Water Research 123 (2017) 642–654

Contents lists available at ScienceDirect

Water Research

journal homepage: www.elsevier.com/locate/watres

Photochemical generation and decay kinetics of superoxide and hydrogen peroxide in the presence of standard humic and fulvic acids

Manabu Fujii*, Erika Otani

Department of Civil and Environmental Engineering, Tokyo Institute of Technology, 2-12-1-M1-22 Ookayama, Tokyo 152-8552, Japan

ARTICLE INFO

Article history:
Received 3 May 2017
Received in revised form
7 July 2017
Accepted 7 July 2017
Available online 9 July 2017

Keywords:
Reactive oxygen species
Photochemistry
Humic substance
Aromatic moiety

ABSTRACT

Reactive oxygen species (ROS) such as superoxide (O_2^-) and hydrogen peroxide (H_2O_2) can be photochemically generated in aerobic waters containing natural organic matters (NOM) such as humic substances (HS). To investigate the effect of NOM molecular composition on the kinetics and mechanism of ROS transformation, photochemical O_2^- generation and subsequent H_2O_2 production via catalyzed and uncatalyzed (bimolecular dismutation) O_2^- decay were examined in the presence of 14 types of HS (pH 8.0). By using chemiluminescence and colorimetric techniques, the photochemical O_2^- generation rate, quasi-steady-state O_2^- concentration, catalyzed and uncatalyzed O_2^- decay rates, and H_2O_2 production rate were found to vary significantly by factors of 72, 18, 14, 320, and 7.7, respectively, depending on the type of HS and degree of photolysis. For more than half of the HS samples, both uncatalyzed and catalyzed reductive decay of photogenerated O_2^- were significantly involved in H_2O_2 generation, and their rates were comparable to those for O_2^- oxidative decay in which H_2O_2 is not generated. These results suggest that the chemical quality of HS influenced the H_2O_2 generation pathway. Correlation analyses indicated that rate constants associated with HS-mediated photochemical O_2^- and H_2O_2 generation are significantly correlated with HS molecular composition including total and aromatic C contents. In particular, practical indices representing NOM aromaticity including specific ultraviolet absorbance (SUVA) can be useful for predicting NOM-mediated ROS generation and decay kinetics. Overall, the present work suggests that NOM concentration and its quality influence NOM-mediated ROS dynamics in aqueous systems.

1. Introduction

Sequential reductions of dissolved triplet dioxygen ($^3O_2$) produce superoxide (O_2^-), hydrogen peroxide (H_2O_2), hydroxyl radicals ($OH^\bullet$) and ultimately water molecules. These intermediate products, in addition to singlet dioxygen ($^1O_2$), are commonly observed reactive oxygen species (ROS) in natural and effluent waters (Rusak et al., 2011; Vione et al., 2014; Zhang et al., 2014). Due to their high reactivity in aquatic solutions, ROS mediate a range of redox reactions that involve transition metals (Fujii et al., 2006; Millero and Sotolongo, 1989), natural organic matter (NOM) (Cory et al., 2010; Goldstone and Voelker, 2000), engineered nanoparticles (Aiken et al., 2011; Li et al., 2016) and organic contaminants (Pignatello et al., 2006; Porras et al., 2016; Rosario-Ortiz et al., 2010). Therefore, ROS are involved in a variety of important processes that determine the solubility, bioavailability, and toxicity of metals in addition to the fates of organic compounds in both natural and engineered aqueous systems.

In the last three decades, H_2O_2 dynamics in natural waters have been extensively investigated. The concentration of this relatively stable intermediate, with a half-life of a few hours to days, is typically observed up to several hundred nanomolars in a range of surface waters (Table 1). The quasi-steady-state concentration of H_2O_2 can be controlled by the balance of generation including photochemical reactions of colored dissolved organic matter (CDOM) such as humic substances (HS), microbial activity, and catalytic reactions (e.g., enzymatic or inorganic redox reactions such as those with Cu, Mn, Fe, and Cr) with the significance of each factor varying temporally and spatially (Cooper and Zika, 1983; Cooper et al., 1988; Garg et al., 2011; Moffett and Zafiriou, 1993; Moffett and Zika, 1987; Rusak et al., 2011; Shaked et al., 2010; Vermilyea et al., 2010b; Wilson et al., 2000; Wuttig et al., 2013b). For example, irradiation by near-ultraviolet (near-UV) light of

---

* Corresponding author.
E-mail address: fujii.m.ah@m.titech.ac.jp (M. Fujii).

http://dx.doi.org/10.1016/j.watres.2017.07.015

Table 1
Superoxide and hydrogen peroxide concentrations and their rate constants for generation and decay in natural waters.[a]

