had been added showed very similar decay curves with time. Had organoperoxides been present then, we would have expected an intermediate decay rate. These data suggest that the measured concentrations are indeed attributed to H_2O_2 and not to organic peroxides.

Both H_2O_2 and $O_2\cdot^-$ are known to affect biological systems (*10*) and geochemical cycles (*11*). At the concentration reported herein, it is very likely that H_2O_2 and $O_2\cdot^-$ are important factors in the maintenance of the *Eh* (redox potential) of natural waters high in organic matter. In addition, the occurrence of H_2O_2 and $O_2\cdot^-$ implicate other reactive transients (for example, OH^- and organic radicals and metastable intermediates of many transition metals and nonmetallic elements) in the overall chemistry of natural waters. Whether these transients exert significant effects on surface water quality remains to be shown.

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References and Notes

1. G. L. Kok, *Atmos. Environ.* **14**, 653 (1980); R. G. Zika, E. Saltzman, W. L. Chameides, D. D. Davis, *J. Geophys. Res.* **87**, 5015 (1982).
2. C. Van Baalen and J. E. Marler, *Nature (London)* **211**, 951 (1966).
3. R. G. Zika, *Eos* **61**, 1010 (1980).
4. V. E. Sinel'nikov, *Gidrobiol. Zh.* **7**, 115 (1971); W. J. Cooper, R. G. Zika, R. G. Petasne, paper presented at the American Water Works Association Conference, Miami Beach, Fla., 16 to 21 May 1982.
5. W. L. Chameides and D. D. Davis, *J. Geophys. Res.* **87**, 4863 (1982).
6. R. G. Zika, P. Zelmer, R. Petasne, in preparation.
7. The ultraviolet absorbance showed differences between samples that resulted in the formation of H_2O_2 and those in which no (or little) H_2O_2 was formed. There is a linear relation between the absorbance at specific wavelengths and TOC (R. G. Zika, W. J. Cooper, R. Petasne, in preparation).
8. D. Klug, J. Rabani, I. Fridovich, *J. Biol. Chem.* **247**, 4839 (1972).
9. B. J. Chance, *ibid.* **179**, 1311 (1949).
10. J. P. McCormick, J. R. Fischer, J. P. Pachlatko, A. Eisenstark, *Science* **191**, 468 (1976); I. Fridovich, *ibid.* **201**, 875 (1978).
11. W. G. Breck, in *The Sea*, E. D. Goldberg, Ed. (Interscience, New York, 1974), vol. 5, pp. 153–179; R. Parsons, *The Nature of Seawater* (Department of Physical Chemistry, University of Bristol, Bristol, England, 1975).
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Adaptations for Climbing in North American Multituberculates (Mammalia)

Abstract. *A recently discovered skeleton of* Ptilodus *exhibits several specializations for climbing. A survey of postcranial bones of Cretaceous and early Cenozoic multituberculates from North America reveals similar locomotor specializations. Multituberculates possessed distinctive tarsal adaptations for a range of pedal mobility characteristic of arboreal mammals that descend trees headfirst. The divergent hallux could move independently of the other digits. The long robust tail of* Ptilodus *possessed musculoskeletal features that, among living mammals, are associated with prehensility.*

Multituberculates are an extinct, holarctic group of nontherian mammals that ranged in geologic history from the Late Jurassic to early Oligocene. They are particularly diverse in Late Cretaceous and Paleocene strata, where they are abundantly represented by teeth and jaws. The postcranial skeleton of multituberculates is, however, poorly known, and a variety of locomotor habits were postulated by early workers from limited evidence (*1*). The discovery of a nearly complete and well-preserved skeleton of *Ptilodus kummae* in the Paleocene Ravenscrag Formation of southeastern Saskatchewan (*2*) provides an opportunity to reassess hypotheses concerning the locomotor adaptations of North American multituberculates. Examination of all North American genera of Cretaceous and early Cenozoic multituberculates for which adequate postcranial material is available leads us to conclude that they possessed adaptations suited for arboreal life.

The articulated portion of the skeleton of *P. kummae* is virtually complete posterior to the anterior part of the rib cage. Portions of the dentition, pectoral girdle, and forelimbs were also recovered. Our analysis is based primarily on this skeleton as well as on a specimen of the hind limbs and pelvis of a multituberculate referred to the genus *Eucosmodon* by Granger and Simpson (*3*). We also examined all available postcranial remains of North American multituberculates of the suborders Ptilodontoidea and Taeniolabidoidea (*4*). These consist primarily of isolated limb bones, most of which have not been described.

The skeletal proportions of multituberculates are comparable to those of generalized, noncursorial mammals such as opossums and tree shrews (*5*). However, specializations in the structure of the ankle, in the joint between the entocuneiform and the hallucal metatarsal, and in the tail are similar to those in certain arboreally adapted Recent mammals.

A number of mammals that climb, many of which are arboreal, possess an unusual range of pedal mobility (particularly abduction and plantar flexion) that permits headfirst descent on vertical surfaces such as tree trunks (*6*). During such activity, the hind foot is reoriented so as to point the toes backward and position