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# Simultaneous photoinduced generation of $\text{Fe}^{2+}$ and $\text{H}_2\text{O}_2$ in rivers: An indicator for photo-Fenton reaction

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## ARTICLE INFO

### Article history:

Received 16 October 2015

Revised 26 December 2015

Accepted 28 December 2015

Available online 13 February 2016

### Keywords:

Photo-Fenton reaction

$\text{Fe}^{3+}$

$\text{Fe}^{2+}$

Dissolved organic matter

$\text{H}_2\text{O}_2$

Light

## ABSTRACT

The photo-Fenton reaction is a key source of the highly reactive hydroxyl radical ( $\text{HO}^\cdot$ ) that is produced by the reaction of simultaneous photo-induced generation of  $\text{Fe}^{2+}$ -dissolved organic matter (DOM) with  $\text{H}_2\text{O}_2$  in sunlit surface waters as well as in the treatment of organic pollutants in the advanced oxidation processes (AOPs). Concentrations of both  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ -DOM were dependent on time and total solar intensity flux, and their levels were highest in the diurnal samples collected at noon compared with the samples collected during the period before sunrise and after sunset.  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ -DOM concentrations during monthly readings were also found higher in comparison with the diurnal samples, shortly before sunrise or after sunset. A  $\pi$ -electron bonding system is formed between Fe and the functional groups in DOM (Fe-DOM), through electron donation from the functional groups of DOM to an empty  $d$ -orbital of Fe. The  $\pi$ -electron is loosely bound and is highly susceptible to a rapid excitation upon light exposure that will provide better understanding of the formation of aqueous electrons, superoxide radical anions,  $\text{H}_2\text{O}_2$  and finally, photo-Fenton reactions, too. Our results imply that simultaneous generation of  $\text{H}_2\text{O}_2$  and  $\text{Fe}^{2+}$ -DOM upon sunlight exposure during the daytime is most likely to be the key photo-Fenton reaction pathway, taking place in surface waters.

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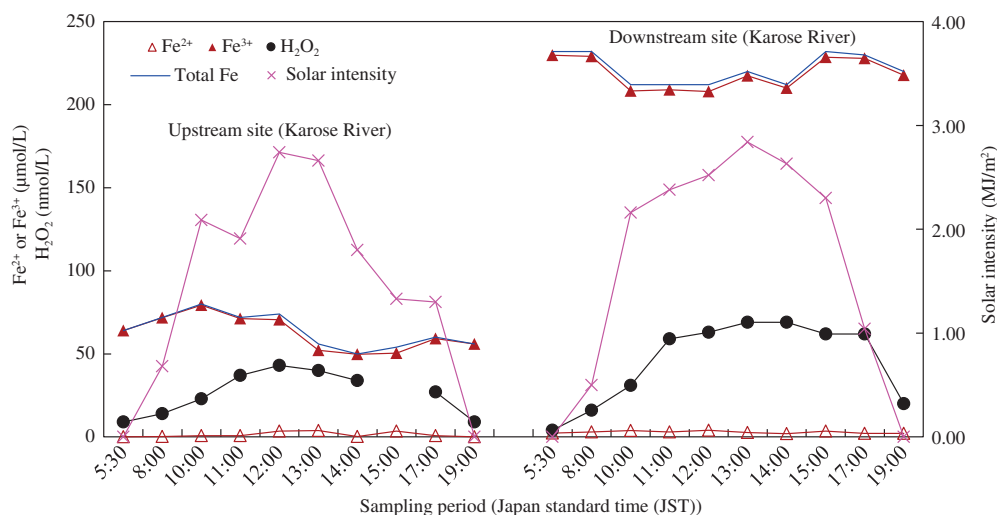
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## Introduction

