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Photobiogeochemistry of Organic Matter

Principles and Practices in Water Environments

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Khan M.G. Mostofa, Takahito Yoshioka, Abdul Mottaleb, Davide Vione

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Zu Inhaltsverzeichnis

Photoinduced and Microbial Generation of Hydrogen Peroxide and Organic Peroxides in Natural Waters

Khan M. G. Mostofa, Cong-qiang Liu, Hiroshi Sakugawa, Davide Vione, Daisuke Minakata and Fengchang Wu

1 Introduction

The concentration of hydrogen peroxide (H_2O_2) in natural waters has been determined for the first time in 1925 by Harvey (Harvey 1925), who studied inshore and offshore water from the English Channel. The concentration of H_2O_2 has been determined in seawater in the 1970's (van Baalen and Marler 1966) and in some Russian freshwaters in the 1980's (Sinel'nikov 1971; Sinel'nikov and Demina 1974). In the same period the occurrence and concentration of H_2O_2 was being studied in air (Penkett et al. 1979; Lazrus et al. 1986; Sakugawa and Kaplan 1987), rain and cloud water, freshwater and coastal and open ocean waters (Cooper and Zika 1983; Draper and Crosby 1983; Helz and Kieber 1985; Lazrus et al. 1985;

K. M. G. Mostofa (✉) · C. Q. Liu
State Key Laboratory of Environmental Geochemistry, Institute of Geochemistry,
Chinese Academy of Sciences, Guiyang 550002, China
e-mail: mostofa@vip.gyig.ac.cn

H. Sakugawa
Department of Environmental Dynamics and Management,
Graduate School of Biosphere Science, Hiroshima University, 1-7-1, Kagamiyama,
Higashi-Hiroshima 739-8521, Japan

D. Vione
Dipartimento Chim Analit, University Turin, I-10125 Turin, Italy

Centro Interdipartimentale NatRisk, I-10095 Grugliasco, (TO), Italy

D. Minakata
School of Civil and Environmental Engineering, Brook Byers Institute for Sustainable Systems,
Georgia Institute of Technology, 828 West Peachtree Street, Suite 320, Atlanta, GA 30332, USA

F. C. Wu
State Environmental Protection Key Laboratory of Lake Pollution Control,
Chinese Research Academy of Environmental Sciences, Chaoyang 100012, China

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Zika et al. 1985a, b; Moffett and Zika 1987a; Palenic and Morel 1988; Cooper and Lean 1989; Hellpointner and Gäb 1989; Johnson et al. 1989). Starting from the 1980's, organic peroxides (ROOH) have been detected in air (Sakugawa and Kaplan 1987; Lazrus et al. 1985; Hellpointner and Gäb 1989; Sauer et al. 2001), cloudwater and rain (Kelley and Reddy 1986). The ROOH concentrations have also been determined in freshwater (Mostofa 2005; Sakugawa et al. 2006; Mostofa and Sakugawa 2009) and seawater (Sakugawa et al. 2000; Gerringa et al. 2004).

Recent studies have demonstrated that natural sunlight or solar radiation is a key factor for the generation of H_2O_2 and ROOH in the atmosphere and in natural waters. Microbial processes can produce small amounts of both H_2O_2 and ROOH in living organisms (Kim and Portis 2004; Boveris et al. 2006; Grivennikova et al. 2008; Roy and Atreja 2008) as well as in the deeper water layers (i.e., under dark conditions) of river, lake and marine environments (Komissarov 2003). H_2O_2 is found to link with the occurrence of oxygenic photosynthesis in both higher plants (Komissarov 1994, 1995, 2003) and natural waters (Mostofa et al. 2009a, b). Therefore, H_2O_2 generated mostly by solar radiation and microbial processes could simultaneously be important for the occurrence of photosynthesis in terrestrial higher plants and for the production of organic matter (ca. algae, cyanobacteria, etc.) in water environments. There is evidence that the microbial processing of vascular-plant spoils in the terrestrial soil environment can produce humic substances (fulvic and humic acids), which are then released into river, lake and marine waters (Mostofa et al. 2009a). The action of sunlight on fulvic and humic acids correspondingly produces H_2O_2 that, by favoring photosynthesis in the surface layer of rivers, lakes and oceans, would induce the generation of algae and other aquatic organisms. These organisms are then able to produce autochthonous DOM via photorespiration (or photo-assimilations) and microbial respiration or processes (Mostofa et al. 2009b; Collen et al. 1995; McCarthy et al. 1997; Rosenstock and Simon 2001; Medina-Sánchez et al. 2006; Nieto-Cid et al. 2006; Zhang et al. 2009; Fu et al. 2010). The photoinduced reactions of autochthonous DOM also yield H_2O_2 in natural waters. The production of H_2O_2 would mostly depend on the amount of DOM and on solar irradiance. Global warming with the associated increase in water temperature would enhance the production of H_2O_2, simultaneously affecting both the photodegradation of DOM and the photosynthesis (Mostofa et al. 2009b). Photosynthesis in higher plants and in natural waters can be significantly increased by rain, also because of the elevated concentration of H_2O_2 and ROOH in rainwater. Therefore, the photoinduced and microbial generation of H_2O_2 is a key factor for the occurrence of many photoinduced, biological, physical and geochemical processes. Such processes include the production of hydroxyl radical and other free radical species, photosynthesis, production of chlorophyll and of autochthonous DOM, photodegradation of DOM, CDOM and FDOM, and complexation of DOM with trace elements in natural water environments. On the other hand, production of ROOH could be a marker of microbial modification of bulk organic matter and of DOM under dark conditions. A few studies have previously been conducted to examine the photoinduced and microbial production of ROOH, their chemical nature and relationships with DOM.

Despite the universal and unique functions that H_2O_2 and ROOH may play in water ecosystems, their roles on some key biogeochemical functions in natural waters have hardly been investigated. This chapter will provide a general overview on the biogeochemical functions of H_2O_2 and ROOH, their production mechanisms and the controlling factors for formation and decay, as well as their significance and impact in natural waters.

1.1 Hydrogen Peroxide and its Biogeochemical Functions

Hydrogen peroxide (H_2O_2) is a simple chemical compound (H–O–O–H) that appears like water (H–O–H) in its chemical formula, with an additional oxygen atom. Hydrogen peroxide can undergo dismutation into water and oxygen:

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

H_2O_2 is a universal constituent of the hydrosphere and occurs in freshwater, seawater, mineral water, rain, dew, cloud, snow, air, and in all living organisms. H_2O_2 also finds effective application in experiments as well as in treatment processes. It acts as an useful indicator for a variety of photoinduced, biological and abiotic processes in the aquatic environment.

The various biogeochemical functions of H_2O_2 can be classified as follows: (i) H_2O_2 is the most stable reactive oxygen species (ROS) and is used as an indicator of photoinduced activity, because it is for instance photolytically generated through irradiation of various dissolved organic matter (DOM) components in natural waters (Cooper and Zika 1983; Zika et al. 1985a, b; Mostofa and Sakugawa 2009; Obernosterer et al. 2001; Fujiwara et al. 1993; Moore et al. 1993; Scully et al. 1996). (ii) H_2O_2 and its precursor superoxide ($O_2^{\bullet -}$) can be both oxidising and reducing agents and are, therefore, potentially important for a number of redox reactions in natural waters (Moffett and Zika 1987a, b; Petasne and Zika 1987; Moffett and Zafiriou 1990; Zafiriou 1990; Zepp et al. 1992; Zafiriou et al. 1998; Voelker et al. 2000; Jeong and Yoon 2005). (iii) H_2O_2 is a natural tracer of the surface-water mixing zone or of stratification processes in lake and marine environments (Johnson et al. 1989; Sikorsky and Zika 1993a, b; Sarthou et al. 1997; Scully and Vincent 1997). (iv) H_2O_2 is an indicator of the photodegradation of dissolved organic matter (DOM) and of organic pollutants in surface natural waters (Gao and Zepp 1998; Westerhoff et al. 1999; Southworth and Voelker 2003). (v) H_2O_2 is involved in oxidative stress in biota/living cells, because of its elevated reactivity by both oxidation and reduction (Berlett and Stadtman 1997; Paradies et al. 2000; Blokhina et al. 2003; Richard et al. 2007). (vi) H_2O_2 can be helpful in the identification of biological activity, in particular in coastal waters where higher biological activity with rapid decay of H_2O_2 is commonly observed compared to the open oceans (Fujiwara et al. 1993; Moffett and Zafiriou 1990; Cooper and Zepp 1990; Petasne and Zika 1997). (vii) H_2O_2 is a useful tracer of the vertical advection transport or the convective overturn, which is usually caused by nocturnal cooling in the upper ocean and can transport significant amounts of H_2O_2 to deep waters (Johnson et al. 1989; Sarthou et al. 1997; Scully and Vincent 1997; Yuan and Shiller 2001). (viii) H_2O_2 is thought to play an important role in the occurrence of photosynthesis in higher plants (Komissarov 1994, 1995; 2003) and in natural waters (Mostofa et al. 2009a, b), by which effect it can induce the production of autochthonous DOM in the aqueous environment. (ix) H_2O_2 can react with CO_2 under irradiation to produce various organic substances in aqueous solution (Lobanov et al. 2004), with a potentially significant role in biogeochemical processes in natural waters. (x) H_2O_2 plays an important role in controlling the physiology of plants, including the activity of some enzymes and the photophosphorylation and photorespiration rates; it is also responsible for fungitoxicity of the leaf surface (Lobanov et al. 2008). (xi) H_2O_2 is generated inside cells by peroxisomes and mitochondria; the formation of H_2O_2 is caused by the reduction of O_2 absorbed in intracellular fluid during the photorespiration (Komissarov 2003; Lobanov et al. 2008). (xii) H_2O_2 acts as an oxidant in the conversion of SO_2 to $SO_4{}^{2-}$ in rainwater, thereby contributing to the acid rain phenomenon that is a harmful threat which damages plant tissues and contributes to forest decline worldwide (Calvert et al. 1985; Sakugawa et al. 1990, 1993). (xiii) The environmental concentration of H_2O_2 is influenced by algae, which simultaneously cause its decay and induce its photoinduced production by exposure of algal suspensions to sunlight (Zepp et al. 1987). (xiv) The photoinduced generation of H_2O_2 from algal suspensions plays a key role in the oxidation of anilines; the latter are able to decrease H_2O_2 production, possibly by consuming it on the surface of algal cells (Zepp et al. 1987; Zepp and Schlotzhauer 1983). (xv) Elevated levels of H_2O_2 induce damage and cell lysis in microorganisms (Gonzalez-Flecha and Demple 1997; Weinbauer and Suttle 1999); H_2O_2 is also implicated as a cause of mortality of fecal indicator bacteria in marine sewage fields (Mitchell and Chamberlin 1975; Clark et al. 2008). (xvi) Bioelectrochemical oxidation of wastewater organic matter can effectively produce H_2O_2 on an industrial scale, with an overall 83 % efficiency that could be useful for industrial purposes (Rozendal et al. 2009). (xvii) H_2O_2 produced from DOM may contribute approximately 1–50 % of hydroxyl radical ($HO^{\bullet}$), a strong oxidizing agent, which is responsible for indirect photoinduced changes in the DOM components in natural waters (Mostofa and Sakugawa 2009; Takeda et al. 2004; Nakatani et al. 2007; Page et al. 2011).

1.2 Organic Peroxides (ROOH) and Their Biogeochemical Functions

Organic peroxides (ROOH) are organic compounds containing the peroxide functional group (–O–O–), and may be considered as derivatives of hydrogen peroxide (H–O–O–H) where one or both of the hydrogen atoms have been replaced by organic radicals. Organic peroxides can commonly be denoted as ROOH, where

R can be CH_3–, CH_3–CH_2–, etc. and H can be H or R. The organic peroxides are ubiquitously distributed in air, cloud, dew, rain, mineral water, freshwater and seawater (Sakugawa and Kaplan 1987; Lazrus et al. 1985; Hellpointner and Gäb 1989; Sauer et al. 2001; Kelley and Reddy 1986; Mostofa 2005; Sakugawa et al. 2006; Mostofa and Sakugawa 2009; Sakugawa et al. 2000; Gerringa et al. 2004).

The major ROOH compounds identified in the aquatic environments are methyl hydroperoxide (CH_3OOH), hydroxymethyl hydroperoxide ($HOCH_2OOH$), ethyl hydroperoxide (CH_3CH_2OOH), 1-hydroxyethyl hydroperoxide ($CH_3CH(OH)OOH$), 2-hydroxyethyl hydroperoxide ($CH_2(OH)CH_2OOH$), 1-hydroxypropyl hydroperoxide ($CH_3CH_2CH(OH)OOH$), 2-hydroxypropyl hydroperoxide ($CH_3CH(OH)CH_2OOH$), 3-hydroxypropyl hydroperoxide ($CH_2(OH)CH_2CH_2OOH$), and bis(hydroxymethyl) peroxide ($HOCH_2OOCH_2OH$) (Hellpointner and Gäb 1989; Hewitt and Kok 1991). The concentration levels of ROOH compounds are commonly low (~<390 nM) in natural waters, and their concentrations are also low when they are generated in photoexperiments conducted on natural waters or on aqueous solutions of standard DOM components.

The various biogeochemical functions of ROOH can be categorized as follows: (i) Production of ROOH compounds would be a marker of microbial changes in bulk organic matter or DOM under dark conditions, which are usually occurring in deeper layers of lake or seawater (Sakugawa et al. 1995, 2000; Hayase and Shinozuka 1995; Mostofa et al. 2005). (ii) ROOH compounds are readily decomposed and correspondingly generated, so that they reach a steady-state concentration in natural waters. (iii) ROOH compounds might be important transformation intermediates of DOM and may be chemically converted into stable DOM components in natural waters. (iv) The photoinduced and thermal decomposition of organic peroxides generally yields organic peroxide radicals; they may combine with other organic substances to form new compounds, or can form polymeric compounds in aqueous solution (Mageli and Kolczynski 1966; Mill et al. 1980; Kieber and Blough 1990; Faust and Allen 1992). Future research is expected to further highlight the importance of ROOH in natural waters.

1.3 Nature and Characteristics of H_2O_2 and ROOH

In natural waters, H_2O_2 shows several characteristic properties that can be listed as follows: (i) The photoinduced generation of H_2O_2 follows a regular trend of increasing concentration with increasing irradiation time, in photoexperiments conducted under a solar simulator (Fig. 1a, b). It suggests that the formation rate is higher than the transformation one. (ii) Photogenerated H_2O_2 is gradually consumed in aqueous media in the absence of solar radiation (Fig. 2a). It suggests that H_2O_2 in aqueous solution is presumably decomposed by chemical and/or enzymatic reactions. (iii) The rate of H_2O_2 photoproduction is higher in filtered than in unfiltered natural waters samples (Fig. 2a), suggesting that particulate matter may rapidly consume H_2O_2 in aqueous solution. (iv) The photoinduced generation of

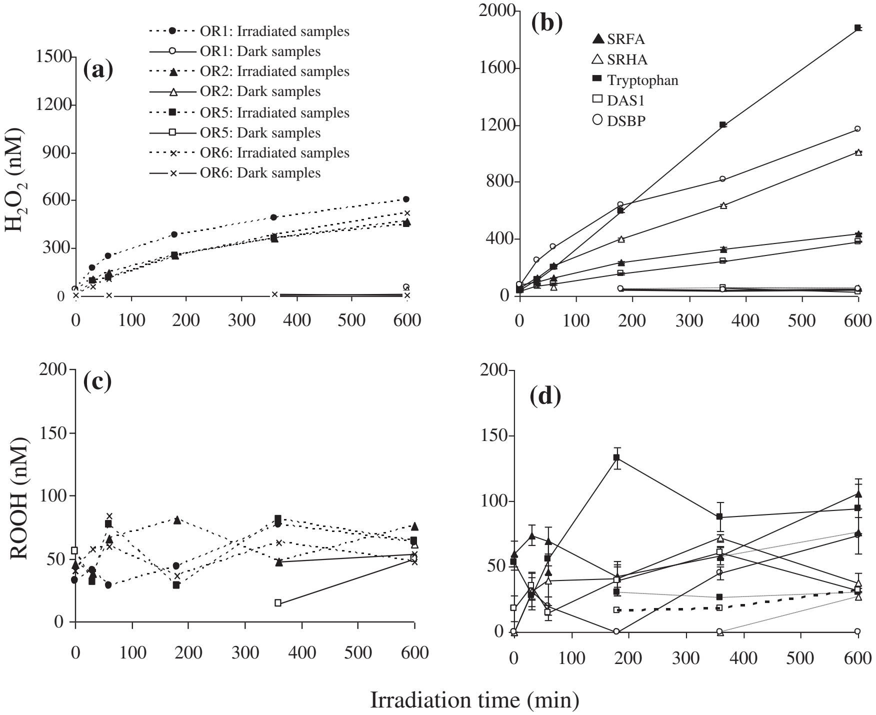


Fig. 1 Production of H_2O_2 (**a**, **b**) and ROOH (**c**, **d**) as a result of solar irradiation on the Ohta River waters (sites OR1, OR2, OR5, and OR6) and on various standard substances, respectively, in photo-experiments conducted using a solar simulator. *Data source* Mostofa and Sakugawa (2009)

H_2O_2 is highly variable in the presence of various standard organic substances in aqueous media (Fig. 1b), which suggests that the concentration of H_2O_2 depends on the nature of the DOM components. (v) The photoinduced generation of H_2O_2 increases with an increase in the contents of fulvic acid in photo-irradiated samples under a solar simulator (Fig. 3), which suggests that H_2O_2 production depends on the DOM amount. (vi) When photogenerated H_2O_2 in unfiltered river water is incubated in the dark, it is entirely decomposed in the first day of incubation and it is not produced further during the incubation period (Fig. 2b). Therefore, microbial reactions may be more effective in consuming than in producing H_2O_2 in river water.