References	Study sites/media	$[O_2^-]_{QSS}$ (nM)	$[H_2O_2]_{QSS}$ (nM)	k_{decay} ($\times 10^{-2}$, s^{-1})	$k_{decay\text{-}DTPA}$ ($\times 10^{-2}$, s^{-1})	$d[O_2^-]/dt$ (pM s^{-1})	$d[H_2O_2]/dt$ (pM s^{-1})
Present study	HS solutions (1 mg L^{-1})[b]	1.6–22			0.017–0.21	4.8–350[d]	1.8–14[d]
Garg et al. (2011)	SRFA solution (0.1–1.0 mg L^{-1})	~10–40			0.66[b]	48–480[d]	~3–~65[d]
Goldstone and Voelker (2000)	Chesapeake Bay	0.01–0.07			30–140[c]		
	Cape Cod Bay				11–70		
	HS solutions (1 mg L^{-1})[b]				1.0–7.4[b]		
Petasne and Zika (1987)	Biscayne Bay	55–86		0.058		78–170[d]	25–62[d]
Zafiriou (1990)	Orinoco River				240–560		
	Gulf of Paria				350–370		
	Caribbean seawater				<110		
Rose et al. (2010)	Great Barrier Reef lagoon[m]	0.087–1.1	5–107	0.7–4.3[f]		1–16[e]	
	Great Barrier Reef lagoon[o]			~20[f,g]			
Rose et al. (2008)	Equatorial Pacific Ocean	0.015–0.17		<0.01–0.97[f]			<0.3[e]
Rusak et al. (2011)	Seawater east of New Zealand[m]	<0.2–33	8.5–139	1.9–2.8		0.01–1.3[e]	0.47–16[d]
Hansard et al. (2010)	Gulf of Alaska	<0.02–0.55		0.2–1.6		<0.28–5.6[e]	<0.03–~0.67[e]
Heller and Croot (2010a)	Eastern Tropical North Atlantic				0.93–3.4		
Heller and Croot (2010b)	Antarctic seawater, Southern Ocean			0.36–7.5[c,f]			
Wuttig et al. (2013a)	Eastern Tropical North Atlantic			0.9–8.6[f,g]	0.6–8.9		
Micinski et al. (1993)	Eastern Caribbean[m]					0.03–2.2[d]	
Shaked et al. (2010)	Gulf of Aqaba, Red Sea		10–90	2.5–4.6[f]			
Cooper and Zika (1983)	Freshwaters (inc. Chechessee River)		88–320				
	Ground waters (inc. Wells in Miami)		ND[h]				
Cooper et al. (1988)	Freshwaters (inc. Volga River)		90–320				
	Seawaters (inc. Gulf of Mexico)		8–240				
	Estuarine waters (inc. Chesapeake Bay)		3–75				
	Freshwaters (inc. Peacock River)						0-2056[d,i]
Cooper and Lean (1989)	Jacks Lake[j,n]		200–400				
	Jacks Lake[k,n]		<10				
Vermilyea et al. (2010b)	Gulf of Alaska[n]		31–224				<0.14–2.2[e]
Vermilyea et al. (2010a)	Freshwaters (pond and lakes)[n]		414–512				8.1–34[e]
Wilson et al. (2000)	Hot springs (Yellowstone National Park)[j,n]		200–600				
	Hot springs (Yellowstone National Park)[k,n]		<50				
Others [l]	Seawaters						0.58–2.7
	Coastal seawaters						1.0–84

[a] All references are listed in the reference section. $[O_2^-]_{QSS}$ and $[H_2O_2]_{QSS}$ represent quasi-steady-state concentrations for O_2^- and H_2O_2, respectively; k_{decay} is the decay rate for O_2^-; $k_{decay\text{-}DTPA}$ is the decay rate for O_2^- in the DTPA-amended medium; $d[O_2^-]/dt$ represents photochemical or dark O_2^- production rates; and $d[H_2O_2]/dt$ represents photochemical and dark H_2O_2 production.
[b] Values were standardized by using a 1 mg L^{-1} HS solution.
[c] Uncatalyzed dismutation dominates in O_2^- decay in the DTPA-amended solution.
[d] Photochemical production dominates.
[e] Nonphotochemical production dominates.
[f] Catalyzed by trace metals (e.g., Cu, Mn, and Fe).
[g] Catalyzed by organic matter.
[h] Lower than detection limit (subnanomolar).
[i] Filtration of samples insignificantly affected the results.
[j] Measurement in daytime.
[k] Measurement at night.
[l] Summary of H_2O_2 production rates presented in Table 1 of the work by Vermilyea et al. (2010b).
[m] Both filtered and unfiltered samples.
[n] Unfiltered samples.
[o] In case of $[O_2^-]$ concentration greater than 10 nM.

ground waters, whose H_2O_2 concentration is typically negligible compared to those observed in surface waters, significantly generates H_2O_2 with the generation rate positively correlating with the initial organic carbon concentration (Cooper and Zika, 1983). In such waters, organoperoxide production may be minor compared with that of H_2O_2. Concentration of H_2O_2 is more prone to increase under conditions where a higher O_2^- concentration is achieved or superoxide dismutase (SOD) is concurrently present (Cooper and Zika, 1983; Garg et al., 2011; Rose et al., 2010). This evidence indicates that O_2^- is most likely the key intermediate in H_2O_2 generation, although O_2^- decay does not necessarily produce H_2O_2. Field observations indicate that H_2O_2 concentration in surface waters is generally elevated during the daytime and decreases during the night (Cooper and Lean, 1989; Shaked et al., 2010; Wilson et al., 2000). Therefore, photochemical processes are considered to be important in H_2O_2 generation in natural and effluent surface waters where light attenuation by the water column is minimized (Cooper and Zika, 1983; Rusak et al., 2011; Shaked et al., 2010; Wilson et al., 2000; Zhang et al., 2014). In contrast, more recent findings suggest that the dark (i.e., biological) H_2O_2 generation associated with particles, such as chlorophyll present in unfiltered samples, is as important to or, in some cases, supersedes photochemical generation in surface seawaters (Hansard et al., 2010; Vermilyea et al., 2010a, 2010b), brackish and freshwater ponds (Zhang et al., 2016) and agricultural headwater streams (Dixon et al., 2013).

Compared to H_2O_2, O_2^- in natural waters has been less studied