The photo-Fenton reaction, an advanced oxidation technology, is one of the key processes for the production of hydroxyl radicals ( $\text{HO}^\cdot$ ) and can be extensively used in the treatment of organic pollutants or recalcitrant organic compounds (e.g., bisphenol A) in wastewater (Nakatani et al., 2007; White et al., 2003; Zepp et al., 1992). Correspondingly, this process is also responsible for the photooxidation of high and low molecular weight dissolved organic matter (DOM), thereby producing low molecular weight intermediates, as well as other mineralisation products such as  $\text{CO}_2$ , dissolved inorganic

carbon (DIC: dissolved  $\text{CO}_2$ ,  $\text{H}_2\text{CO}_3$ ,  $\text{HCO}_3^-$ , and  $\text{CO}_3^{2-}$ ),  $\text{NH}_4^+$ ,  $\text{PO}_4^{3-}$ , and so on (Mostofa et al., 2013). These photoproducts play an important role in the cycling of carbon, nitrogen, and phosphorus, and participate in the food chains for the growth of microbes in the aquatic environment. It has been shown that the photo-Fenton reaction accounts for more than 70% of total photochemical  $\text{HO}^\cdot$  production in Satilla River water (White et al., 2003). This process is expected to be the main contributor to  $\text{HO}^\cdot$  photo-production in iron-rich waters, either in rivers or lakes (Nakatani et al., 2007; Vione et al., 2006; White et al., 2003). Conversely, rivers generally contain high amounts (up to 80% of total DOM) of humic substances

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**Fig. 1** –  $\text{Fe}^{2+}$  (a, d),  $\text{Fe}^{3+}$  (b, e) and  $\text{H}_2\text{O}_2$  (c, f) concentrations as a function of time and total solar intensity ( $\text{MJ}/\text{m}^2\cdot\text{hr}$ ) in the upstream waters (site KR2, Shouri) on 21 August 2003 and in the downstream waters (site KR6, Hinotsume) on 26 September 2003 of the Kurose River.

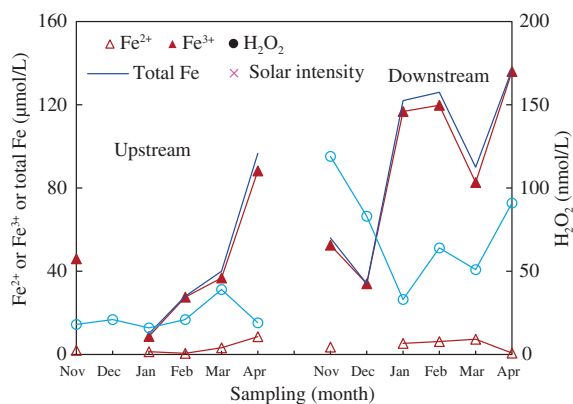
(fulvic and humic acids), which can form complexes with dissolved  $\text{Fe}^{2+}$  (Hopwood et al., 2015; Mostofa et al., 2013; White et al., 2003). Note that over 99% of dissolved Fe is strongly complexed with the functional groups of DOM in marine waters (Kondo et al., 2012; Su et al., 2015). The conditional complexation (or binding) constants of  $\text{Fe}^{2+}$  with DOM that is leached by water from vegetation and detritus is in the order of  $\log K_{\text{Fe(II)}-\text{DOM}} = 7-8$  (Hopwood et al., 2015). Moreover, it has been shown that approximately 87% of the iron can be removed from the dissolved phase after 30 days, but iron does not flocculate until a major fraction of DOM is removed by photochemical degradation and flocculation (>10 days) (Helms et al., 2013). It was also suggested that during the initial 10 days, there were sufficient organic ligands present or the pH was low enough to keep iron in the solution (Helms et al., 2013). The binding of DOM with dissolved Fe is, therefore, a regular phenomenon that

could play an important role in photochemistry as well as in other biogeochemical phenomena. On the other hand, hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) is ubiquitously present in natural waters and is essential for several redox reactions. Fulvic acid is thought to be a dominant source of  $\text{H}_2\text{O}_2$  in river waters, accounting for 23%–70% of  $\text{H}_2\text{O}_2$  production (Mostofa and Sakugawa, 2009). Therefore, it is vital to simultaneously detect of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  to better understand the importance of the photo-Fenton reaction during the daytime, which still remains unclear in field conditions.