ROOH compounds typically show the following features in natural waters: (i) The photoinduced generation of ROOH does not follow a regular trend of increasing concentration with increasing irradiation time, in photoexperiments conducted using a solar simulator; in contrast, produced ROOH is very low and fluctuates heavily without any observable trends (Fig. 1c, d). It is suggested that ROOH compounds are readily decomposed in aqueous solution. (ii) The photoinduced generation of ROOH compounds is typically higher in filtered than in

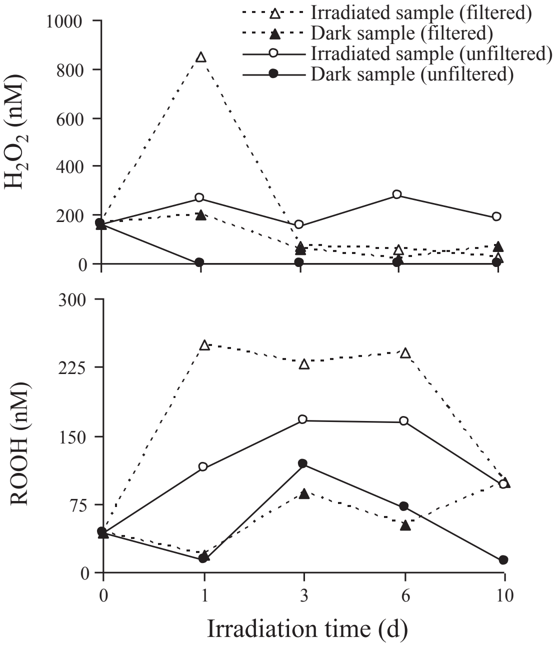


Fig. 2 Production of H_2O_2 and ROOH as a result of photoinduced and microbial incubation on filtered and unfiltered river waters. *Data source* Mostofa et al. (Manuscript in preparation)

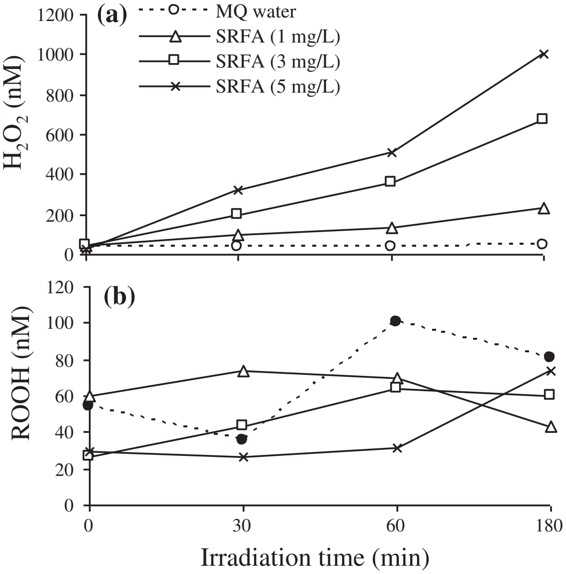


Fig. 3 Production of H_2O_2 and ROOH as a result of solar irradiation on the aqueous solutions of fulvic acid in photoexperiments conducted using a solar simulator

unfiltered samples of river water (Fig. 2b), which suggests that particulate matter (or microbes) in unfiltered river water are susceptible to rapidly degrade ROOH. (iii) ROOH compounds were frequently generated under dark incubation (which followed irradiation) in unfiltered and filtered river waters (Fig. 1b), which indicates that dark production pathways of ROOH are operational in natural waters. (iv) The photoinduced generation of ROOH compounds is typically higher for low concentration of fulvic acid (FA, 1 mg L^{-1}), and decreases with increasing FA concentration (3 and 5 mg L^{-1}, Fig. 3b). This finding suggests that the formation of ROOH compounds does not depend on DOM concentration which, on the contrary, might favor ROOH decomposition. These results indicate that ROOH compounds are quickly decomposed, which might be due to their inherently unstable chemical nature. ROOH compounds are sensitive to acid, alkali, redox and light in aqueous solution (Mostofa and Sakugawa 2009).

1.4 Steady State Concentration and Half-Life of H_2O_2 and ROOH

The concentration levels of H_2O_2 and ROOH are often measured in natural waters or in irradiated aqueous solutions, and they are often in a steady state. Steady-state concentrations of H_2O_2 and ROOH compounds in natural waters are mostly dependent on three major phenomena. First, enzymes (catalase, peroxidase and superoxide dismutase) in microbes, phytoplankton and algae present in natural waters are active agents for the rapid decay of peroxides (Mostofa 2005; Fujiwara et al. 1993; Moffett and Zafiriou 1990; Petasne and Zika 1997). These processes limit the occurrence of organic peroxides in natural waters. Second, the incident solar irradiance may be involved into the production of peroxides in waters (Cooper and Zika 1983; Moore et al. 1993; Baxter and Carey 1983; Mostofa and Sakugawa 2003). Third, the organic peroxides may take part to the generation of free radicals ($HO^{\bullet}$ or $RO^{\bullet}$) by direct photolysis or photo-Fenton reactions in natural waters (Zepp et al. 1992; Jeong and Yoon 2005; Southworth and Voelker 2003; Voelker et al. 1997). The free radicals then cause the photodegradation of DOM (Gao and Zepp 1998; Brezonik and Fulkerson-Brekken 1998; Goldstone et al. 2002). A general scheme for the steady-state concentration of H_2O_2 and ROOH in aqueous media can be expressed as follows (Fig. 4):

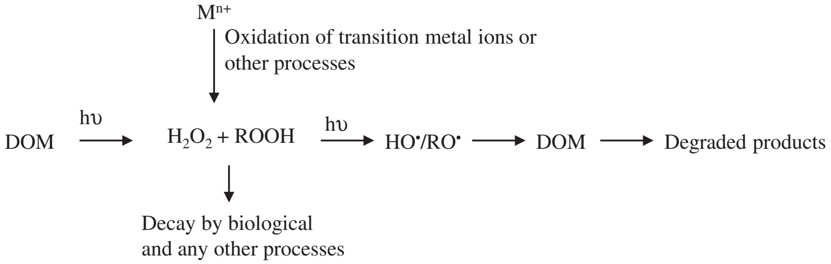


Fig. 4 A schematic diagram of steady state concentration of photoinduced generation of H_2O_2 and ROOH from DOM in natural waters

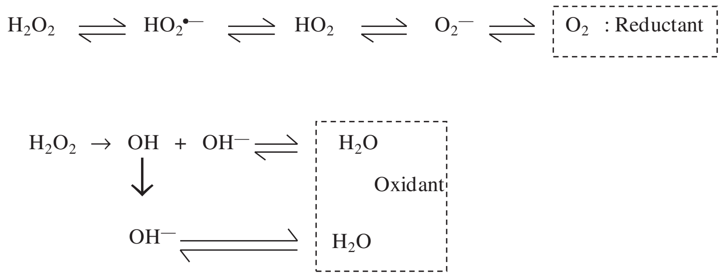


Fig. 5 Electron transfer and proton transfer reactions in the reduction of O_2 from H_2O_2 to H_2O, demonstrating the intermediates involved *Data source* Moffett and Zafiriou (1990)

More simply, "Peroxides$_{SSC}$ = produced peroxides—(decay by microbles and any other processes + contribution to DOM photo degradation)", where SSC = Steady-State Concentration. Therefore, enzymes might be an important factor in regulating the occurrence of H_2O_2 and ROOH compounds in natural waters.

The decay rates of H_2O_2 and ROOH, expressed as half-life times ($t_{1/2}$), are hours to days depending on the presence of enzymes in natural waters (Harvey 1925; Mostofa 2005; Richard et al. 2007; Cooper and Zepp 1990; Cooper and Lean 1992). For example, the half-life of H_2O_2 is gradually increased from unfiltered to filtered lake waters, from 4.4 h for unfiltered water to 4.7 h for 64 μm filtered water (zooplakton removed), 6.4 h for 12 μm filtered water (large algae removed), 19.1 h for 1.0 μm filtered water (small algae removed), and 58.7 h for 0.2 μm filtered water (bacteria removed) (Cooper and Lean 1992). Similarly, the half-lives are approximately 3 h or less for highly biologically productive coastal waters or freshwaters, and hundreds of hours for oligotrophic unfiltered waters (Mostofa 2005; Fujiwara et al. 1993; Moore et al. 1993; Richard et al. 2007).

1.5 H_2O_2 Acts as a Reductant and Oxidant-REDOX

H_2O_2 acts as a reductant and oxidant (REDOX) in many reactions occurring in natural waters (Moffett and Zika 1987a; b; Moffett and Zafiriou 1990; Zepp et al. 1992; Jeong and Yoon 2005). When H_2O_2 acts as a reductant, O from H_2O_2 is transformed into O_2. When H_2O_2 acts as an oxidant, O from H_2O_2 is converted into H_2O (Moffett and Zafiriou 1990). The chain reactions of H_2O_2 as reductant and oxidant are schematically depicted below (Fig. 5) (Moffett and Zafiriou 1990).

1.6 Concentration Levels of H_2O_2 and ROOH Compounds in Natural Water

The levels of H_2O_2 and ROOH are greatly variable for a variety of natural waters (Table 1) (van Baalen and Marler 1966; Sinel'nikov 1971; Sinel'nikov and Demina 1974; Cooper and Zika 1983; Helz and Kieber 1985; Lazrus et al. 1985;

Zika et al. 1985a, b; Moffett and Zika 1987a; Palenic and Morel 1988; Cooper and Lean 1989; Johnson et al. 1989; Sakugawa et al. 2000, 2006; Mostofa and Sakugawa 2009; Gerringa et al. 2004; Obernosterer et al. 2001; Fujiwara et al. 1993; Moore et al. 1993; Sikorsky and Zika 1993a, b; Sarthou et al. 1997; Richard et al. 2007; Petasne and Zika 1997; Lobanov et al. 2008; Sakugawa et al. 1995; Cooper and Lean 1992; Moffett and Zika 1983; Szymczak and Waite 1991; Resing et al. 1993; Miller and Kester 1994; Amouroux and Donard 1995; Fujiwara et al. 1995; Kieber and Heltz 1995; Herut et al. 1998; Cooper et al. 2000; Akane et al. 2004, 2005; Avery et al. 2005; Croot et al. 2005; Miller et al. 2005; O'Sullivan et al. 2005; Olasehinde et al. 2008; Boehm et al. 2009; Clark et al. 2010a, b; Rusak et al. 2010). H_2O_2 concentrations in surface freshwater are 6–68 nM in upstream rivers and 9–501 nM in rivers in Japan, 1300–3200 nM in rivers and 700–1300 nM in reservoirs in Russia, 88–320 nM in rivers in the USA, and 10–1300 nM in several lakes in USA and Canada (Table 1). H_2O_2 concentrations in surface seawater are 11–440 nM in estuaries in USA and Japan, 0–496 nM in coastal Bay and coastal seawaters in Japan, 25–360 nM in Amazon and Orinoco River plume, 3–1700 nM in Chesapeake Bay, 22–256 nM in Bay of Biscay (Atlantic Ocean), 124–275 nM in Biscayne Bay and Gulf Stream, <200 nM in Port Aransas seawater, <150 nM in Florida west coast, 8–50 nM in Peru upwelling area (Coastal and offshore), 8–100 nM in the Mediterranean (Israeli coastal waters) and the Red Sea (Gulf of Aqaba), 20–80 nM in Baltic Sea (German Coastal waters), 15–110 nM in Great Barrier Reef seawater (Australia), 120–280 nM in Gulf of Mexico, 50–420 nM in Caribbean Sea, 95–175 nM in Sargasso Sea and Western Mediterranean, 16–220 nM in Atlantic Ocean, and 5–25 nM in Southern Ocean in Antarctic regions (Table 1). H_2O_2 concentrations are remarkably higher in Russian rivers and reservoir (700–3200 nM) than in other rivers (6–501 nM) and lakes (10–1300 nM) in the freshwater environments. High concentrations (0–420 nM) are commonly observed in estuaries, bays and coastal seawaters, and an exceptionally high concentration (1700 nM) was detected in Cheasapeake Bay. H_2O_2 concentrations are apparently lowest in the Southern Ocean, Antactic (5–25 nM). On the other hand, the occurrence of ROOH compounds is not often studied in natural waters (Table 1). ROOH concentrations are 9–73 nM in upstreams, 0–200 nM in rivers, 32–389 nM in coastal seawaters, and 1–6 nM in the eastern Atlantic Ocean (Table 1).

1.7 Production Rates and Sources of H_2O_2

Production rates of H_2O_2 are greatly variable among upstreams (245–903 nM h^{-1}), groundwater (0–4800 nM h^{-1}), rivers (390–7400 nM h^{-1}), lakes (81–2400 nM h^{-1}), coastal waters (4536–35640 nM h^{-1}), and seawaters (0–161 nM h^{-1}) (Table 2) (Mostofa and Sakugawa 2009; Obernosterer et al. 2001; Scully et al. 1996; Richard et al. 2007; Miller and Kester 1994; Cooper et al. 1988; Moffett and Zafiriou 1993; Yocis et al. 2000; Clark et al. 2009; Mostofa KMG and Sakugawa H, unpublished;

Table 1 Hydrogen peroxide (H_2O_2) and organic peroxides (ROOH) concentrations reported in natural waters (rivers, lakes, seawaters), and rainwater

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2 (nM)	ROOH (nM)	Solar intensity (MJm^{-2})	DOC (µM C)	References
Rivers							
Upstream waters (3 sites), Hiroshima Prefecture	Japan	Monthly (12 months)	6.0–68.0	9.0–73.0	0.50–2.88	43–146	Mostofa and Sakugawa (2009)
Ohta Rivers (2 sites), Hiroshima Prefecture	Japan	Monthly (12 months)	38–171	1.0–80.0	0.24–3.19	40–164	Mostofa and Sakugawa (2009)
Kurose Rivers (2 sites), Hiroshima Prefecture	Japan	Monthly (12 months)	9–213	0.0–67.0	0.48–3.13	130–383	Mostofa and Sakugawa (2009)
Upstream waters, Hiroshima Prefecture	Japan	Diel (August)	9.0–43.0	–	0–2.74	118–239	Mostofa and Sakugawa (2009)
Kurose downstream waters, Hiroshima Prefecture	Japan	Diel (September)	4.0–69.0	–	0–2.84	326–384	Mostofa and Sakugawa (2009)
Kurose Rivers (2 sites), Hiroshima Prefecture	Japan	Summer (August)	345–501	74–78	2.70	299–329	Mostofa and Sakugawa (2009)
Ohta River, Hiroshima Prefecture	Japan	December and June	66–107	33–200	–	–	Sakugawa et al. (2006)
Stream, water of Leith	New Zealand	October	15–491	–	–	–	Richard et al. (2007)
Stream, water of Leith	New Zealand	September 2003–March 2006	688 ± 8.9–72 ± 2.7	–	–	–	Rusak et al. (2010)
Ashida River, Fukuyama	Japan	December and June	91–169	80–178	–	–	Sakugawa et al. (2006)
Fuji River, Onomichi	Japan	December and June	98–301	87–125	–	–	Sakugawa et al. (2006)
Nuta River, Mihara	Japan	December and June	78–249	78–105	–	–	Sakugawa et al. (2006)
Gohno River, Miyoshi	Japan	December and June	17–101	55–69	–	–	Sakugawa et al. (2006)
Saijo River, Shoubara	Japan	December	72	65	–	–	Sakugawa et al. (2006)
Volga River	Russia	Surface water	1300–3200	–	–	–	Sinel'nikov (1971)
Chechessee River, S·C.	USA	Surface water	88	–	–	183	Cooper and Zika (1983)
Combahee River, S.C.	USA	Surface water	160	–	–	1225	Cooper and Zika (1983)

(continued)

Table 1 (continued)

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2	ROOH	Solar intensity (MJm^{-2})	DOC (µM C)	References
			(nM)				
Newman River, Fla.	USA	Surface water	170	–	–	1392	Cooper and Zika (1983)
Peacock River, Ga.	USA	Surface water	320	–	–	1483	Cooper and Zika (1983)
Tamiami Canal, Fla.	USA	Surface water	90	–	–	1033	Cooper and Zika (1983)
Lakes and reservoir							
Jacks Lake, Ontario	Canada	Surface water	10–800	–	–	–	Cooper and Lean (1992)
Lake Erie	USA	Surface water	50–200	–	–	–	Cooper and Lean (1992)
Lake Ontario	USA	Surface water	100	–	–	–	Cooper and Lean (1992)
Jacks Lake, Ontario	44°N	Diel	10–800	–	–		Cooper and Lean (1989)
VH Pond, Miami, Fla.	USA	Surface water	140	–	–	–	Cooper and Zika (1983)
Reservoir	Russia	Surface water	700–1300	–	–	–	Sinel'nikov and Demina (1974)
Estuaries							
Patuxent Estuary	38–39°N	Diel (Feb: 14:30–10:00)	25–61	–	–	–	Kieber and Heltz (1995)
Patuxent Estuary	38–39°N	Diel (Aug: 09:30–07:30)	177–350	–	–	–	Kieber and Heltz (1995)
Patuxent Estuary	38–39°N	Diel (Sept: 11:40–09:00)	11–194	–	–	–	Kieber and Heltz (1995)
Patuxent Estuary	38–39°N	Diel (Nov: 09:00–08:30)	39–95	–	–	–	Kieber and Heltz (1995)
Estuary of Ohta River, Japan	34°N	Summer	<400	–	–	–	Fujiwara et al. (1995)
Estuary of Ohta River, Japan	34°N	Winter	60–140	–	–	–	Fujiwara et al. (1995)
Coastal seawater off Rhode Island	USA	Surface waters	60–280	–	–	–	Miller et al. (2005)
Estuarine, Chesapeake Bay	USA	Surface waters	440	–	–	–	O'Sullivan et al. (2005)
Coastal waters	USA	Surface waters	110–260	–	–	–	Cooper et al. (2000)

(continued)

Table 1 (continued)

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2	ROOH	Solar intensity (MJm^{-2})	DOC (μM C)	References
			(nM)				
Gironde estuary, France	France	Surface waters	22–256	–	–	–	Amouroux and Donard (1995)
Sea beaches, southern California	USA	Surf zone	49–175	–	–	–	Clark et al. (2010)
Sea Beach, southern California (n = 4)	USA	Diel	25–200	–	–	–	Clark et al. (2010)
Sea beach, Santa Catalina Island	USA	Surface waters	93–329	–	–	–	Boehm et al. (2009)
Seawaters							
Hiroshima Bay, Japan	34°N	Surface water	143–348	–	–	–	Olasehinde et al. (2008)
Hiroshima Bay, Japan	34°N	Surface water (0–20 m)	39–496	–	–	78–212	Akane et al. (2004)
Hiroshima Bay, Japan	34°N	Diel and surface water (5:00–19:00)	143–448	–	–	–	Akane et al. (2004)
Hiroshima Bay, Japan	34°N	Diel and surface water (20:00–4:00)	85–259	–	–	–	Akane et al. (2004)
Hiroshima Bay, Japan	34°N	Diel and surface water (20:00–4:00)	0–195	32–389	–	100–150	Sakugawa et al. (2000)
Iyo-Nada Bay, Japan	33°N	Diel and surface water (20:00–4:00)	7–146	38–296			Sakugawa et al. (2000)
Seto Inland Sea, Japan	33°N	Diel and surface water (20:00–4:00)	40–191	–	–	–	Sakugawa et al. (1995)
Tokyo Bay	35°N	Diel and surface water	20–207	50–130	–	–	Sakugawa et al. (1995)
Sagami Bay	35°N	Diel and surface water	40–80	40–90	–	–	Sakugawa et al. (1995)
Seto Inland Sea, Japan	34°N	Surface water	60–400	–	–	–	Fujiwara et al. (1993)
Hiroshima Bay, Japan	34°N	Surface water (day time)	143–448				Fujiwara et al. (1993)
Hiroshima Bay, Japan	34°N	Surface water (night time)	85–259				Fujiwara et al. (1993)

(continued)

Table 1 (continued)