## 1. Materials and methods

The Kurose River is approximately 43 km long and originates in mountains that are largely covered by dense forest. The Kurose River flows over both urban and agricultural areas of the Kamo plateau region including the Higashi-Hiroshima City, then into the Seto Inland Sea. Water samples were collected from one upstream site, Shoriki, and one downstream site, Hinotsume, in the Kurose River on 21 August and 26 September 2003, respectively, from before sunrise (5:30, Japan Standard Time (JST)) to after sunset (7:00 JST). The upstream water (Shoriki) is mostly affected by pine forests in mountains (up to 670 m elevation). While downstream water (Hinotsume) is located near rice fields and low populated areas, crossing the Higashi-Hiroshima City, and about 25 km from the upper reach of the Kurose River. A description of each sampling site and mapping of the river is provided elsewhere (Mostofa et al., 2005).

$\text{H}_2\text{O}_2$  was measured with a fluorometric method using a flow injection analyzer (auto sampler: TOSOH, model AS8020; plunger pump: Sanuki Ind. Co., model 4P2U-4016; fluorescence detector: Shimadzu: RF-10AXL, recorder: Shimadzu: C-R5A Chromatopac) described elsewhere (Fujiwara et al., 1993). In brief, 1 mL of a sample was first treated with catalase (20  $\mu\text{L}$ , 500 units/mL) for 6 min and was used as a blank. Similarly, 1 mL of the same sample, wherein the catalase was



**Fig. 2** – Variation of the  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{H}_2\text{O}_2$  concentrations during monthly readings in the upstream (site KR2) and downstream (site KR6) waters of the Kurose River. These monthly readings were conducted from November 2002 to April, 2003 (see Mostofa and Sakugawa, 2009 for a detailed description).

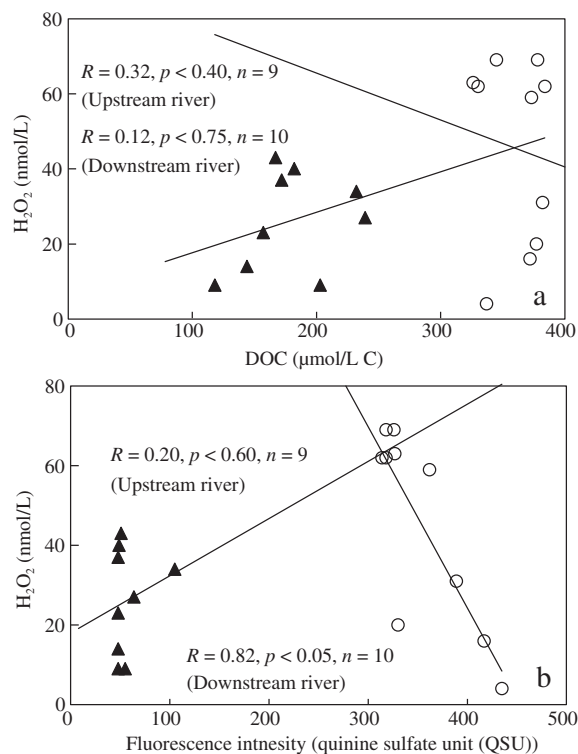
replaced with 20  $\mu\text{L}$  of MQ water, was used to obtain the signal from  $\text{H}_2\text{O}_2$ . The reactions were stopped using peroxidisemixed *p*-hydroxyphenylacetic acid. The difference in the fluorescence values (measured at excitation/emission = 320/400 nm) between samples treated with catalase and without the enzyme provided the estimate of  $\text{H}_2\text{O}_2$  concentration. Detailed methods of the  $\text{H}_2\text{O}_2$  have been discussed elsewhere (Mostofa and Sakugawa, 2009).

Dissolved Fe(II) and total Fe content were measured using the 1,10-phenanthroline method. In this method, Fe(III) was estimated as the difference between Fe(II) and total Fe after reduction of Fe(III) by 5% hydroxyl amine. Ferrous ammonium sulfate was used as a standard. The river and standard samples were processed following an earlier method (Zuo, 1995). The absorbance of the samples was then measured at wavelength ranges of 450–550 nm using UV–VIS spectrophotometer (Shimadzu UV-2401, Shimadzu, Japan). The maximum absorbance at a specific wavelength was used for determination of Fe(II) and total Fe concentrations in samples.