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2	ROOH	Solar intensity (MJm^{-2})	DOC (μM C)	References
			(nM)				
Taira Bay, Japan	26°N	Surface (diel, red-soil polluted)	40–160	–	–	73–118	Arakaki et al. (2005)
Sesoko Island Bay, Japan	26°N	Surface (diel, red-soil polluted)	30–110	–	–	70–118	Arakaki et al. (2005)
Amazon plume	10°S–40°N	Surface water	25–165	–	–	–	Yuan and Shiller (2001)
Bay of Biscay, France	France	Surface waters	138–186	–	–	–	Amouroux and Donard (1995)
Grizzly Bay, California	USA	Surface waters	37	–	–	–	O'Sullivan et al. (2005)
Plume of Orinoco River	9–11°N	Surface water (fall and spring)	~75–360	–	–	–	Sikorsky and Zika (1993)
Biscayne Bay & Gulf Stream	9–11°N	Surface (late afternoon)	124–275	–	–	–	Petasne and Zika (1997)
Peru upwelling area (Coastal and offshore)	9–11°N	Surface (late afternoon)	8.0–50.0	–	–	–	Zika et al. (1985b)
Chesapeake Bay	9–11°N	Surface (late afternoon)	3–1700	–	–	–	Helz and Kieber (1985)
Marine bathing water, Southern California	USA	Surf zone waters (noon)	49–175				Clark et al. (2010a)
Marine bathing water, Southern California	USA	Diel	20–200	–	–	–	Clark et al. (2010b)
Florida west coast	25°N	Surface water (April)	<150	–	–	–	Moffett and Zika (1987a)
Port Aransas seawater	USA	Surface water	<200	–	–	–	van Baalen and Marler (1966)
Mediterian, Israeli coastal waters	32–33°N	Diel	10.0–80.0	–	–	–	Herut et al. (1998)
Red Sea, Gulf of Aqaba	29°N	Diel	8–100	–	–	–	Herut et al. (1998)
Baltic Sea, German coastal waters	54°N	Surface water	20–80	–	–	–	Herut et al. (1998)

(continued)

Table 1 (continued)

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2	ROOH	Solar intensity (MJm^{-2})	DOC (μM C)	References
			(nM)				
Bay of Biscay, Atlantic Ocean	France	Surface water (May)	24–256	–	–	–	Amouroux and Donard (1995)
Bay of Biscay, Atlantic Ocean	France	Surface water (December)	22–69	–	–	–	Amouroux and Donard (1995)
Great Barrier Reef seawater	Australia	Surface water (December)	15–110	–	–	–	Szymczak and Waite (1991)
Gulf of Mexico	22–30°N	Surface water	150–197	–	–	–	van Baalen and Marler (1966)
Gulf of Mexico	22–30°N	Surface water	120–140	–	–	–	Moffett and Zika (1983)
Gulf of Mexico	22–30°N	Surface water	180–280	–	–	–	Zika et al. (1985)
Caribbean Sea	10°N	Surface water	95–420	–	–	–	Moore et al. (1993)
Eastern Caribbean Sea	10°N	Near surface	60–120	–	–	–	Moore et al. (1993)
Eastern Caribbean Sea	15–19°N	Surface water (fall & spring)	~75–150	–	–	–	Sikorsky and Zika (1993)
Eastern Caribbean Sea	12–15°N	Surface water (fall & spring)	~50–180	–	–	–	Sikorsky and Zika (1993)
Sargasso Sea	32°N	Surface water (fall & spring)	95–175	–	–	–	Miller and Kester (1994)
Saragasso Sea	32°N	Surface water (June)	<150	–	–	–	Palenic and Morel (1988)
Western Mediterranean	36–38°N	Surface water (May)	100–140	–	–	–	Johnson et al. (1989)
Subtropical Atlantic Ocean	12–34°N	Surface water	75–220	–	–	77–91 (50 m)	Obernosterer et al. (2001)
Subtropical Atlantic Ocean	12–34°N	Deeper water	5.0–10.0	–	–	57–71 (150 m)	Obernosterer et al. (2001)

(continued)

Table 1 (continued)

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2	ROOH	Solar intensity (MJm^{-2})	DOC (μM C)	References
			(nM)				
South and Tropical Atlantic	10°S–40°N	Surface water	16–68	–	–	70–110	Yuan and Shiller (2001)
Atlantic Ocean	10–20°N	Surface water	37–48	–	–	–	Yuan and Shiller (2001)
Eastern Atlantic Ocean	–	Surface water	20–80	1.0–6.0	–	–	Gerringa et al. (2004)
Lagrangian, Atlantic Ocean	10°S–40°N	Diel	23–55	–	–	70–110	Yuan and Shiller (2001)
Underway, Atlantic Ocean	10°S–40°N	Diel	27–47	–	–	70–111	Yuan and Shiller (2001)
Bermuda Atlantic Time Series Station	Bermuda	Diel (6:00–14:00)	25–84	–	–	–	Avery et al. (2005)
Southern Ocean: Coasta & Cintinental Shelf Zone	61–70°N	Surface water	13–20	–	–	–	Sarthou et al. (1997)
Southern Ocean: Seasonal Ice Zone	61°N	Surface water	7.0–11.0	–	–	–	Sarthou et al. (1997)
Southern Ocean: Permanently Open Ocean Zone	55°N	Surface water	7.0–10.0	–	–	–	Sarthou et al. (1997)
Southern Ocean: Polar Front Zone	48–57°N	Surface water	~5	–	–	–	Sarthou et al. (1997)
LTER-6000, transect, Antarctic	64°N	Surface water	12.0–21.0	–	–	–	Resing et al. (1993)
Paradise Harbor, Antarctic	Antarctic	Surface water	8.5–25.0	–	–	–	[996]
Southern Ocean	48°N	Surface water (20 m)	18–25	–	–	–	Croot et al. (2005)
Rainwaters							
Rainwater, Freising/Munich	Germany	Diel (March)	2300–8600	400–1100	–	–	Hellpointner and Gäb (1989)
Rainwater, Freising/Munich	Germany	Diel (May)	9000–110600	1400–1600	–	–	Hellpointner and Gäb (1989)
Rainwater, Central Europe	Europe	Summer	500–71000	–	–	–	Sakugawa et al. (1990)
Rainwater, Central Europe	Europe	Winter	10–200	–	–	–	Sakugawa et al. (1990)

(continued)

Table 1 (continued)

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2	ROOH	Solar intensity (MJm^{-2})	DOC (µM C)	References
			(nM)				
Rainwater, Dortmund, W. Germany	Germany	Summer	700–65000	–	–	–	Sakugawa et al. (1990)
Rainwater, Dortmund, W. Germany	Germany	Winter	0– 8500	–	–	–	Sakugawa et al. (1990)
Rainwater, The Netherlands	Netherland	–	<8200	–	–	–	Sakugawa et al. (1990)
Rainwater, Salvador area, Bahia	Brazil	March–April	17000–199000	–	–	–	Sakugawa et al. (1990)
Rainwater, Research Triangle Park, NC	USA	Summer	<5800	–	–	–	Sakugawa et al. (1990)
Rainwater, Research Triangle Park, NC	USA	Winter	60–240	–	–	–	Sakugawa et al. (1990)
Rainwater, Claremont, Los Angeles Basin	USA	–	30–46800	–	–	–	Sakugawa et al. (1990)
Rainwater, Southern Florida	USA	–	10000–70000	–	–	–	Sakugawa et al. (1990)
Rainwater, Eastern U.S.	USA	–	100–63000	–	–	–	Sakugawa et al. (1990)
Rainwater, Long Island, NY	USA	April–June	<120000	–	–	–	Sakugawa et al. (1990)
Rainwater, Summit of Whitetop Mountain, VA	USA	Spring-fall	40–39800	–	–	–	Sakugawa et al. (1990)
Rainwater, Westwood, Los Angeles Basin	USA	–	100–95000	–	–	–	Sakugawa et al. (1990)
Rainwater, Philadelphia	USA	Spring	500–5000	–	–	–	Sakugawa et al. (1990)
Rainwater, Northwestern New York state	USA	Winter	100–50000	–	–	–	Sakugawa et al. (1990)

(continued)

Table 1 (continued)

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2	ROOH	Solar intensity (MJm^{-2})	DOC (µM C)	References
			(nM)				
Rainwater, New York	USA	No indication	2900–28800	–	–	–	Lazrus et al. (1985)
Rainwater, Niwot Ridge, Colorado	USA	10:30–17:00	16100–52500	1780–5820	–	–	Hewitt and Kok (1991)
Rainwater, Niwot Ridge, Colorado	USA	8:00–10:00	300–1300	60–80	–	–	Hewitt and Kok (1991)
Rainwater, Westwood, Los Angeles	USA	Summer	43000 (mean, n = 9)	<6500	–	<1908	Sakugawa et al. (1993)
Rainwater, Westwood, Los Angeles	USA	Winter	4300 (mean, n = 53)	–	–	17–758	Sakugawa et al. (1993)
Rainwater, Wilmington, NC	USA	Aug–Sept: 11:00–3.30	1200–11600			5–238	Miller et al. (2008)
Rainwater, North Bay, Ontario	Canada	Jan–Feb	500–5000	–	–	–	Sakugawa et al. (1990)
Rainwater, Jacks Lake, Ontario	44°N	Diurnal (no lightening)	4400–29600				Cooper and Lean (1989)
Rainwater, Jacks Lake, Ontario	44°N	One sample (lightening)	34000				Cooper and Lean (1989)
Jacks Lake	Canada	–	1300–34000	–	–	–	Cooper and Lean (1992)
Rainwater, Kanagawa	Japan	–	10300–25300	–	–	–	Sakugawa et al. (1990)
Rainwater, Tokyo	Japan	–	200–31300	–	–	–	Sakugawa et al. (1990)
Rainwater, Higashi-Hiroshima	Japan	Monthly (Jul–Jan)	39–56400	–	–	–	Sakugawa et al. (2006)
Rainwater, Mt. Gokurakuji (site 1)	Japan	Monthly (Aug–Nov)	24–1050	–	–	–	Sakugawa et al. (2006)

(continued)

Table 1 (continued)

Sampling sites/Regions	Latitude/ Country	Sample type /Time/Period	H_2O_2	ROOH	Solar intensity (MJm^{-2})	DOC (μM C)	References
			(nM)				
Rainwater, Mt. Gokurakuji (site 3)	Japan	Monthly (Aug–Nov)	189–10100	–	–	–	Sakugawa et al. (2006)
Rainwater, South and Central Atlantic Ocean	10–11°S	8:30–12:30	3500–9200	–	–	–	Yuan and Shiller (2000)
Rainwater, South and Central Atlantic Ocean	3.4°N	16:30–17:10	46200–49300	–	–	–	Yuan and Shiller (2000)
Rainwater, South and Central Atlantic Ocean	4.7°N	23:00– 0.30	14000–14200	–	–	–	Yuan and Shiller (2000)
Rainwater, South and Central Atlantic Ocean	6.79°N	15:30–16:15	6000–12400	–	–	–	Yuan and Shiller (2000)
Rainwater, South and Central Atlantic Ocean	8°N	14:30–23:00	46000–70900	–	–	–	Yuan and Shiller (2000)
Rainwater, Gulf of Mexico	Marine areas	–	11400–82000	–	–	–	Cooper and Lean (1992)
Rainwater, Western Atlantic	Marine areas	–	8400–20600	–	–	–	Cooper and Lean (1992)
Rainwater, Florida Keys	Marine areas	–	24300–31900	–	–	–	Cooper and Lean (1992)

Vermilyea et al. 2010).Variations in production rates of H_2O_2 are likely to be caused by the amount and the molecular nature of DOM (Table 2). This fact can be easily understood from a significant difference in the production rates of H_2O_2 estimated in the presence of various standard organic substances (Table 2). The major source of H_2O_2 in river water is fulvic acid, which contributed 23–61 % in upstream rivers, 28–63 % in polluted Kurose waters, and 67–70 % in clean Ohta river waters (Mostofa and Sakugawa 2009). Tryptophan-like substances are a minor source of H_2O_2 (~1 %) in all river waters. The contribution of the fluorescent whitening agents (DAS + DSBP) to H_2O_2 production was minor (2 %), although they were dominant FDOM components in the downstream waters of the Kurose river. The 4-biphenyl carboxaldehyde (4BCA), one photoproduct of DSBP, showed that the percent contribution to total H_2O_2 production was 2.0–5.0 % in the downstream waters of the Kurose river (Mostofa and Sakugawa 2009). Unknown sources of H_2O_2 (other than fulvic acid-like and tryptophan-like substances or FWAs) accounted for 34–68 % of H_2O_2 in the upstream waters of the Kurose, 35–67 % in the upstream areas of the Ohta, 14–15 % in the downstream sites of the Ohta, and 51–70 % in the downstream sites of the Kurose (Mostofa and Sakugawa 2009). The unknown sources of H_2O_2 may be other fluorescent and non-fluorescent substances (Kramer et al. 1996), which can originate from forest ecosystems in the upstream regions of a river and from various anthropogenic sources affecting the downstream regions. The production rate of H_2O_2 for Suwannee River Fulvic Acid (SRFA) is relatively low (344 nM h^{-1}) compared to DSBP (1073 nM h^{-1}), tryptophan (648 nM h^{-1}), and Suwannee River Humic Acid, SRHA, (644 nM h^{-1}, Table 2). However, fulvic acids may be important H_2O_2 sources due to their significant occurrence (30–80 % of total DOM) in the aquatic environments (Mostofa et al. 2009; Malcolm 1985; Peuravuori and Pihlaja 1999).

1.8 Diurnal Cycle or Diel Variation of H_2O_2 and its Controlling Factors in Natural Waters

A diurnal cycle is a regular and ubiquitous phenomenon of H_2O_2 production and decay. H_2O_2 concentration in natural waters gradually increases as incident solar radiation increases during the period from dawn to noon. The solar radiation reaches a peak at noon time and then the concentration gradually decreases with the decrease of sunlight intensity (Fig. 6). The amplitude of the H_2O_2 diurnal cycle (highest concentration at noon time minus concentration during the period before sunrise) was 35 nM in upstream and 65 nM in Kurose River (Fig. 6) (Mostofa and Sakugawa 2009), 790 nM in Jacks Lake (Cooper and Lean 1989), 36 nM (February), 173 nM (August), 183 nM (September), and 56 nM (November) in Patuxent Estuary (Kieber and Heltz 1995), 187 nM in Seto Inland Sea (Sakugawa et al. 1995), 305 nM in Hiroshima Bay (Akane et al. 2004), 120 nM in Taira Bay and 80 nM in Sesoko Island Bay (Arakaki et al. 2005), 70 nM in Mediterranean (Israeli) coastal waters, 92 nM in Red Sea in Gulf

Table 2 Production rates of H_2O_2 reported from natural waters, and standard fluorescent dissolved organic substances

Type of samples/substances	Source of light/ wavelength (nm)	Production rate of		References
		H_2O_2 (nM h^{-1})	DOC (µM C)	
Rivers				
Upstream waters (Ohta River, OR1 & OR2: Aug), Japan	Xe lamp[a]	400–768	88–101	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Upstream waters (Kurose River, KR1: May), Japan	Xe lamp[a]	342	111	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Upstream waters (Kurose River, KR1: Aug), Japan	Xe lamp[a]	903	152	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Upstream waters (Kurose River, KR2: May), Japan	Xe lamp[a]	723	134	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Upstream waters (Kurose River, KR2: Aug), Japan	Xe lamp[a]	761	106	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Surface stream, Water of Leith, New Zealand	Full solar spectrum	245–444	–	Richard et al. (2007)
Ohta River (midstreams waters, OR3 & OR4: Aug), Japan	Xe lamp[a]	390–485	112–116	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Ohta River (downstream waters, OR5 & OR6: Aug), Japan	Xe lamp[a]	427–468	115–124	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)

(continued)

Table 2 (continued)

Type of samples/substances	Source of light/ wavelength (nm)	Production rate of		References
		H_2O_2 (nM h^{-1})	DOC (μM C)	
Kurose River (Izumi): polluted site (KR5: May), Japan	Xe lamp[a]	1931	505	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Kurose River (Izumi): polluted site (KR5: Aug), Japan	Xe lamp[a]	1401	310	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Kurose River (Hinotsume): polluted site (KR6: May), Japan	Xe lamp[a]	1429	445	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Kurose River (Hinotsume) polluted site (KR6: Aug), Japan	Xe lamp[a]	1363	276	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Kurose River (Machida): downstream (KR7: May), japan	Xe lamp[a]	545	368	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Kurose River (Shinkeiji): downstream (KR8: May), Japan	Xe lamp[a]	739	392	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Kurose River (Shinkeiji): downstream (KR8: Aug), Japan	Xe lamp[a]	623	299	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Eastern Caribbean, Orinoco River	Xe lamp[a]	33		Moffett and Zafiriou (1993)
Chechesse River, SC (USA)	Sunlight	830	183	Cooper et al. (1988)
VH Pond, Miami, FL	Sunlight	1600	575	Cooper et al. (1988)
VH Pond, Miami, FL (unfiltered)	Sunlight	1400	575	Cooper et al. (1988)
Tamiami Canal, Miami, FL	Sunlight	3800	1033	Cooper et al. (1988)
Tamiami Canal, Miami, FL (unfiltered)	Sunlight	2700	1033	Cooper et al. (1988)

(continued)

Table 2 (continued)

Type of samples/substances	Source of light/ wavelength (nm)	Production rate of		References
		H_2O_2 (nM h^{-1})	DOC (μM C)	
Combahee River, SC	Sunlight	4400	1225	Cooper et al. (1988)
Peacock River, GA	Sunlight	7400	1483	Cooper et al. (1988)
Ground water				
Tucson, Ariz	Sunlight	0	18	Cooper et al. (1988)
Spring water, Coudersport, PA	Sunlight	270	44	Cooper et al. (1988)
Spring water, Sodus, NY	Sunlight	0	78	Cooper et al. (1988)
Well 18, Miami, FL	Sunlight	590	242	Cooper et al. (1988)
Preston Well 5, Miami, FL	Sunlight	1600	517	Cooper et al. (1988)
Well 23, Miami, FL	Sunlight	1700	858	Cooper et al. (1988)
Northwest Well 5, Miami, FL	Sunlight	4800	1100	Cooper et al. (1988)
Northwest Well 1, Miami, FL	Sunlight	4600	1467	Cooper et al. (1988)
Lake				
Amituk (75°N)	Quartz Halogen lamp	81	133	Scully et al. (1996)
Small (74°N)	Quartz Halogen lamp	413	167	Scully et al. (1996)
Char (74°N)	Quartz Halogen lamp	96	117	Scully et al. (1996)
Muretta (74°N)	Quartz Halogen lamp	249	167	Scully et al. (1996)
Drinking Water (55°N)	Quartz Halogen lamp	587	858	Scully et al. (1996)
West Twin (52°N)	Quartz Halogen lamp	451	342	Scully et al. (1996)
Boulder (45°N)	Quartz Halogen lamp	925	525	Scully et al. (1996)
Bat Bog (45°N)	Quartz Halogen lamp	–	700	Scully et al. (1996)
Spruce Bog (45°N)	Quartz Halogen lamp	–	1125	Scully et al. (1996)
Wolf Howl Bog (45°N)	Quartz Halogen lamp	–	1117	Scully et al. (1996)
Cromwell (45°N)	Quartz Halogen lamp	2120	650	Scully et al. (1996)
Croche (45°N)	Quartz Halogen lamp	1222	558	Scully et al. (1996)
Deer Fen (45°N)	Quartz Halogen lamp	–	1667	Scully et al. (1996)

(continued)

Table 2 (continued)

Type of samples/substances	Source of light/ wavelength (nm)	Production rate of		References
		H_2O_2 (nM h^{-1})	DOC (μM C)	
Vernon (45°N)	Quartz Halogen lamp	1322	408	Scully et al. (1996)
Dawson Bog (44°N)	Quartz Halogen lamp	1620	633	Scully et al. (1996)
Sharpes Bay (44°N)	Quartz Halogen lamp	695	492	Scully et al. (1996)
Brookes Bay (44°N)	Quartz Halogen lamp	1315	633	Scully et al. (1996)
Bay of Quinte (44°N)	Quartz Halogen lamp	1473	633	Scully et al. (1996)
Lake Ontario 401 (43°N)	Quartz Halogen lamp	193	242	Scully et al. (1996)
Lake Ontario 403 (43°N)	Quartz Halogen lamp	161	292	Scully et al. (1996)
Lake Ontario 007 (43°N)	Quartz Halogen lamp	175	233	Scully et al. (1996)
Lake Ontario 206 (43°N)	Quartz Halogen lamp	234	225	Scully et al. (1996)
Hamilton Harbor (43°N)	Quartz Halogen lamp	790	325	Scully et al. (1996)
Newnans Lake, Gainesville, FL	Sunlight	2400	967	Cooper et al. (1988)
Coastal waters				
Source waters: San Juan Creek outlet (33°N)	Xe lamp[a]	35640	1500 < 1 kDa	Clark et al. (2009)
Source waters: Upper Newport Back Bay (33°N)	Xe lamp[a]	10260	1400 < 1 kDa	Clark et al. (2009)
Source waters: Talbert Marsh (33°N)	Xe lamp[a]	4536	600 < 1 kDa	Clark et al. (2009)
Surf zone waters: Huntington Beach pier (33°N)	Xe lamp[a]	35640	400 < 1 kDa	Clark et al. (2009)
Surf zone waters: Newport Beach pier (33°N)	Xe lamp[a]	28800	400 < 1 kDa	Clark et al. (2009)
Surf zone waters: San Clemente Beach pier (33°N)	Xe lamp[a]	22320	500 < 1 kDa	Clark et al. (2009)

(continued)

Table 2 (continued)

Type of samples/substances	Source of light/ wavelength (nm)	Production rate of H_2O_2 (nM h^{-1})	DOC (μM C)	References
Seawater				
Seto Inland Sea (Near Coastal area: site 2)	Xe lamp[a]	161	107	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Seto Inland Sea (Far from Coastal area: site 11)	Xe lamp[a]	54	89	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Seto Inland Sea (Near open ocean: site 23)	Xe lamp[a]	58	99	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Gulf of Alaska	Xe lamp[a]	0.5–8	–	Vermilyea et al. (2010)
Eastern Caribbean, coastal	Xe lamp[a]	17	–	Moffett and Zafiriou (1993)
Eastern Caribbean, estuarine	Xe lamp[a]	25	–	Moffett and Zafiriou (1993)
Sargasso Sea	–	4 ± 1	–	Miller and Kester (1994)
Antactic waters	Xe lamp[a]	2.1–9.6	–	Yocis et al. (2000)
Subtropical Atlantic Ocean (14°N): 5 m	Xe lamp[a]	5.5	90.6	Obernosterer et al. (2001)
10 m	Xe lamp[a]	3.6	90.6	Obernosterer et al. (2001)
20 m	Xe lamp[a]	1.3	90.6	Obernosterer et al. (2001)
30 m	Xe lamp[a]	1.7	90.6	Obernosterer et al. (2001)
40 m	Xe lamp[a]	1.0	90.6	Obernosterer et al. (2001)
50 m	Xe lamp[a]	0.0	90.6	Obernosterer et al. (2001)
Subtropical Atlantic Ocean (23°N): 5 m	Xe lamp[a]	5.2	80.5	Obernosterer et al. (2001)
10 m	Xe lamp[a]	2.1	80.5	Obernosterer et al. (2001)
20 m	Xe lamp[a]	2.5	80.5	Obernosterer et al. (2001)
30 m	Xe lamp[a]	1.3	80.5	Obernosterer et al. (2001)
40 m	Xe lamp[a]	1.5	80.5	Obernosterer et al. (2001)

(continued)

Table 2 (continued)

Type of samples/substances	Source of light/ wavelength (nm)	Production rate of		References
		H_2O_2 (nM h^{-1})	DOC (µM C)	
50 m	Xe lamp[a]	0.0	80.5	Obernosterer et al. (2001)
Subtropical Atlantic Ocean (34°N): 5 m	Xe lamp[a]	4.8	78	Obernosterer et al. (2001)
10 m	Xe lamp[a]	4.1	78	Obernosterer et al. (2001)
Subtropical Atlantic Ocean (34°N): 5 m	Xe lamp[a]	3.6	81	Obernosterer et al. (2001)
10 m	Xe lamp[a]	1.8	81	Obernosterer et al. (2001)
Standard fluorescent organic substances				
Suwannee River Fulvic Acid (SRFA)	Xe lamp[a]	344	49	Mostofa and Sakugawa 2009 and Mostofa KMG and Sakugawa H (unpublished)
Suwannee River Humic Acid (SRHA)	Xe lamp[a]	644	49	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Tryptophan	Xe lamp[a]	648	69	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Fluorescent whitening agents, DAS1	Xe lamp[a]	190	38	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Fluorescent whitening agents, DSBP	Xe lamp[a]	1073	34	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Tyrosine	Xe lamp[a]	275	33	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)

(continued)

Table 2 (continued)

Type of samples/substances	Source of light/ wavelength (nm)	Production rate of		References
		H_2O_2 (nM h^{-1})	DOC (μM C)	
Phenylalanine	Xe lamp[a]	39	47	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
Phenol	Xe lamp[a]	69	21	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
4-Biphenyl carboxaldehyde (4BAC)	Xe lamp[a]	224	74	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)
2-Sulfonic acid benzaldehyde (2SAB)	Xe lamp[a]	153	80	Mostofa and Sakugawa (2009) and Mostofa KMG and Sakugawa H (unpublished)

[a] production rate is normalized to sunlight intensity (noon time) at the Campus of Hiroshima University, Japan

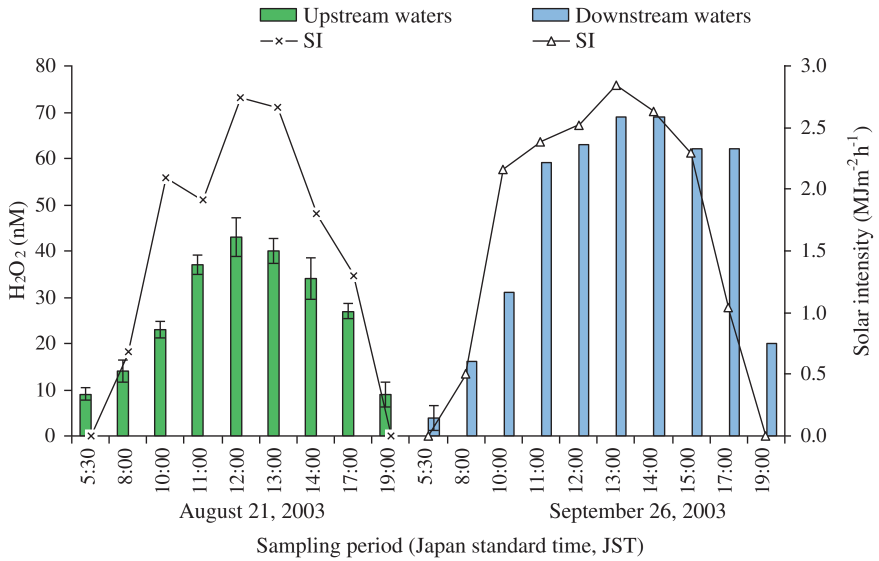


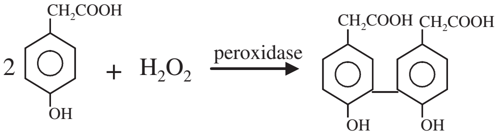
Fig. 6 Diurnal variations of H_2O_2 concentrations in the upstream waters (site KR2) on 21August 2003 and in the downstream waters (site KR6) on 26 September 2003, in the Kurose River. *Data source* Mostofa and Sakugawa (2009)

of Aqaba (Herut et al. 1998), 32 nM in Lagrangian-Atlantic Ocean, 20 nM in Underway-Atlantic Ocean (Yuan and Shiller 2001), 59 nM in Bermuda, Atlantic Time Series Station (Avery et al. 2005), 491 in a shallow freshwater stream (Richard et al. 2007), and 365 nM in marine bathing waters at Huntington State Beach (Clark et al. 2010).

The magnitude of the diurnal cycle of H_2O_2 production shows seasonal and spatial variations in natural waters, depending on several factors. First, the solar intensity varies greatly among tropical, sub-tropical, Arctic and Antarctic regions. The diurnal cycle of H_2O_2 is in fact the best paradigm for the dependence of its production on solar intensity. Second, the contents and nature of DOM components are widely different for a variety of waters and cause correspondingly variable production rates of H_2O_2. For example, H_2O_2 concentration is almost doubled in waters having high DOC concentration (326–384 µM C) than in waters with low DOC (118–239 µM C), even in the presence of similar solar irradiance (Mostofa and Sakugawa 2009). A third factor is the presence of catalase and peroxidase enzymes associated with microbes or algae. Biological processes are widely variable for a variety of natural waters and can control the steady-state concentration by rapidly decomposing H_2O_2 (Fujiwara et al. 1993; Petasne and Zika 1987; Moffett and Zafiriou 1990; Mostofa (Manuscript in preparation). Fourth, iron (Fe) can reduce the steady-state H_2O_2 concentration by producing $HO^\bullet$ through the photo-Fenton or other photoinduced reactions in natural waters (Moffett and Zafiriou 1990; Zepp et al. 1992; Southworth and Voelker 2003).

2 Fluorometric Method for Determining H_2O_2 and ROOH in Natural Waters

Theory: The fluorometric method described here has been developed by Fujiwara et al. (1993) and Sakugawa et al. (2000) by implementation of earlier methods (Lazrus et al. 1986; Guilbault et al. 1968; Miller and Kester 1988). The compounds H′OOH (where H′ = H or CH_3–, –OCH_3, etc.) react with p-hydroxyphenyl acetic acid in the presence of peroxidase, to produce the 6,6′-dihydroxy-3,3′-biphenyldiacetic acid (POPHA dimer: Eq. 2.1). The latter is detected using a fluorometer at excitation/emission = 320/400 nm.



(2.1)

$$2H_2O_2 \xrightarrow{\text{catalase}} 2H_2O + O_2 \qquad (2.2)$$

A sodium hydroxide solution is used to increase the pH to approximately 12, which largely enhances the fluorescence intensity of the POPHA dimer. In this way it is possible to detect few nano molar (nM) levels of H_2O_2 in natural waters. To make the analytical blanks and to distinguish H_2O_2 from ROOH, one should add catalase to the samples, which causes the rapid decomposition of H_2O_2 (Eq. 2.2).

2.1 Chemicals Preparation

Note: ultrapure water should be used throughout. It should be kept in the dark for 3 days before use to allow for the decomposition to undetectable levels of H_2O_2 and ROOH, which could possibly be present.

Preparation of *p*-hydroxyphenyl acetic acid solution:

(i) Take potassium hydrogen phthalate (71.48 g) in approximately 650 mL water in a 1-L beaker, and dissolve it at approximately 40 °C under gentle stirring.
(ii) Dissolve 12 g NaOH in approximately 50 mL water in a 100 mL beaker.
(iii) The pH of the solution (i) is adjusted to 5.5 upon addition of solution (ii) under constant stirring.
(iv) Add 18.62 g of di-sodium dihydrogen ethylenediamine tetraacetate dehydrate (EDTA) to the solution (iii) under constant stirring. The EDTA is added to eliminate the effect of metal ions, particularly Fe^{2+}, and to prevent the formation of a $Mg(OH)_2$ precipitate after addition of NaOH to seawater samples (Fujiwara et al. 1993). It can be noted that without EDTA, 1 mg/mL Fe^{2+} can reduce the signal intensity by 80 % (Fujiwara et al. 1993).
(v) Add 0.304 g of *p*-hydroxyphenyl acetic acid to the solution (iv) under constant stirring, then adjust the total solution to 1-L in a volumetric flask.

Preparation of the catalase solution: For 50,000 units of catalase solution, add 5 mg of catalase to 2 mL water in a 10 mL glass bottle, then mix up by shaking gently. This solution can be used for one week by keeping it in a refrigerator. For 500 units of catalase solution, add 100 μL of 50,000 units catalase solution to 10 mL water. Such a solution must be freshly prepared each time.

Preparation of peroxidase solution: Add 0.022 mg of peroxidase to 5 mL water in a 10 mL glass bottle, then mix up by shaking gently. This solution can be used for two weeks by keeping it in a refrigerator. Add 250 μL of the peroxidase solution to approximately 100 mL of *p*-hydroxyphenyl acetic acid solution.

NaOH solution: Prepare a fresh 0.6 M NaOH solution.

Preparation of standard H_2O_2 solution: Original H_2O_2 (30 %; KANTO Chemical Co., Japan) was considered as 10 M, then 1 mL of that H_2O_2 solution was used to prepare 100 mM H_2O_2. The 100 mM H_2O_2 solution was then diluted to concentrations of 0, 100, 200, 300, 500, and 1000 nM, as standards for H_2O_2 determination.

Preparation of standard ROOH solution: Original peracetic acid (9 % in diluted acetic acid; KANTO Chemical Co., Japan) was considered as 1 M, then 10 mL of that peracetic acid solution was used to prepare 100 mM ROOH. The 100 mM solution was then diluted to concentrations of 0, 100, 200, 300, 500, and 1000 nM as standards for ROOH determination.

2.2 Analytical Procedure

A flow injection apparatus should be used, of which a scheme is provided in Fig. 6 (Sakugawa et al. 2000; Fujiwara et al. 1993). The instrument shown consists of an auto sampler (TOSOH, model AS8020), fluorescence detector (Shimadzu: RF-10AXL), plunger pump (Sanuki Ind. Co., model 4P2U-4016), and recorder (Shimadzu: C-R5A Chromatopac) (Fig. 7) (Fujiwara et al. 1993).

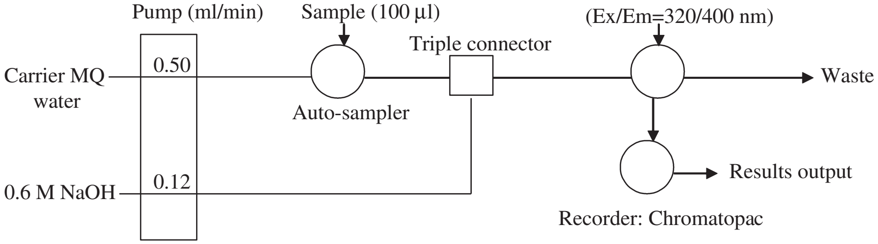


Fig. 7 Modified flow diagram for measuring H_2O_2 and ROOH concentrations in natural waters. *Data source* Fujiwara et al. (1993)

The flow lines were made of Teflon tubing (i.d. = 0.5 mm). After filling up with carrier ultrapure water and 0.6 M NaOH solution, all flow lines should be freed from air bubbles before starting. The fluorescence detector should be set at Ex/Em = 320/400 nm, and the zero level of fluorescence recorded. After completion of the baseline one should set again the fluorescence level to zero, then the analysis can be started. After completion of the measurements, before turning off the plunger pump, one should wash the flow lines. In particular, the NaOH line should be flushed with water and the outgoing flow should be checked for pH until neutrality.

In sample preparation, 1 mL sample in a Teflon or glass container is first treated with catalase (20 μL, 500 units mL^{-1}) in order to decompose all the H_2O_2 present (Eq. 2.2), shaking well for a few seconds and keeping still for six minutes. This solution can be used as a blank. Moreover, 1 mL of the same sample where catalase is replaced with 20 μL of ultrapure water is used to obtain the signal from H_2O_2. Fluorescence can be induced upon addition (300 μL) of peroxidase mixed with *p*-hydroxyphenylacetic acid. The difference in the fluorescence values (Ex/Em = 320/400 nm) between samples treated with catalase and those without the enzyme will provide the estimate of H_2O_2 concentration. Calibration can be carried out by use of the external standards already described (Fig. 8a). A typical example of calibration curves for standard H_2O_2 and peracetic acid

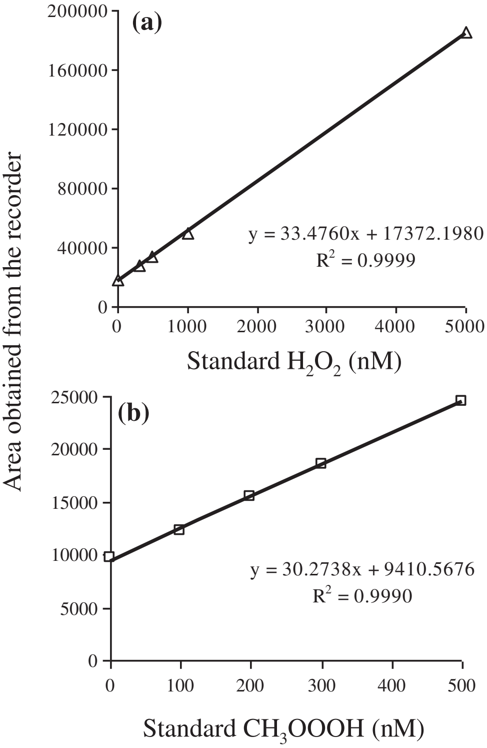


Fig. 8 A typical example of calibration curve for aqueous solutions of standards H_2O_2 (**a**) and peracetic acid (CH_3OOOH) (**b**) measured using this fluorometric method

(CH_3OOOH) is reported in earlier studies (Fig. 8). For ROOH measurement, 50,000 units mL^{-1} catalase solution was used to decompose nearly all of the ROOH in the samples during the same six minute reaction. In this way it is possible to provide only the signal of the background DOM or water fluorescence. The fluorescence-developing reagent is peroxidase mixed with *p*-hydroxyphenylacetic acid also in this case. The difference between the fluorescence measurements using 500 and 50,000 units mL^{-1} of catalase (decomposition of H_2O_2 alone and of H_2O_2 and ROOH, respectively) provides an estimate of the ROOH concentrations in the samples. Also in this case it is possible to use the external standards for calibration (Fig. 8b).

The production of H_2O_2 and ROOH in water samples is normalized as a function of natural sunlight using the following (Eq. 2.3) (Mostofa and Sakugawa 2009):

$$r_{(H_2O_2,Is)} = \frac{D_{(2-NB,Is)} \times r_{(H_2O_2,Ixe)}}{D_{(2-NB,Ixe)}} \tag{2.3}$$

where $r_{(H_2O_2,Is)}$ is the rate of H_2O_2 production, corrected for the intensity of natural sunlight (at noon under clear-sky conditions, on 6 July 2004 at Hiroshima University Campus), in natural water samples and standard DOM materials, $D_{(2\text{-}NB,Is)}$ and $D_{(2\text{-}NB,Ixe)}$ are the degradation rates of 2-NB (2-nitro-benzaldehyde) estimated using the intensity of natural sunlight and the adopted irradiation device, respectively, and $r_{(H_2O_2,Ixe)}$ is the observed H_2O_2 production rate under the adopted irradiation device.