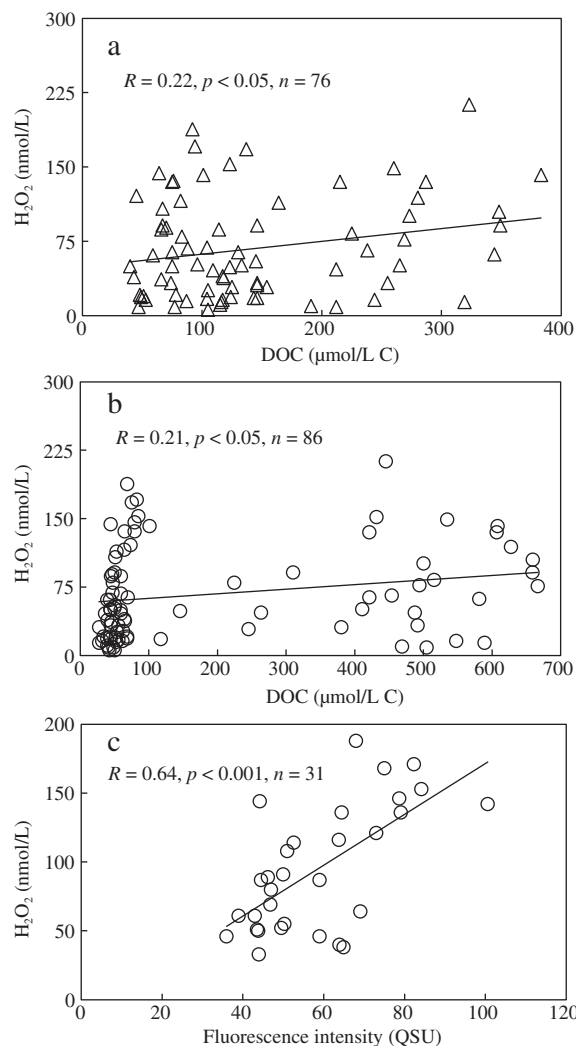
## 2. Results and discussion

Diurnal variations of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  as a function of time and solar intensity were examined in water samples collected from upstream and downstream sites in the Kurose River (Fig. 1). The sunlight intensity reached a peak at noon and then the intensity gradually decreased with time. Correspondingly, concentrations

of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  were gradually increased during the period before sunrise to noon and then gradually decreased after sunset. The conversion of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  upon sunlight exposure in river waters involved 0.3–3.8  $\mu\text{mol/L}$  (0.4%–6.8%) of total dissolved Fe in the upstream waters and 2.0–4.0  $\mu\text{mol/L}$  (0.9%–1.9%) in the downstream waters. Such photo-conversion of  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  was also observed during monthly readings, contributing 2%–13% and 1%–8% of total dissolved iron, respectively, in the same upstream and downstream waters (Fig. 2). Similar results are also found in other freshwater river-estuarine systems, ranging from 0.012 to 3.6  $\mu\text{mol/L}$  (7%–30% of total dissolved Fe) (Hopwood et al., 2015).  $\text{Fe}^{2+}$  concentrations in a variety of marine waters are substantially varied, accounting for up to 65% of total dissolved Fe (Hopwood et al., 2015 and references therein). Conversely, the magnitude of the  $\text{H}_2\text{O}_2$  diurnal cycle (highest concentration at noon minus concentration during the period before sunrise) was 35 nmol/L (79% higher than the level shortly before sunrise) in the



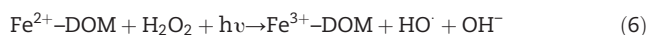
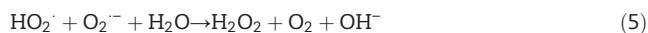
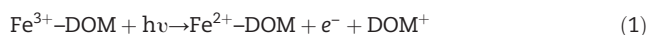
**Fig. 3 – Relationship between the  $\text{H}_2\text{O}_2$  concentration and dissolved organic carbon (DOC) concentration (a) or the fluorescence intensity of peak C (b) for the dissolved organic matter (DOM) in the diurnal samples of upstream water and downstream water.**