The production rate of H_2O_2 in irradiated water samples can be determined from the net production of H_2O_2 (final concentration minus initial concentration) measured for the initial 60 min of the irradiation period. The rate of H_2O_2 generation is then normalised to sunlight intensity with (Eq. 2.3). The normalised rate of H_2O_2 production of a specific fluorescent DOM component (identified by parallel factor modeling on DOM) is estimated on the basis of its fluorescence intensity observed in waters and can be determined using (Eq. 2.4) (Mostofa and Sakugawa 2009):

$$r_{Fi(DOM)} = \frac{FI_{Fi(DOM)} \times r_{RS}}{FI_{RS}} \tag{2.4}$$

where $r_{Fi\ (DOM)}$ is the normalised production rate of H_2O_2 of an identified fluorescent DOM component in natural waters, $FI_{Fi(DOM)}$ is the fluorescence intensity of the identified fluorescent DOM component in natural waters, FI_{RS} is the fluorescence intensity of the relevant standard substance in the aqueous solution, and r_{RS} is the normalised production rate of H_2O_2 of the relevant standard substance in solution. Finally, percentages of each identified DOM component contributing to the rate of production of H_2O_2 are calculated using the following (Eq. 2.5) (Mostofa and Sakugawa 2009):

$$F_{i(DOM)} = \frac{r_{Fi(DOM)} \times 100}{r_{net(DOM)}} \tag{2.5}$$

where $F_{i(DOM)}$ is the contribution percentage to the normalised net H_2O_2 production rate in the water (%) by each identified fluorescent DOM component, $r_{Fi(\mathrm{DOM})}$ is the normalised H_2O_2 production rate generated by each identified DOM component, and $r_{net(DOM)}$ is the whole, normalised net H_2O_2 production rate in the water samples. The percent contributions of unknown sources of H_2O_2 in the water samples are estimated using a simple formula: $F_{unknown} = 100$—$(F_{FA} + F_{TRYP} + F_{OTHERS})$. In the formula, the sum of the normalized H_2O_2 production rate of FA-like substances (F_{FA}), tryptophan-like substances (F_{TRYP}), and other organic substances if any (F_{OTHERS}) is subtracted from the normalised, net H_2O_2 production rate that is assumed as 100 %.

2.3 Advanced Analytical Method for H_2O_2 Determination in Natural Waters

Theory: This method is based on the Fenton reaction, where H_2O_2 reacts with Fe^{2+} in acidic solution to yield $HO^\bullet$. The latter is scavenged by an aromatic compound (e.g. benzene) to produce the respective phenolic compound (e.g. phenol) according to the following reactions (Eqs. 2.6, 2.7) (Olasehinde et al. 2008; Lee et al. 1994; Liu et al. 2003):

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^\bullet + OH^- \tag{2.6}$$

$$HO^\bullet + C_6H_6 \rightarrow C_6H_5OH \tag{2.7}$$

where the rate constant of the first reaction (Eq. 2.6) is $k = 63$ at pH 3, 1.2×10^2 at pH 4 and 5.7×10^2 M^{-1} s^{-1} at pH 5, respectively (Kwan and Voelker 2002). Phenol produced by the second reaction (Eq. 2.7) is determined by high performance liquid chromatography (HPLC) with fluorescence detector (Olasehinde et al. 2008). The amount of phenol produced is directly proportional to the H_2O_2 concentration present in the sample solution.

Based on this theoretical framework, Olasehinde and his co-workers (Olasehinde et al. 2008) developed a new method for the measurement of H_2O_2 in the aqueous solution, which is highly sensitive and simpler than any other enzymatic process applied earlier to natural waters. The chemicals preparation, analytical procedure and HPLC instrumentation for this method are depicted below (Olasehinde et al. 2008):

Chemicals preparation

Benzene stock solution: 2×10^{-2} M benzene solution is prepared by adding 88.8 μL of 99.7 % benzene in 50 mL of ultrapure water.

Fe^{2+} solution: A 0.1 M Fe^{2+} solution is prepared by dissolving 1.39 g ferrous sulphate pentahydrate into 50 mL of 0.07 M H_2SO_4 solution.

H_2SO_4 solution: A 3.0 M sulphuric acid stock solution is prepared by diluting 16.3 mL of 98 % H_2SO_4 to 100 mL with ultrapure water.

H_2O_2 standard solution: A 1 × 10^{-2} M H_2O_2 standard stock solution is prepared by diluting 1.0 mL of 30 % H_2O_2 to 100 mL with ultrapure water. The concentration of H_2O_2 is determined based on the molar extinction coefficient at 240 nm ($\varepsilon = 38.1$ L mol^{-1} cm^{-1}) (Miller and Kester 1988).

HPLC system: An HPLC-fluorescence system is adopted. The separation is carried out on a RP-C18 column with acetonitrile–water mixture as eluent. Tentative elution conditions are (CH_3CN/H_2O 40/60 v/v) at a flow rate of 1 mL min^{-1} (note: optimal conditions may vary depending on the actual system adopted). For the detection of phenol, the fluorescence detector is operated at 270 and 298 nm for excitation and emission, respectively.

Analytical procedure: 3.0 mL of water sample (natural water or standard H_2O_2) is first treated with 200 µL of 2 × 10^{-2} M benzene in a 5 mL amber vial and then mixed by gently shaking. It is then added 50 µL of 0.1 M Fe^{2+} in 0.07 M H_2SO_4 solution, waiting 5 min at room temperature for completion of the Fenton reaction. The final pH of the solution should be adjusted to ca. 4 with addition of sulphuric acid solution. It can be noted that the rate constant of the Fenton reaction is much higher at pH 4 to 5 than at pH 3, thus the reaction can be conducted in these pH ranges. An aliquot of the solution (e.g. 150 µL) is then injected into the HPLC system for analysis. Phenol and benzene are separated by reverse-phase chromatography. The standard phenol and H_2O_2 concentrations might be 0, 100, 200, 300, 500 and 1000 nM, and can be prepared freshly by diluting their stock solutions. The H_2O_2 concentration is determined by calibration of the peak areas of phenol produced in each standard solution against the H_2O_2 concentration of the sample. It can be noted that the addition of 10 µM NO_2^- to the water samples shows no significant interference on the fluorescence intensity of phenol. In contrast, addition of 50 µM NO_2^- to the samples decreases the fluorescence intensity signal of phenol by almost 40 %.

3 Mechanism of Production of H_2O_2 and ROOH in Natural Waters

3.1 Photoinduced Formation of H_2O_2 and ROOH

H_2O_2 and ROOH are photolytically produced by several pathways in the aquatic environments. First, H_2O_2 and ROOH are photogenerated by chromophoric or fluorescent dissolved organic matter (CDOM or FDOM) in aqueous media (Cooper and Zika 1983; Mostofa and Sakugawa 2009; Moore et al. 1993; Richard et al. 2007; Baxter and Carey 1983; Clark et al. 2009; Cooper et al. 1989a, b; Dalrymple et al. 2010). A second pathway is linked with the redox cycling of transition metal ions in aqueous media (Moffett and Zika 1983; Moffett and Zika 1987a, b). An additional process is the intracellular H_2O_2 formation in chloropigments in aquatic organisms (Lobanov et al. 2008; Hong et al. 1987; Bazanov et al. 1999). Finally, various chemical reactions cause the production of H_2O_2 and ROOH in the gaseous and aqueous phases in the atmosphere.

In the gas phase, H_2O_2 and ROOH compounds are formed through several chain reactions (Eqs. 3.1–3.5) as a combined effect of solar radiation on organic substances, nitrogen oxides (NO_x), and oxygen (O_2) (Sakugawa et al. 1990, 1993; Zuo and Hoigné 1992, 1993). The relevant processes are shown below:

$$\mathrm{RCHO} + h\nu \overset{O_2}{\rightarrow} 2\mathrm{RO}^\bullet + \mathrm{CO}\ \ (\mathrm{R = H, methyl, alkyl, etc}) \tag{3.1}$$

$$\mathrm{NO_3}^- + \mathrm{HCHO} \rightarrow \mathrm{HNO_3} + \mathrm{HO_2}^\bullet + \mathrm{CO} \tag{3.2}$$

$$\mathrm{HO_2}^\bullet + \mathrm{RO_2}^\bullet \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{3.3}$$

$$\mathrm{HO_2}^\bullet + \mathrm{HO_2}^\bullet \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{3.4}$$

$$\mathrm{HO_2}^\bullet + \mathrm{RO_2}^\bullet \rightarrow \mathrm{ROOH} + \mathrm{O_2} \tag{3.5}$$

In atmospheric waters the formation and decomposition of H_2O_2 is mechanistically different compared to the gas-phase reactions (Eqs. 3.6–3.9). A general scheme can be expressed as follows below (Sakugawa et al. 1990):

$$\mathrm{HO_2}^\bullet(\mathrm{aq}) + \mathrm{O_2} \xrightarrow{\mathrm{H_2O}} \mathrm{H_2O_2}(\mathrm{aq}) + \mathrm{O_2} + \mathrm{OH}^- \tag{3.6}$$

$$\mathrm{HSO_3}^- + \mathrm{H_2O_2}(\mathrm{aq}) + \mathrm{H}^+ \rightarrow \mathrm{SO_4}^{2-} + 2\mathrm{H}^+ + \mathrm{H_2O} \tag{3.7}$$

$$\mathrm{H_2O_2}(\mathrm{aq}) + \mathrm{HO}^\bullet(\mathrm{aq}) \rightarrow \mathrm{H_2O} + \mathrm{HO_2}^\bullet(\mathrm{aq}) \tag{3.8}$$

$$\mathrm{H_2O_2}(\mathrm{aq}) + h\nu \rightarrow 2\mathrm{HO}^\bullet(\mathrm{aq}) \tag{3.9}$$

H_2O_2 is also formed by photodecomposition of Fe(III) complexes with oxalic, glyoxalic and pyruvic acids, under the typical acidic conditions that can be found in atmospheric waters (Zuo and Hoigné 1992, 1993; Faust et al. 1993. A general mechanism for the formation of H_2O_2 via this route is reported below (Eqs. 3.10–3.12) (Sakugawa et al. 1990; Kim et al. 2003):

$$\mathrm{Fe(III)\text{-}L} + h\nu \rightarrow \mathrm{Fe(II)} + \mathrm{L}^\bullet \tag{3.10}$$

$$\mathrm{L}^\bullet + \mathrm{O_2} \rightarrow \mathrm{O_2}^{\bullet-} + \mathrm{oxidized\,L} \tag{3.11}$$

$$\mathrm{O_2}^{\bullet-} + 2\mathrm{H}^+ \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \tag{3.12}$$

In (Eqs. 3.10, 3.11), Fe(III)-L is a complex of Fe(III) with an organic ligand, hυ is the energy of a photon, and $L^\bullet$ is the organic radical of L. Superoxide ion ($O_2^{\bullet-}$) is a major intermediate in many O_2-mediated oxidations, such as the well-known Haber–Weiss mechanism of iron oxidation (Haber and Weiss 1934).

In natural waters, the main sources of H_2O_2 are fulvic acid (FA), humic acid, tryptophan amino acid, fluorescent whitening agents (DSBP and DAS1) and their photoproducts, as well as various unknown organic substances belonging to DOM (Mostofa and Sakugawa 2009). There is evidence that H_2O_2 may be a photoproduct of reaction chains involving dissolved organic matter (DOM) components in the presence of dissolved oxygen under natural sunlight (Eqs. 3.13–3.18) (Mostofa and Sakugawa 2009; Moore et al. 1993; Richard et al. 2007; O'Sullivan et al. 2005; Cooper et al. 1988; Clark et al. 2009; Fischer et al. 1985; Fischer et al. 1987; Power et al. 1987; Cabelli 1997). In these chain reactions, the functional groups of DOM absorb photons and are promoted to the singlet excited states ($^1DOM^*$). The latter can undergo intersystem crossing (ISC) and be converted into the triplet states ($^3DOM^*$) (Eq. 3.13). The reaction of oxygen with photo-excited DOM might generate the superoxide radical anion ($O_2^{\bullet -}$) (Eq. 3.14) in equilibrium with its conjugate acid perhydroxyl radical ($HO_2^{\bullet}$) (Eq. 3.15). Both $O_2^{\bullet -}$ and $HO_2^{\bullet}$ disproportionate to form H_2O_2 (Eqs. 3.17 and 3.18, respectively). The scheme of the reaction chain is reported below:

$$\mathrm{DOM} + h\nu \rightarrow {}^1\mathrm{DOM}^* \xrightarrow{\mathrm{ISC}} {}^3\mathrm{DOM}^* \tag{3.13}$$

$$^3\mathrm{DOM}^* + \mathrm{O_2} \rightarrow \mathrm{DOM}^{\bullet} + \mathrm{O_2}^{\bullet -} \tag{3.14}$$

$$\mathrm{O_2}^{\bullet -} + \mathrm{H}^+ \rightarrow \mathrm{HO_2}^{\bullet} \quad \mathrm{p}K_a = 4.8 \tag{3.15}$$

$$2\mathrm{O_2}^{\bullet -} \rightarrow \mathrm{O_2}^{2-} \; + \mathrm{O_2} \quad \mathrm{p}K_a =< 0.35\,\mathrm{M^{-1}\,s^{-1}} \tag{3.16}$$

$$\mathrm{HO_2}^{\bullet} + \mathrm{HO_2}^{\bullet} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} \quad k = 8.6 \times 10^5\,\mathrm{M^{-1}\,s^{-1}} \tag{3.17}$$

$$\mathrm{HO_2}^{\bullet} + \mathrm{O_2}^{\bullet -} + \mathrm{H_2O} \rightarrow \mathrm{H_2O_2} + \mathrm{O_2} + \mathrm{OH}^- \quad k = 1.0 \times 10^8\,\mathrm{M^{-1}\,s^{-}} \tag{3.18}$$

The reaction of $HO_2^{\bullet}$ with $O_2^{\bullet -}$ (Eq. 3.28) is faster than that of $HO_2^{\bullet}$ with $HO_2^{\bullet}$ (Eq. 3.17), and the termination reaction of two $O_2^{\bullet -}$ radicals is too slow to be significant (Clark et al. 2009). The acidic constant of $HO_2^{\bullet}$ ($pK_a = 4.8$) supports the generation of the perhydroxyl radical ($HO_2^{\bullet}$) in coastal waters (Clark et al. 2009; Cabelli 1997). Therefore, the steady-state concentrations of $O_2^{\bullet -}$ and H_2O_2 (Eq. 3.18) are the result of the photoinduced activity of DOM components in sunlit surface freshwater and oceanic environments, as well as in other aqueous media (Inoue et al. 1982; Cooper et al. 1994; Millington and Maurdev 2004). $DOM^{\bullet +}$ is susceptible to further photoinduced degradation by photoinduced generation of hydroxyl radical, and the relevant pathways are depicted in the DOM degradation chapter (see chapter "Photoinduced and Microbial Degradation of Dissolved Organic Matter in Natural Waters"). It can be noted that the excitation of DOM would involve its functional groups (chromophores or fluorophores) that are the easiest to be excited. Therefore, the reactivity of DOM toward H_2O_2 production will often resemble that of simple photoactive organic molecules. Recent evidence highlights that DOM can form complexes with trace elements by a strong π–electron bonding system (Mostofa et al. 2009a, b). The metal-DOM complexes are susceptible to undergoing rapid photoinduced excitation that would finally result into the production of H_2O_2.

In studies mimicking the process of intracellular H_2O_2 formation, it has been found that the synthetic analogues of chlorophyll, metal complexes of porphyrins and phthalocyanines, act as photoactive species that produce H_2O_2 under irradiation in aqueous solutions saturated with dioxygen (Lobanov et al. 2008;

Hong et al. 1987; Bazanov et al. 1999). The highest photoinduced activity has been reported for porphyrin and phthalocyanine complexes with metals such as Mg, Zn, Al, and Cd (Komissarov 2003; Vedeneeva et al. 2005), which can typically produce long-lived triplet excited states (lifetimes up to 1 ms) with a high quantum yield (60–90 %) (Parmon 1985). Photosynthetically produced organic matter (e.g. algae) can enhance the production of H_2O_2 by natural sunlight in aquatic ecosystems (Zepp et al. 1987). It can be hypothesized that the photoinduced and microbial assimilation of algae produce autochthonous fulvic acid and other DOM components (Mostofa et al. 2009b; Fu et al. 2010; Mostofa et al. (Manuscript In preparation), which may induce H_2O_2 photoproduction by the pathways already described for DOM.

In natural waters, ROOH compounds are formed upon photodegradation of DOM (including both CDOM and FDOM) via pathways that also induce the production of H_2O_2 (Mostofa and Sakugawa 2009; Sakugawa et al. 1990; Faust and Hoigne 1987; Perkowski et al. 2006). A generalized chain-reaction scheme for the formation of ROOH from DOM in natural waters can be depicted as follows (Eqs. 3.19–3.24):

$$H_2O_2 + h\nu \rightarrow 2HO^\bullet \tag{3.19}$$

$$DOM^{\bullet+} + HO^\bullet \rightarrow R^\bullet + H^\bullet \tag{3.20}$$

$$R^\bullet + O_2 \rightarrow RO_2{}^\bullet \tag{3.21}$$

$$RO_2{}^\bullet + O_2{}^{\bullet-} + H^+ \rightarrow ROOH + O_2 \tag{3.22}$$

$$RO_2{}^\bullet + R^\bullet \rightarrow ROOR \tag{3.23}$$

$$RO_2{}^\bullet + RO_2{}^\bullet \rightarrow ROOR + O_2 \tag{3.24}$$

First, the photodecomposition of H_2O_2 generates the hydroxyl radical, $HO^\bullet$ (Eq. 3.19), which subsequently oxidizes DOM or $DOM^{\bullet+}$ (the latter is formed by $^3DOM^*$ and O_2, see Eq. 3.20) to form the organic radical $R^\bullet$ (Eq. 3.20) (Mostofa and Sakugawa 2009). Afterwards, $R^\bullet$ reacts with O_2 to form the organo peroxide radical $RO_2{}^\bullet$ (Eq. 3.21). The reduction of $RO_2{}^\bullet$, e.g. by $O_2{}^{\bullet-}$, can form ROOH in natural waters (Eq. 3.22) whereas $O_2{}^{\bullet-}$ is formed using (Eq. 3.14). Organic radicals ($R^\bullet$ and $RO_2{}^\bullet$) can rapidly associate with one another (Eq. 3.23), and organo peroxide radicals can combine (Eq. 3.24) to terminate the chain reactions. The termination reactions (Eqs. 3.23, 3.24) are competitive with (3.21, 3.22), which leads to complicated reaction kinetics (Perkowski et al. 2006).

Oxidation–reduction of transition metal ions is an important pathway for the formation of organic peroxides in natural waters. A general mechanistic scheme for these oxidation–reduction chain reactions (Eqs. 3.25–3.27) can be expressed as follows:

First, oxidation of the metal ions (M^{n+}) forms the superoxide radical anion ($O_2{}^{\bullet-}$) (Eq. 3.25). $O_2{}^{\bullet-}$ then combines with H^+ or with an alkyl ion (R^+=H^+, positively charged alkyl group, etc.) to form an hydro-peroxide or organo-peroxide radical ($RO_2{}^\bullet$, R = H or alkyl group, Eq. 3.26). $RO_2{}^\bullet$ can then associate with H^+ or a metal ion ($M^{(n+1)+}$), to form ROOH (where R = H or an alkyl group) and a further oxidized $M^{(n+2)+}$ ion (Eq. 3.27). Therefore, formation of $O_2^{\bullet-}$ is an important step in the generation of organic peroxides in natural waters.

$$M^{n+} + O_2 \rightarrow M^{(n+1)} + O_2^{\bullet-} (M = Fe^{2+}, Cu^{+}, etc) \tag{3.25}$$

$$O_2^{\bullet-} + R^{+} \rightarrow RO_2^{\bullet} \quad (R = H^{+}/CH_3^{+}, etc) \tag{3.26}$$

$$RO_2^{\bullet} + M^{(n+1)+} + H^{+} \rightarrow ROOH + M^{(n+2)+} \quad (R = H^{+}/CH_3^{+}) \tag{3.27}$$

3.2 Microbial Formation of H_2O_2 and ROOH

H_2O_2 and ROOH compounds are typically produced under dark incubation by microbial activity in natural waters (Fig. 2) (Palenic and Morel 1988; Moffett and Zafiriou 1990; Vermilyea et al. 2010a, b). They are susceptible to be formed by several biological processes. Biota is thought to be the main source of dark H_2O_2 and ROOH production in natural waters (Fig. 2b) (Paradies et al. 2000; Forman and Boveris 1982). For instance, dark production of H_2O_2 in seawater is particle-dependent and the production rates are in the range of 0.8–2.4 nM h^{-1} (Moffett and Zafiriou 1990). Recent studies demonstrate the high dark production rate (29–122 nM h^{-1}) of H_2O_2 in several lake waters (Vermilyea et al. 2010). Moreover, H_2O_2 and ROOH may be formed extracellularly by marine phytoplankton or cyanobacteria (Palenic and Morel 1988; Zepp et al. 1986). Extracellular H_2O_2 can be produced under dark conditions by enzymatic reduction of oxygen at the cell surface (Palenic et al. 1987) and upon oxygen reduction by other electron transport chains. The latter include the mitochondrial reduction of oxygen followed by H_2O_2 diffusion out of the cell (Forman and Boveris 1982; Frimer et al. 1983). Also the autooxidation of organic material may produce H_2O_2 and ROOH in the aquatic environment (Stevens et al. 1973). In seawater, H_2O_2 may be produced by particle-dependent and light-independent microbial processes (Moffett and Zafiriou 1990). For example, a net H_2O_2 production (dark production minus dark consumption) of 1–3 nM h^{-1} has been observed at 40–60 m in an in situ experiment conducted in the Sargasso Sea (Palenic and Morel 1988). Finally, ROOH compounds are produced in bulk natural-water DOM by light-independent microbial processes (Fig. 2) (Sakugawa et al. 2000). For example, net ROOH production has been observed in both filtered and unfiltered river waters (2b), while H_2O_2 is merely produced in filtered river waters (Fig. 2a). ROOH compounds are typically more concentrated in deep seawaters than in surface waters (Sakugawa et al. 2000).

4 Factors Controlling the Production and Decay of H_2O_2 and ROOH in Natural Waters

Concentration levels of H_2O_2 and ROOH as well as production rates of H_2O_2 differ in a variety of natural waters (Table 1). The magnitude of the H_2O_2 production decreases from coastal waters to open oceans (Zika et al. 1985a, b; Fujiwara et al.

1993). The influence of riverine fluxes having high DOM plays an important role in the production of H_2O_2 in coastal seawaters. The lowest H_2O_2 concentration was seasonally detected in southern oceans (5–25 nM), which was 10 to 20 times lower compared to other oceanic environments (Table 1). The major factors behind the low H_2O_2 concentration in the southern ocean are thought to be: (i) Low incident solar intensity and penetration efficiency in the surface water layer (Zika et al. 1985), solar irradiance being a major factor for the photoinduced formation of H_2O_2 in natural waters. (ii) Water temperature that is normally below <5 °C in the southern ocean. (iii) Vertical mixing (Johnson et al. 1989). (iv) DOC concentration (Zika et al. 1985a, b). (v) Distinct latitude or solar zenith angle, considering that H_2O_2 photoproduction decreases with increasing apparent-noon solar zenith angle (Sikorsky and Zika 1993a, b).

Therefore, the production and decay of H_2O_2 and ROOH and their lifetimes in the aquatic environment (Table 1) generally depend upon a complex set of factors, which can be distinguished as: (1) Effects and variation of solar radiation; (2) Contents and molecular nature of DOM; (3) Presence of phytoplankton, algae and microbes; (4) Photodegradation; (5) Photosynthesis; (6) Photolytic and chemical processes; (7) Physical processes; and (8) Precipitation (e.g. rain).

4.1 Effects and Variation of Solar Radiation

Solar radiation is one of the key factors in the generation of H_2O_2 and ROOH in natural waters (Mostofa and Sakugawa 2009; Obernosterer et al. 2001; Richard et al. 2007; Rusak et al. 2010; Holm-Hansen et al. 1993). The diurnal cycle of H_2O_2, where an increase of solar radiation intensity increases the production of H_2O_2 and vice versa, is a typical example of the strong dependence between solar intensity and H_2O_2 generation (Fig. 6). It has been estimated that the production of H_2O_2 and ROOH is usually higher by several times in the summer season than in the winter one. Production of H_2O_2 is higher in summer by 55–79 % in upstream waters, 162–364 % in polluted waters, and 137–146 % in clean river waters. In the case of ROOH the summer production is higher by 116–240 %, 521–1322 %, and 244–550 %, respectively, compared to the winter one. Such effects are mostly considered to be the effect of variation in solar intensity, which is much higher in the summer season (by 84 %, 32 %, and 216 %, respectively) compared to winter during a sampling day (Fig. 9) (Mostofa and Sakugawa 2009). Therefore, an increase in solar intensity would enhance the production of H_2O_2 in aqueous solution (Mostofa and Sakugawa 2009).

The solar intensity is highly variable in different regions. In the subtropical zone, ultraviolet (UV) B radiation (280–320 nm) is stable, but it is much higher (≈ten fold) than that in the Antarctica (Holm-Hansen et al. 1993). Depletion of the stratospheric ozone layer increases the ground-level UV B radiation in the polar regions (Crutzen 1992) as well as at temperate latitudes (Stolarski et al. 1992). H_2O_2 formation is largely dependent on the radiation wavelengths (Obernosterer

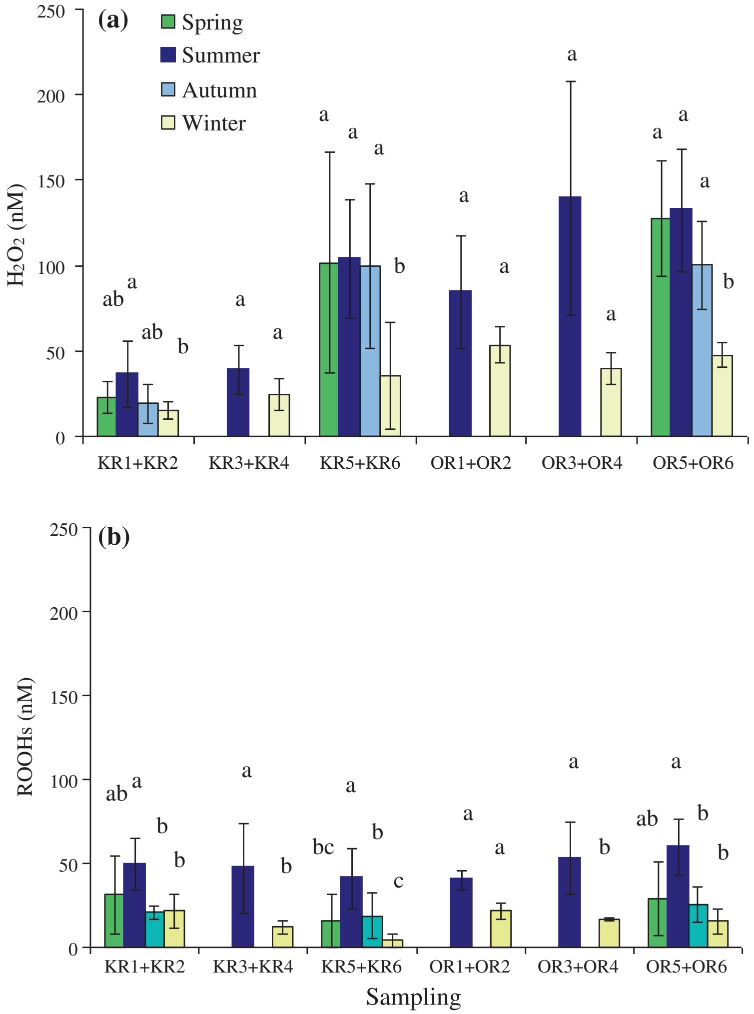


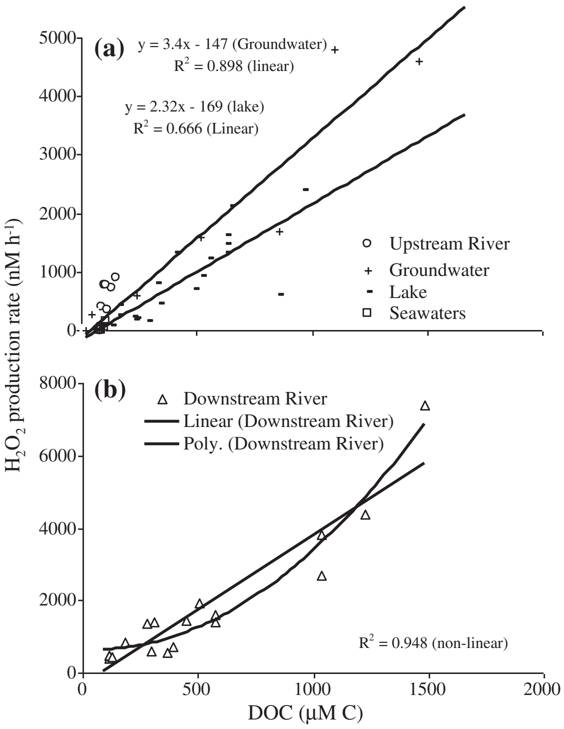
Fig. 9 Seasonal variations of the H_2O_2 (**a**) and ROOH (**b**) concentrations in the waters of the Kurose River and Ohta River in the Hiroshima prefecture, Japan. The error bar indicates the standard deviation of seasonal average value of peroxides. Mean values labelled with different letters are significantly different at $P < 0.05$ (Fisher's l.s.d. analysis). *Data source* Mostofa and Sakugawa (2009)

et al. 2001; Richard et al. 2007), and the contribution of UV-B, UV-A and photosynthetically active radiation (PAR) is 40, 33 and 27 %, respectively (Richard et al. 2007). Production of H_2O_2 at vertical depths depends on the penetration of solar radiation, and decreases with an increase in depth of lakes or oceans (Obernosterer et al. 2001). A model study on a freshwater stream shows that the H_2O_2 concentrations over time significantly depend on photoinduced production rates from ultraviolet-B (UVB), UVA and photosynthetically active radiation (PAR), and loss rates from temperature-dependent and temperature-independent processes (Rusak et al. 2010). The retrieved model terms confirm that H_2O_2 is produced by both UVB and UVA radiation. These results demonstrate that changes in solar radiation reaching the study site are closely correlated with the observed seasonal pattern in H_2O_2 concentrations in the water (Rusak et al. 2010).

4.2 Production and Decay Affected by Contents and Molecular Nature of DOM

The production and decay of H_2O_2 and ROOH in natural waters are significantly affected by the total contents and molecular nature of DOM (Mostofa and Sakugawa 2009; Scully et al. 1995). An increase in standard Suwannee River Fulvic Acid (SRFA) contents in aqueous solution increases the photoinduced production of H_2O_2, but the production of ROOH decreases with an increase in SRFA concentration. It is suggested that the photoinduced generation of H_2O_2 depends on the total contents of DOM components in natural waters. It is demonstrated that the production rates of H_2O_2 are greatly different for a variety of waters, and the production rates for various standard organic substances are also widely variable (Table 2). The photoinduced generation of H_2O_2 by natural waters and standard organic substances is generally much higher at short irradiation times (60 min), after which it often decreases. Such an effect has been observed in upstream waters as well as in aqueous solutions of Suwannee River Fulvic Acid (SRFA), Suwannee River Humic Acid (SRHA), tryptophan, DSBP and DAS1, during photo experiments carried out with a solar simulator (Fig. 1a, b) (Mostofa and Sakugawa 2009). The production of H_2O_2 and its disappearance for prolonged irradiation times has suggested two important phenomena. Firstly, H_2O_2 is initially generated as a consequence of the excitation of highly efficient functional groups of organic substances. These groups are effectively excited and transformed by solar radiation, after which the effectiveness of the functional groups to yield H_2O_2 gradually decreases. This effect, combined with consumption processes, causes a decrease of H_2O_2 concentration at the end of the long-term irradiation period. Secondly, H_2O_2 produced upon irradiation is photolytically converted to $HO^{\bullet}$, which can degrade the parent organic substances and yields a variety of photoproducts in the aqueous solution (Southworth and Voelker 2003; Kramer et al. 1996; Legrini et al. 1993; von Sonntag et al. 1993; Corin et al. 1996; Schmitt-Kopplin et al. 1998; Wang et al. 2001; Leenheer and Croué 2003). These results suggest that the photoinduced generation of H_2O_2 and ROOH depends on the molecular nature of DOM components in natural waters. The relationship between DOC concentration and production rates of H_2O_2 (Fig. 10) shows that the rate is higher for upstreams and groundwater, and increases non-linearly with an increase of DOC concentration in rivers (Fig. 10) and lakes (Scully et al. 1996). It can be considered that the highly reactive DOM is photolytically and rapidly degraded into photoproducts in

Fig. 10 Relationship between DOC concentration and production rates of H_2O_2 generated from photoexperiments conducted on upstream river, groundwater, lake and seawaters (**a**); as well as on the waters of the downstream river (**b**)



stagnant lake or seawaters or during the transportation of water from the source to the lake or ocean (Moran et al. 2000; Mostofa et al. 2005a, 2007a, b; Wu et al. 2005). Indeed, previous photoprocessing is a likely reason for the photostability of DOM sampled in surface lake environments (Vione et al. 2009). H_2O_2 production is less efficient in the presence of DOM from lake or seawater, which suggests that the generation of hydrogen peroxide depends also on the nature and not only on the total amount of DOM in natural waters. Therefore, H_2O_2 production follows the order: upstreams > groundwater > rivers > lake > coastal sea > open ocean.

Fluorescent DOM (FDOM) or chromophoric DOM (CDOM) plays an active role in the generation of H_2O_2 and ROOH in natural waters (Table 1) (Mostofa and Sakugawa 2009; Obernosterer et al. 2001; Fujiwara et al. 1993; Moore et al. 1993; O'Sullivan et al. 2005). It can be noted that CDOM or FDOM moieties undergo rather efficient photoionization under sunlight (Wu et al. 2005; Senesi 1990). For example, a significant correlation has been observed between fluorescence intensity (FI) of fulvic acid and the photoproduction of hydrated electrons (Fujiwara et al. 1993). Similarly, the production rates of H_2O_2 are highly correlated with the fluorescence of fulvic acid present in river (Mostofa 2005) and lake waters, rather than with DOC concentrations (Scully et al. 1996). Moreover, the production of H_2O_2 by a variety of river waters is highly different due to a variation in their DOM components such as fulvic acid, fluorescent whitening agents and tryptophan-like compounds (Mostofa and Sakugawa 2009). Thus, production of H_2O_2 and ROOH significantly depends on the molecular nature and composition of FDOM or CDOM rather than on DOC concentration.

4.3 Production and Decay Affected by Phytoplankton, Algae and Microbes

Production and decay of H_2O_2 and ROOH are greatly influenced by marine phytoplankton, algae and microbes. Two phenomena are involved. First, marine phytoplankton, algae and microbes may produce autochthonous DOM, which is then involved into the photoinduced or microbiological (the latter being highlighted under dark incubation) generation of H_2O_2 and ROOH compounds in natural waters. Second, the decay of H_2O_2 and ROOH compounds may be caused by catalase, peroxidase and superoxide dismutase produced by phytoplankton, algae and microbes.

A variety of marine organisms or phytoplankton can produce or excrete organic compounds such as riboflavin (Dunlap and Susic 1985; Mopper and Zika 1987), amino acids including tryptophan, proteins, carbohydrates and saturated and unsaturated fatty acids (McCarthy et al. 1997; Rosenstock and Simon 2001; Nieto-Cid et al. 2006). All of these organic compounds are photolytically reactive. For example, 1 nM riboflavin added to seawater can produce approximately 10 nM H_2O_2 (Mopper and Zika 1987), and tryptophan can produce H_2O_2 at a rate of 648 nM h^{-1} in aqueous media (Table 2). The organisms, 10^5 coccolithophorid cells L^{-1}, can produce H_2O_2 at a rate of 1–2 nM h^{-1} in oligotrophic waters (Palenic et al. 1987). Production of H_2O_2 by the eukaryotic phytoplankton species *Hymenomonas carrterae* is induced by amino acid oxidation by cell-surface enzymes (Palenic et al. 1987). The photorespiration cycle of phytoplankton involves production of H_2O_2 during glycolate oxidation (Lehninger 1970), which can be expressed as follows (Eq. 4.1):

$$\mathrm{CH_2OHCOOH} + \mathrm{O_2} \xrightarrow{\text{glycolate oxidase}} \mathrm{CHOCOOH} + \mathrm{H_2O_2} \tag{4.1}$$

The rate of photorespiration increases with high light intensity, possibly as a way to dissipate the excess light energy (Harris 1979), but its exact role is unclear (Ogren 1984).

The exposure of algae suspensions to sunlight can produce H_2O_2 ((Johnson et al. 1989; Collen et al. 1995; Zepp et al. 1987), possibly by photoinduced excitation of DOM released under photo- and microbial assimilation of algae (Mostofa et al. 2009b; Medina-Sánchez et al. 2006; Fu et al. 2010; Takahashi et al. 1995; Marañòn et al. 2004). This hypothesis is supported by the fact that the H_2O_2 production from algal suspensions is low in the initial two hours of irradiation, and is greatly increased with further irradiation (Zepp et al. 1987). It can be assumed that the high production of H_2O_2 after two hours occurs because of the photodegradation of organic substances newly released from algal suspensions in the reaction media during the initial irradiation period. For example, the production rates of

H_2O_2 due to sunlight effects on algae are 0.04–1.7 × 10^6 M h^{-1} for five algae at a concentration of 0.097–1.0 × 10^{-3} mg m^{-3} Chl *a* (Zepp et al. 1987).

4.3.1 Mechanism of Microbial Decomposition of H_2O_2 and ROOH

Decay of peroxides (H_2O_2 and ROOH) by phytoplankton, algae and microbes is a reverse effect of peroxide production in natural waters. Peroxides ($H'OOH$, $H' = H$ or R) may be decomposed by catalase, peroxidase and superoxide dismutase, produced by phytoplankton, algae and microbes to generate energy for their growth and to eliminate excessive intracellular levels of H_2O_2 and $O_2^{\bullet -}$ (Fujiwara et al. 1993; Moffett and Zafiriou 1990; Zepp et al. 1987; Mostofa et al. (Manuscript in preparation); Wong et al. 2003). Such a decomposition effect induced by phytoplankton, algae and microbes would usually occur constantly, until the concentration of peroxides reaches a minimum level that would afford inefficient further decomposition. Catalase enzymatically activates the peroxides ($H'OOH^*$) to use them as oxidants (electron acceptors) and reductants (electron donors). Afterwards, disproportionation of activated $H'OOH^*$ converts them into water or alcohols and oxygen. A reaction scheme (Eqs. 4.2, 4.3) for the decomposition of peroxides by catalase can be generalized as follows (Moffett and Zafiriou 1990):

$$H'OOH + \text{Catalase} \rightarrow H'OOH^* + \text{Catalase}^{\#} \tag{4.2}$$

$$2H'OOH^* + \text{Catalase}^{\#} \rightarrow H' - O - H + O_2 + \text{Catalase} \tag{4.3}$$

where Catalase$^{\#}$ is the activated state of catalase.

Peroxidase enzymatically activates the peroxides ($H'OOH^*$) to detoxify them to H_2O or any other end product. As reducing species it uses organic compounds (H_2R) other than $H'OOH$. A reaction scheme (Eqs. 4.4, 4.5) for the decomposition of peroxides is presented below (Moffett and Zafiriou 1990):

$$H'OOH + \text{Peroxidase} \rightarrow H'OOH^* + \text{Peroxidase}^{\#} \tag{4.4}$$

$$H'OOH^* + H_2R + \text{Peroxidase}^{\#} \rightarrow H' - O - H + H - O - H + R + \text{Peroxidase} \tag{4.5}$$

where Peroxidase$^{\#}$ is the activated state of peroxidase. It has been shown that the percentage decay of H_2O_2 was 65–80 % by catalase and 20–35 % by peroxidase, as estimated by isotopic measurements in seawater (Moffett and Zafiriou 1990). The sources of catalase and peroxidase in natural waters are bacteria and marine phytoplankton (Kim and Zobell 1974), but these enzymes are also part of the dissolved organic matter (Serban and Nissenbaum 1986). Similarly, chloroplasts have a peroxidase-mediated H_2O_2 scavenging system (Tanaka et al. 1985). Natural marine peroxidases are also capable of catalyzing H_2O_2-mediated halogenation reactions in the oceanic environments (Theiler et al. 1978; Baden and Corbett 1980). The decay of H_2O_2 is usually low (12 % after 5 h incubation) in upstream waters due to the presence of few bacteria (some 10^5 cells mL^{-1}), and much higher in polluted

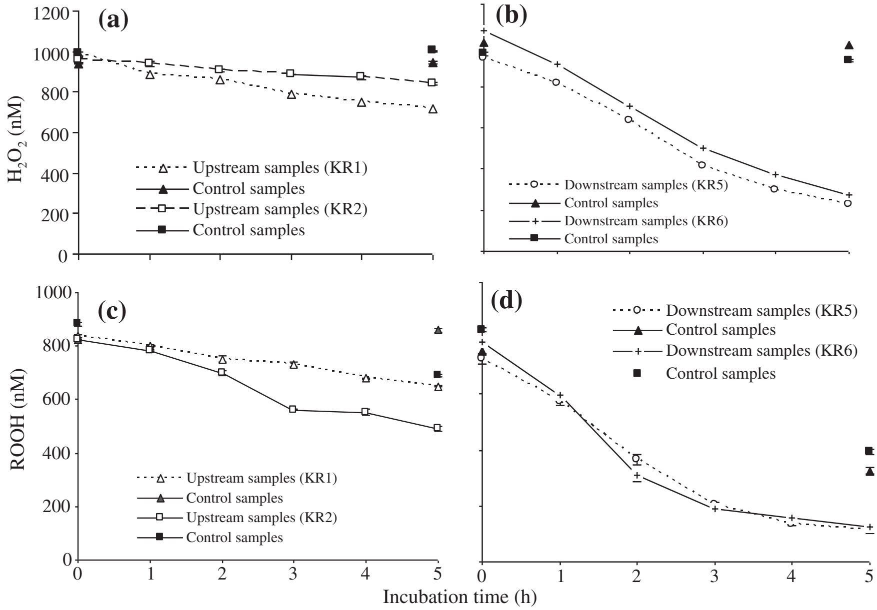


Fig. 11 The decay of peroxides by the occurrence of bacterial incidences in upstream and polluted river waters with an addition of standard 1,000 nM of H_2O_2 (**a**) and 1,000 nM of peracetic acid (**b**) under dark incubation in NK system BIOTRON at controlled temperature (21 °C). Controlled or sterilized samples (addition of 2 % solution of $HgCl_2$) conducted under the same condition and same incubation period. *Data source* Mostofa et al. (Manuscript in preparation)

rivers (74 %) where the bacteria are more numerous (of order 10^6 cells mL^{-1}) (Fig. 11a). Similarly, the decay of peracetic acid (ROOH) was 40 % and 85 %, respectively (Fig. 11b). The initial degradation rate is roughly double for ROOH (peracetic acid) than for H_2O_2, thus the concentrations of ROOH found in rivers are generally lower than those of H_2O_2. It is suggested that ROOH compounds are chemically unstable and more reactive than H_2O_2 in natural waters (Mostofa and Sakugawa 2009). Therefore, enzymatic or microbial degradation of peroxides is a rapid process that may control the steady-state concentrations of both H_2O_2 and ROOH compounds in natural waters (Fujiwara et al. 1993; Cooper and Zepp 1990; Zepp et al. 1987; Serban and Nissenbaum 1986; Tanaka et al. 1985).

It has been shown that the algal-catalyzed decomposition of H_2O_2 under dark conditions is second-order overall, first-order with respect to H_2O_2 and first-order with respect to the algal biomass (Petasne and Zika 1997; Zepp et al. 1987; Cooper and Lean 1992). The median second-order rate constant for nine algae is approximately 4×10^{-3} m^3 (mg Chl *a*)$^{-1}$ h^{-1}. Natural levels of the blue-green *Cyanobacterium sp.* can greatly increase the decay rates of H_2O_2, which follow a second-order rate constant of 3.5×10^{-10} L $cell^{-1}$ h^{-1} (Petasne and Zika 1997). Similar kinetics has been observed for *Vibrio alginolyticus*, in which case the decay of H_2O_2 was second-order overall, and first-order in both H_2O_2 concentration and number of bacterial cells (Cooper and Lean 1992). Such a kinetic can be expressed as follows:

$$\text{Rate} = -d\,[H_2O_2]\,/dt = k_2\,[H_2O_2]\ [\text{Number of bacterial cells}] \qquad (4.6)$$

where $k_2 = 1.6 \times 10^{-9}$ mL cell^{-1}min^{-1}. The freshwater bacterium *Enterobacter cloaceae* showed a similar rate constant, $k_2 = 1.5 \times 10^{-9}$ mL cell^{-1} min^{-1}.

4.4 Production and Decay by DOM Photochemistry

Photodegradation of DOM depends on the incident light intensity, which is directly linked to the production of H_2O_2 and ROOH through photoinduced reactions in natural waters (Cooper and Zika 1983; Moore et al. 1993; Baxter and Carey 1983). For example, H_2O_2 concentration gradually increases with irradiation time in natural waters as well as in aqueous solutions of standard organic substances (Fig. 3) (Obernosterer et al. 2001; Cooper et al. 1988). Similarly, a 10–20 times lower H_2O_2 production was observed in river waters during the cold season compared to summer, and in the Southern Ocean in Antarctic regions (5–25 nM) compared to other oceanic environments, respectively (Fig. 9; Table 1). The photodegradation of DOM is greatly influenced by the stratospheric ozone hole events, particularly in Antarctic waters. The ozone hole can increase the fluxes of solar ultraviolet radiation (UVR, 280–400 nm), which may substantially enhance the photoinduced generation of reactive species (H_2O_2, ROOH, $HO^\bullet$, etc.) in natural waters (Yocis et al. 2000; Rex et al. 1997; Qian et al. 2001). For example, a decrease in stratospheric ozone from 336 to 151 Dobson units during an ozone hole event resulted in an increase by 19–42 % in the production of H_2O_2 at the surface of Antarctic waters (Yocis et al. 2000). An increase in ozone hole events can thus cause a higher degree of DOM photodegradation upon generation of highly reactive free radicals.

4.5 Production and Decay by Photosynthesis

As a result of photodegradation of DOM, along with the production of H_2O_2 and ROOH compounds, several other photoproducts such as CO_2, CO or other forms of dissolved inorganic carbon (DIC = sum of dissolved CO_2, H_2CO_3, $HCO_3{}^-$, and $CO_3{}^{2-}$), low molecular weight (LMW) DOM, and thermal energy, E (±) are simultaneously produced in natural waters (Mostofa et al. 2009; Wu et al. 2005; Amador et al. 1989; Moran and Zepp 1997; Wang et al. 2009; Xie and Zafiriou 2009. A general scheme (Eq. 4.7) for the photodegradation of DOM can be expressed as follows (Mostofa et al. 2009a, b):

$$\text{DOM} + h\upsilon \rightarrow H_2O_2 + CO_2/CO/DIC + \text{LMW DOM} + E\ (\pm) \qquad (4.7)$$

H_2O_2 and CO_2 that are simultaneously produced by DOM photodegradation can take part to photosynthesis, to form carbohydrate-type compounds (Eq. 4.8) (Mostofa et al. 2009a, b):

$$xCO_{2(H_2O)} + yH_2O_{2(H_2O)} + h\upsilon \rightarrow C_x\,(H_2O)_y + O_2 + E\,(\pm) \tag{4.8}$$

$$2H_2O_2 + \text{photo}\,(h\upsilon)\ \text{or biological processes} \rightarrow O_2 + 2H_2O\ \text{or unknown oxidants} \tag{4.9}$$

where $C_x(H_2O)_y$ (Eq. 4.8) represents a generic carbohydrate. In natural waters, H_2O_2 acts as a key component together with carbon dioxide (CO_2) to form carbohydrates and oxygen through photosynthesis (Eq. 4.8). The formation of oxygen in the photosynthesis process might also occur via either H_2O_2 disproportionation or biological processes (Eq. 4.9) (Komissarov 2003; Moffett and Zafiriou 1990; Liang et al. 2006; Buick 2008). Note that the contribution of H_2O_2 decay is 65–80 % by catalase enzyme and 20–35 % by peroxidase enzyme, respectively, as estimated by isotopic measurements in seawater (Moffett and Zafiriou 1990). E (±) is the energy produced during photosynthesis. The new concept of photosynthesis was firstly hypothesized in plants by Komissarov (1994, 2003). He proposed that interaction of CO_2 in air and H_2O_2, instead of H_2O, may form carbohydrate in plants. It is interesting to note that during the diurnal cycle, H_2O_2 production is the highest at noon time, thereby simultaneously causing the maximum production of CO_2 or DIC due to photodegradation by H_2O_2 or photoinduced generation of $HO^\bullet$. The new reaction mechanim for photosynthesis (Eq. 4.2) will be discussed in details in photosynthesis chapter "Photosynthesis in Nature: A New Look".

It is demonstrated that microbial consumption is the dominant sink of oceanic carbon monoxide (CO), and that the rate constant (k_{CO}) of microbial CO consumption is positively correlated with chlorophyll *a* (Chl *a*). It is suggested that Chl *a* concentration can be used as an indicator of CO-consuming bacterial activity in natural waters (Xie et al. 2005). Photodegradation and photosynthesis may be important in natural waters with high contents of DOM; photodegradation induces the production of CO_2 and peroxides, which would in turn favor photosysnthesis in the aquatic environments. This would lead to the multiplication of algae, small aquatic plants and phytoplankton. For example, high algal production is operational in some Chinese Lakes during the summer season, which might also be an effect of high DOM photodegradation that favor photosynthesis in lake ecosystems (Mostofa et al. 2009b).

4.6 Production and Decay by Photolytic and Chemical Processes

Production of H_2O_2 and ROOH by photolytic processes may involve their photoinduced formation from DOM under natural sunlight, as explained earlier. The decay of peroxides by photolytic processes (Moffett and Zafiriou 1990; 1993;

Petasne and Zika 1997) may follow two pathways. First, photolytic decomposition of H_2O_2 can occur in seawater (e.g., filtered Vineyard Sound waters) to yield O_2. The photodecomposition was approximately 5 % of the corresponding photoproduction (Moffett and Zafiriou 1990). However, H_2O_2 decomposition typically does not occur in oligotrophic seawater after 2 h of irradiation. This suggests that the contaminants associated with H_2O_2 synthesis in Vineyard Sound samples might be susceptible to the photolytic decomposition of H_2O_2 (Moffett and Zafiriou 1990). Second, H_2O_2 and ROOH can photolytically form free radicals ($R'OOH + h\upsilon \rightarrow RO^{\bullet\prime} + HO^{\bullet}$ where $R' = H$ or R). For example, ROOH compounds are lower in surface seawater than in the deeper layers (Sakugawa et al. 2000). The ROOH compounds are negatively correlated with solar intensity (Sakugawa et al. 2000). This suggests that ROOH may be decomposed by photolytic processes in surface seawater. This result can be justified by the observation of a significant correlation between H_2O_2 and $HO^{\bullet}$ generated photolytically in experiments conducted on river waters, standard Suwannee River Fulvic Acid and DAS1 using a solar simulator Mostofa KMG and Sakugawa H (unpublished), which indicates the photoinduced formation of $HO^{\bullet}$ from H_2O_2. Therefore, decay of peroxides by photolytic processes is a typical phenomenon that may significantly occur in natural waters.

Formation of H_2O_2 and ROOH by chemical processes may include several chain-reactions among various reactant species (Eqs. (3.2–3.5, 3.10–3.12, 3.27). The decomposition of peroxides by chemical processes may involve the Fenton reaction ($H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$) (Fenton 1894), photo-Fenton reaction ($H_2O_2 + Fe^{2+} + h\nu \rightarrow Fe^{3+} + HO^{\bullet} + OH^{-}$) (Zepp et al. 1992), photoferrioxalate reaction ($Fe^{II}(C_2O_4) + H_2O_2 + h\nu \rightarrow Fe^{III}(C_2O_4) + HO^{\bullet} + OH^{-}$) (Safazadeh-Amiri et al. 1997) and other chain reactions (Eqs. 3.7, 3.8, 3.16). Free radical oxidation of H_2O_2 by transition metal ions is one of the most important chemical decomposition processes of H_2O_2 in natural waters (Jeong and Yoon 2005; Fenton 1894; Millero and Sotolongo 1989).

4.7 Physical Mixing Processes

The rates of production and decay of peroxides may be influenced by physical processes, such as the mixing by strong waves in the surface mixing zone (Mostofa KMG and Sakugawa H, unpublished; Scully et al. 1998). Physical mixing by strong waves can facilitate the contact of the reactants and increase the reaction rates. For example, the production rate of H_2O_2 was increased by mechanical stirring during irradiation of seawater (86 nM h^{-1}) and standard Suwannee River Fulvic Acid (445 nM h^{-1}) samples, compared to the same samples that were not stirred (51 and 211 nM h^{-1}, respectively). The photoexperiments on site were carried out with a solar simulator Mostofa KMG and Sakugawa H (unpublished). Mixing phenomena can contribute to the relatively elevated H_2O_2 concentration that is often observed in the mixing zone or in the upper surface layers of lake or seawater (Johnson et al. 1989; Sakugawa et al. 2000; Sikorsky and Zika 1993a, b; Scully et al. 1998). Similarly the vertical convective overturn, which is usually caused by nocturnal cooling in the upper lake or ocean, may greatly decrease the surface H_2O_2 concentration through distribution in the whole water column (Johnson et al. 1989; Sarthou et al. 1997; Yuan and Shiller 2001).

4.8 Salinity Effect on Production of H_2O_2

The photoproduction of H_2O_2 significantly increases with salinity in natural waters (Osburn et al. 2009). The generation of H_2O_2 upon irradiation of ultrafiltered river DOM substantially increases from 15 to 368 nM h^{-1} with increasing salinity at circumneutral pH values (Osburn et al. 2009). The increase in H_2O_2 production with salinity has a linear trend (Eq. 4.10) (Osburn et al. 2009):

$$H_2O_2\ (\mathrm{nM}) = 83.15 \times \text{ salinity } - 69.16\left(r^2 = 0:99, p = 0:001, n = 10\right) \tag{4.10}$$

The apparent quantum yield of H_2O_2 photoproduction from ultrafiltered river DOM, *Qhp*, also increases with salinity from 1.64×10^{-4} to 37.02×10^{-4} (Osburn et al. 2009).

The mechanism of high production of H_2O_2 with salinity is not well documented in ealier studies. It is hypothesiszed that hydrated electrons ($e_{aq}{}^{-}$) are considerably formed in ionic (saline) solution under irradiation. This phenomenon can substantially increase the production of superoxide radical ($O_2{}^{\bullet -}$) and, through disproportionation, of H_2O_2 in aqueous solution. This is evidenced by the photoinduced formation of aqueous electrons ($e_{aq}{}^{-}$) from organic substances and by their high production in NaCl-mixed solutions compared to pure (Milli-Q) water (Fujiwara et al. 1993; Gopinathan et al. 1972; Zepp et al. 1987b; Nakanishi et al. 2002; Assel et al. 1998; Richard and Canonica 2005). In the presence of high salinity it was also observed a significant increase of CDOM loss (10–40 %) and high photoelectrochemical degradation of methyl orange (~48 % increase in 0.5 M NaCl) (Osburn et al. 2009; Zhang et al. 2010). The mechanisms behind the high photoinduced reactivity of DOM with salinity are discussed in details in other chapters (see chapters "Colored and Chromophoric Dissolved Organic Matter in Natural Waters" and "Fluorescent Dissolved Organic Matter in Natural Waters").

4.9 Production Affected by Precipitation

Precipitation in the form of e.g. rain greatly increases the peroxide concentrations in natural waters (Sakugawa et al. 1995; Avery et al. 2005; Cooper et al. 1987; Yuan and Shiller 2000). This might be caused by the mixing of highly concentrated H_2O_2 in rainwater, where the measured levels are 0–110,600 nM in Europe, 17,000–199,000 nM in Brazil, 30–120,000 nM in the USA, 500–34,000 nM in Canada, 24–56,400 nM in Japan and 3,500–82,000 nM in marine areas (Table 1) (Lazrus et al. 1985; Cooper and Lean 1989; Hellpointner and Gäb 1989; Sakugawa et al. 1990, 1993, 2006; Hewitt and Kok 1991; Cooper and Lean 1992; Yuan and Shiller 2000; Miller et al. 2008). ROOH concentrations in rainwater are 400–1600 nM in Europe and 60–6500 nM in the USA (Table 1) (Hellpointner and Gäb 1989; Sakugawa et al. 1993; Hewitt and Kok 1991). The levels of H_2O_2 and ROOH in rainwater (Table 1) usually show some common trends. First, there are strong diel variations with highest concentrations in the afternoon and lowest ones in the night time and in the early morning. Second, high variations are observed between summer and winter, which are presumably caused by high light intensity in summer that induces elevated H_2O_2 production. Rain drops may scavenge H_2O_2 and ROOH generated in the gas phase or within cloud droplets. Because of the observed diel trend, daytime precipitation might be a more important source of peroxides to natural waters compared to the nighttime one.

5 Significance of H_2O_2 and ROOH in the Aquatic Environment

H_2O_2 and ROOH compounds are uncharged, non-radical active oxygen species that may act as oxidants and reductants in natural waters. These features of peroxides are also of importance for their use in chemical reactions and in our daily life. The main effects of H_2O_2 and ROOH can be distinguished as: (1) Natural purifiers in natural waters; (2) Photo-Fenton reaction for the decomposition of organic pollutants; (3) Indicators of microbial changes in bulk DOM; (4) Function as a redox agents in aqueous solution, (5) Medical treatment and commercial uses; (6) Growth of terrestrial vegetation by rainwater H_2O_2 and ROOH; and (7) Oxygen evolution in photosynthesis.

5.1 Natural Purification in Aquatic Ecosystems

H_2O_2 and ROOH compounds are powerful oxidants, which can directly oxidize the DOM or other reactants in natural waters (Draper and Crosby 1984; Ho 1986; Samuilov et al. 2001). Peroxides are formed photolytically from DOM in natural water, and their productions reach maximum at noon time. The photoinduced generation of $HO^\bullet$ from peroxides can degrade organic pollutants or DOM (Gao and Zepp 1998; Brezonik and Fulkerson-Brekken 1998; Goldstone et al. 2002), which accounts for the role of H_2O_2 and ROOH as purifiers in natural waters.

5.2 *Photo-Fenton Type Reaction for Decomposing Organic Pollutants*

One of the key applications of H_2O_2 is its use in the degradation of organic pollutants in the wastewater treatment industry by means of Fenton's reaction (Fe^{2+} and H_2O_2), photo-Fenton reaction (UV/Visible-Fe^{2+}/H_2O_2, $\lambda < 580$ nm), UV/Visible-ferrioxalate/H_2O_2 reaction and ozone with H_2O_2 (Zepp et al. 1992; Voelker et al. 1997; Fenton 1894; Safazadeh-Amiri et al. 1997; Glaze and Kang 1989; Tizaoui et al. 2007). Among many other applied technologies, these four are major commercialized technologies.

5.3 *Indicators for Microbial Modification of Bulk DOM*

ROOH compounds are significantly produced in natural waters under dark conditions (Figs. 1 and 2) and are more concentrated in deep seawater than in the surface layer (Sakugawa et al. 2000). Net ROOH formation (dark production minus dark consumption) is observed in both filtered and unfiltered river waters (Fig. 2). In contrast, net H_2O_2 formation is only observed in filtered waters. The microbial modification of bulk DOM can yield ROOH compounds in natural waters. Microbially-induced changes in the bulk DOM composition are in agreement with the observation of a red shift of the fulvic acid-like fluorescence (peak C) with an increase in fluorescence in deeper lake or seawaters (Hayase and Shinozuka 1995; Mostofa et al. 2005; Moran et al. 2000). Therefore, dark production of organic peroxides could be a useful indicator for the microbial modification of bulk DOM in aquatic environments.

5.4 *Function of H_2O_2 as an Oxidizing-Reducing Agent in Aqueous Solution*

On the basis of the reduction potential V, the oxidizing agents in aqueous solution can be classified according to the following order: Fluorine ($V = 3.0$) > Hydroxyl radical ($HO^\bullet$) ($V = 2.8$) > Ozone ($V = 2.1$) > Peracetic acid (ROOH) ($V = 1.8$) > H_2O_2 ($V = 1.8$) > Potassium permanganate ($V = 1.7$) > Hypochlorite ($V = 1.5$) > Chlorine dioxide ($V = 1.5$) > Chlorine ($V = 1.4$) (Buettner 1993).

H_2O_2 and ROOH compounds act as intermediates in the reduction of oxygen in natural waters. They can act as oxidants or reductants in their reactions with metal ions (Moffett and Zika 1987a, b). For example, H_2O_2 and ROOH compounds can oxidize Cu(I) and Fe(II) in natural waters (Moffett and Zika 1987a, b), a process that can be schematically generalized as follows:

$$M^{n+} + R'OOH \rightarrow M^{(n+1)+} + R'O^\bullet + OH^- \ (R' = \text{H or R}) \qquad (5.1)$$

$$M^{n+} + R'O^{\bullet} + H^{+} \rightarrow M^{(n+1)+} + R'OH \quad (5.2)$$

On the other hand, the reduction of Cu(II) and Fe(III) by H_2O_2 and ROOH compounds (Moffett and Zika 1987a; Moffett and Zika 1987) can be generalized in the following scheme:

$$R'OOH \rightleftharpoons H^{+} + R'O_2^{-} \left(R' = H \text{ or } R\right) \quad (5.3)$$

$$M^{(n+1)+} + R'O_2^{-} \rightarrow M^{n+} + R'O_2^{\bullet} \quad (5.4)$$

$$HO_2^{\bullet} \rightleftharpoons H^{+} + O_2^{\bullet -} \quad (5.5)$$

$$M^{(n+1)+} + O_2^{\bullet -} \rightarrow M^{n+} + O_2 \quad (5.6)$$

These reactions have already been verified for various chemical and biochemical processes in natural waters.

5.5 *Medical Treatment and Commercial Uses of H_2O_2*

H_2O_2 therapy is commonly used in bio-medical sciences. The singlet oxygen atoms produced from H_2O_2 in the human body ($H_2O_2 \rightarrow H_2O + O_1$) can kill or severely inhibit the growth of anaerobic organisms (bacteria and viruses that use carbon dioxide for fuel and leave oxygen as a by-product) (Gorren et al. 1986). Bacteria and viruses do not have an enzyme coating, thus they are easily oxidized by O_1. Application of H_2O_2 is particularly effective for asthma, leukemia, multiple sclerosis, degenerative spinal disc disease, high blood pressure and wound care (Gorren et al. 1986; Nathan and Cohn 1981). In addition, H_2O_2 is widely used to bleach textiles and paper products, in processing foods, minerals, petrochemicals, consumer products (detergents), and in some daily uses such as cleaning and sanitizing the kitchen, soaking the toothbrush to prevent transfer of germs, cleaning vegetables and fruits for freshness and good taste.

5.6 *Growth of Terrestrial Vegetation by Rainwater's H_2O_2 and ROOH*

High concentrations of H_2O_2 (0–199000 nM) and ROOH (60–6500 nM) in rainwater (Table 1) should be able to promote photosynthesis in plants and algae (Komissarov 1995, 2003; Mostofa et al. 2009a, b). The detailed mechanism in that regard has been discussed in photosynthesis chapter (see chapter "Photosynthesis in Nature: A New Look"). The occurrence of H_2O_2 and ROOH in rainwater could thus contribute to the good health and efficient growth of plants. However, high concentrations of H_2O_2 (50–100 μM) in the presence of iron (Fe) and oxalate can generate $HO^•$ that would decrease the plant productivity and growth (Kobayashi et al. 2002). Furthermore, the ability of H_2O_2 and ROOH compounds to act as anti-bacterial and anti-fungal agents additionally suggests that an optimal level of peroxides could play a positive role toward good health and efficient growth of earth's plants.

5.7 *Role of H_2O_2 in Oxygen Production by Photosynthesis*

Photosynthetic O_2 evolution involves different stages that carry out a gradual accumulation of oxidizing equivalents in the Mn-containing water-oxidizing complex (WOC) (Samuilov et al. 2001). The WOC can exist in different oxidation states (S_n, where high n indicates the most oxidised states), which can be probed by addition of different redox-active molecules. The interaction of H_2O_2 with the S states of the WOC is depicted in the scheme below (Fig. 12) (Samuilov et al. 2001):

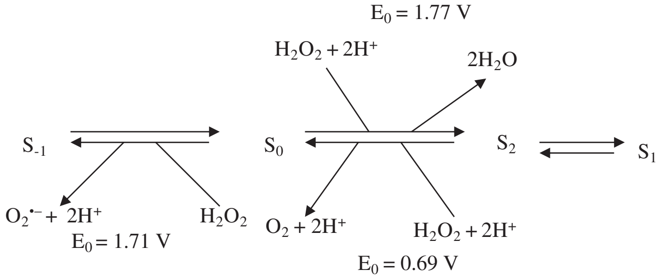


Fig. 12 Different oxidation states of H_2O_2 and its interaction with the S states of the water-oxidizing complex. *Data source* Samuilov et al. (2001)

6 Impacts of H_2O_2 and ROOH in Natural Waters

H_2O_2 and ROOH compounds are uncharged and non-radical active oxygen species, and capable of acting as oxidants and reductants in chemical reactions in natural waters. These properties have some impact on the aquatic organisms, which can be listed as follows: (1) Acid rain; (2) Inhibition of photosynthetic electron transport in cells of cyanobacteria; (3) Effect of H_2O_2 on bacterial growth in waters; and (4) Impact of H_2O_2 on microbial quality of recreational bathing waters.

6.1 Acid Rain

H_2O_2 and ROOH compounds are key components in the conversion of dissolved sulfur dioxide (SO_2) to sulfate (SO_4^{2-}) or sulfuric acid (H_2SO_4) in atmospheric clouds (Sakugawa et al. 1990; Zuo and Hoigné 1993). Sulfuric acid (SO_4^{2-}) can be formed in cloud drops by reaction of HSO_3^- with H_2O_2 (Eq. 3.7) and is a major contributor to acid precipitation to the earth surface.

6.2 Inhibition of Photosynthetic Electron Transport in Cells of Cyanobacteria

H_2O_2 can control a large number of stages of cell metabolism, including those involved in the induction of programmed cell death (Samuilov et al. 2001). H_2O_2 can inhibit growth at concentrations as low as 10^{-5}–10^{-4} M under the conditions of a dialysis culture (Samuilov et al. 2001). H_2O_2 can inhibit the photosynthetic electron transport in cells of cyanobacteria (Samuilov et al. 2001, 2004). It can also destroy the function of the oxygen-evolving complex (OEC) in some chloroplasts and photosystem II preparations, causing release of manganese from the cyanobacterial cells, which inhibits the OEC activity.

6.3 Impact of H_2O_2 on Bacterial Growth in Aquatic Ecosystems

Bacterial growth has a seasonal variability, reaching the maximum in spring to early summer and greatly decreasing in summer, e.g. when water temperature in lakes becomes higher than 25.5 °C (Zhao et al. 2003). Sunlight inactivates bacteria in seawater (Fujioka et al. 1981), which suggests that some photoinduced processes may be involved. The bacterial abundance is commonly affected by water temperature (Zhao et al. 2003; Darakas 2002), but the latter is directly connected with solar radiation that can generate strong oxidizing agents such as peroxides (H_2O_2 and ROOH), $O_2^{\bullet -}$ and $HO^{\bullet}$. These reactive species can reduce the activity of the catalase, peroxidase and superoxide dismutase enzymes present in bacterial cells, DOM, algae and phytoplankton. Bacterial cells protect themselves from the oxidizing species (H_2O_2, $O_2^{\bullet -}$ and $HO^{\bullet}$) by adjusting the level of their enzymes (Chance et al. 1979). An experimental study conducted on marine invertebrates suggests that H_2O_2-scavenging enzymes can protect against external photodynamic effects and internal respiratory by-products (Dykens 1984). It can be assumed that the activity of the enzymes in dealing with the external effects would decrease their ability to scavenge the internal by-products, with harmful effects for the organisms. Low levels of H_2O_2 (~100 nM) affect oxidative stress to bacteria in coastal waters by increasing the concentration of the catalase enzyme. The diurnal periodicity of catalase activity matched the diurnal changes of H_2O_2 (Clark et al. 2008; Angel et al. 1999). The effects of H_2O_2 and peroxides can be particularly important during the summer season when their levels are higher. Moreover, ozone hole events in Antarctic waters may greatly increase photodegradation processes that can generate reactive free radicals and peroxides, with a damaging influence on biogeochemical cycles in Antarctic waters (Diffey 1991; Smith et al. 1992; Randall et al. 2005).

6.4 Impacts of H_2O_2 on Microbial Quality of Recreational Bathing Waters

Microbial water quality is assessed from the concentration of fecal indicator bacteria (FIB) because of their adverse health effects (Cabelli et al. 1979; US Environmental Protection Agency 2000; Wade et al. 2003. Frequent FIB contamination episodes in the surf zone resulted in multiple beach closures in the USA (Boehm et al. 2002). It is shown that elevated levels of H_2O_2, ROOH, superoxide ($O_2^{\bullet -}$) and hydroxyl radical, photolytically produced, can cause damage and cell lysis in microorganisms. This may result into high FIB mortality in recreational bathing waters (Gonzalez-Flecha and Demple 1997; Weinbauer and Suttle 1999; Mitchell and Chamberlin 1975; Clark et al. 2008). It is estimated that approximately ~100 nM of H_2O_2 can cause oxidative stress to bacteria in waters (Angel et al. 1999). Diurnal cycles of FIB mortality in the surf zone (Clark et al. 2008; Boehm et al. 2002), which well resemble the diurnal cycle of H_2O_2, suggest that the FIB mortality may be linked to the photoinduced generation of H_2O_2 and ROOH in sunlit surface waters.

7 Role of H_2O_2 in the Origin of Autochthonous DOM and of other Oxidising Agents

H_2O_2 can contribute to the production of autochthonous DOM by different important processes. First, it is involved in the photosysthesis process that is a major source of organic matter (e.g. algae) (Mostofa et al. 2009a, b). The photoinduced and microbial assimilation of organic matter, including algae, can produce autochthonous DOM in natural waters (Mostofa et al. 2009b; Fu et al. 2010; Harvey et al. 1995; Carrillo et al. 2002; Coble 2007; Yamashita and Tanoue 2004; Yamashita and Tanoue 2008). Coherently, a correlation has been observed between production of organic carbon and concentration of photolytically formed H_2O_2 (Anesio et al. 2005). The autochthonous production of DOM (Mostofa et al. 2005; Yoshioka et al. 2002) is typically observed during the summer season, and a major DOM component that is produced is autochthonous fulvic acid, often termed sedimentary fulvic acid (Hayase and Tsubota 1985). Other produced compounds include marine humic substances (Coble 1996, 2007), carbohydrates and unknown substances (Fu et al. 2010; Mostofa et al. (Manuscript In preparation); Hamanaka et al. 2002; Hayakawa 2004; Farjalla et al. 2006).

Second, H_2O_2, formed photolytically from water using UV radiation, can react with CO_2 under abiogenic conditions to produce various organic substances (CH_2O, HCOOH, CH_3OH, CH_4, and $C_6H_{12}O_6$; Eqs. 7.1–7.5, respectively) in the aqueous solutions (Lobanov et al. 2004). The reactions between H_2O_2 and CO_2 as well as their thermodynamic parameters such as enthalphy changes (ΔH^0) and the Gibbs free energy changes (ΔG^0) are mentioned as follows (Lobanov et al. 2004):

$$H_2O_2 + CO_2 \rightarrow CH_2O + 3/2O_2 \tag{7.1}$$

$$\Delta H^0 = 465\,\text{kJ}, \Delta G^0 = 402\,\text{kJ}$$

$$H_2O_2 + CO_2 \rightarrow HCOOH + O_2 \tag{7.2}$$

$$\Delta H^0 = 172\,\text{kJ}, \Delta G^0 = 166\,\text{kJ}$$

$$2H_2O_2 + CO_2 \rightarrow CH_3OH + 5/2O_2 \tag{7.3}$$

$$\Delta H^0 = 530\,\text{kJ}, \Delta G^0 = 464\,\text{kJ}$$

$$2H_2O_2 + CO_2 \rightarrow CH_4 + 3O_2 \tag{7.4}$$

$$\Delta H^0 = 649\,\text{kJ}, \Delta G^0 = 580\,\text{kJ}$$

$$H_2O_2 + CO_2 \rightarrow 1/6C_6H_{12}O_6 + 3/2O_2 \tag{7.5}$$

$$\Delta H^0 = 426\,\text{kJ}$$

Therefore, these organic substances produced photolytically may play an important role in biogeochemical processes in natural waters.

Third, H_2O_2 can react with nitrous acid to yield peroxynitrous acid, a powerful nitrating agent and an important intermediate in atmospheric chemistry (Vione et al. 2003). The kinetics of the reaction is compatible with a rate-determining step involving either $H_3O_2^+$ and HNO_2, with rate constant $179.6 \pm 1.4\ M^{-1}\ s^{-1}$, or H_2O_2 and protonated nitrous acid, with rate constant $1.68 \pm 0.01 \times 10^{10}\ M^{-1}\ s^{-1}$ (diffusion-controlled reaction) (Vione et al. 2003). Thus, H_2O_2 might be a key environmental factor in atmospheric oxidative chemistry.

8 Scope of the Future Challenges

The determination of H_2O_2 and ROOH as well as their spatial–temporal variations, sources, production and decay mechanisms have been examined in natural waters. Compared to H_2O_2, relatively little attention is paid to the determination of ROOH compounds and their concentrations in natural waters. Investigations based on the detection of ROOH would be crucial to improve the understanding of the photoinduced processes along with H_2O_2 generation in natural waters. Limited attention is also devoted to what fractions of DOM are most involved in the photoinduced production of peroxides in freshwater and marine environments. Other important research demands for future challenges are the following: (i) Identification of the DOM components involved into the production of H_2O_2 in freshwater and marine water. (ii) Elucidation of the temperature and pH effect on the production of H_2O_2 and ROOH compounds by aquatic DOM components and standard organic substances. (iii) Clarification of the correlation between diurnal variations of H_2O_2 and ROOH levels in natural waters and DOM concentration. (iv) Investigation of the role of the photo-Fenton reaction in the production of peroxides in iron-rich waters. (v) Elucidation of the relationship between peroxides and free radicals. (vi) Study of the dark production of H_2O_2 and ROOH by phytoplankton, algae and bacteria in fresh and marine waters. (vii) Effect of variable diurnal levels of H_2O_2 on bacteria in DOM-rich waters. (viii) Detection of ROOH compounds generated photochemically by standard organic substances in aqueous solution and by DOM components in natural waters.

Problems

(1) Explain the nature and biogeochemical function of H_2O_2 and ROOH in natural waters.
(2) Discuss the steady-state concentration of H_2O_2 and ROOH in natural waters
(3) Explain how H_2O_2 acts as REDOX agent.
(4) Explain the mechanisms of photoinduced generation of H_2O_2 and ROOH in the gas phase and in natural waters.
(5) How does fulvic acid photolytically produce H_2O_2 and ROOH in natural waters?
(6) What are the sources of H_2O_2 in natural waters?
(7) What factors are involved in the diurnal cycle of H_2O_2 production in natural waters?
(8) Explain the controlling factors for the decay of H_2O_2 and its decay mechanism by biological processes in natural waters.
(9) What is the importance of H_2O_2 and ROOH?
(10) Which is the impact of H_2O_2 on organisms?
(11) What is the link between H_2O_2, photosynthesis and the autochthonous production of DOM in natural waters?
(12) How does H_2O_2 differ chemically from ROOH?
(13) What is the principle of H_2O_2 and ROOH measurement by the fluorometric method?
(14) In a diurnal cycle in river water, the concentration of H_2O_2 gradually increased from 4 to 69 nM in the period from before sunrise to noon and

then gradually decreased to 20 nM. What is the concentration of H_2O_2 accounted for by diurnal effects in the river waters?

(15) What is the steady state concentration of H_2O_2 in natural waters? Find out the production of H_2O_2 in a natural water when its steady-state concentration is 350 nM, microbial degradation 20 nM, and consumption by DOM photodegradation 30 nM.

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