**Fig. 4 – Relationship between the  $\text{H}_2\text{O}_2$  concentration and DOC concentration (a) or the fluorescence intensity of peak C (b) for the DOM in the monthly samples of the two rivers (Kurose and Ohta), Hiroshima Prefecture, Japan. Relationship between the  $\text{H}_2\text{O}_2$  concentration and the fulvic acid-like fluorescence intensity of peak C (c) alone in the monthly samples of the Ohta River.**

upstream waters and 65 nmol/L (94% higher than the level shortly before sunrise) in the downstream waters of the Kurose River. Such magnitude of the  $\text{H}_2\text{O}_2$  diurnal cycle was measured in different ecosystems and results were equal to 35–65 nmol/L in rivers, 790 nmol/L in lakes, 36–183 nmol/L in estuaries and 20–476 nmol/L in the coastal and open ocean (Arakaki et al., 2005; Richard et al., 2007; Mostofa et al., 2013 and references therein). The highest concentrations of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  were observed between 12:00 and 14:00 pm in river waters. Modeling shows that  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  as a function of solar intensity are produced simultaneously and react with each other, thereby triggering the photo-Fenton reaction.

So the big question now is: what is the mechanism for the photo-Fenton reaction in freshwater rivers? Relatively high binding constants of  $\text{Fe}^{3+}$  to DOM (Hopwood et al., 2015) may pave the way to produce a rapid photochemical process in sunlit surface waters. A rapid excitation upon light exposure would predominantly occur from the  $\pi$ -electron bonding system of  $\text{Fe}^{3+}$ -DOM complex. The latter would be formed by a donation of electrons from O- or S-containing functional groups of DOM, mostly humic substances (fulvic and humic acids) (Mostofa et al., 2013) to an outer unpaired  $d$ -orbital of  $\text{Fe}^{3+}$  ( ${}^{25}\text{Fe}^{2+}$ :  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2_{xy} 3d^2_{xz} 3d^1_{yz} 3d^1_{x^2-y^2} 3d^1_{z^2} 4s^0$ ). Note that fulvic acid is a major component (approximately 40%–80% of total DOM) in rivers and has molecular structures with diverse functional groups (Mostofa et al., 2013). Photochemical excitation can cause a rapid release of aqueous electrons ( $e^-$ ) from DOM, which would generally react with dissolved oxygen ( $\text{O}_2$ ) to produce the superoxide radical anion ( $\text{O}_2^-$ ) in equilibrium with its conjugate acid perhydroxyl radical ( $\text{HO}_2^\cdot$ ). Both  $\text{O}_2^-$  and  $\text{HO}_2^\cdot$  are disproportionate to form  $\text{H}_2\text{O}_2$ . Based on these results, we propose the following reaction mechanism for the occurrence of the photo-Fenton reaction upon sunlight exposure of surface waters (Eqs. (1)–(6)):



Continuing irradiation may recycle  $\text{Fe}^{3+}$ -DOM (Eq. (6)) to  $\text{Fe}^{2+}$ -DOM (Eq. (1)) in the reaction media and is thus possible to continuously generate  $\text{HO}^\cdot$  under irradiation without any net consumption of  $\text{Fe}^{2+}$ , which significantly accelerates the overall reaction rate in the photo-Fenton reaction system. The net effect of the photo-Fenton reaction is the ultimate photodegradation of the DOM ( $\text{DOM}^+$ ) by  $\text{HO}^\cdot$  (Eq. (5)). It can be noted that under exposure to light,  $\text{Fe}^{2+}$ -DOM instead of free  $\text{Fe}^{2+}$  would be highly susceptible to react with  $\text{H}_2\text{O}_2$ . This is most likely due to the production of  $\text{H}_2\text{O}_2$  during the conversion of  $\text{Fe}^{3+}$ -DOM to  $\text{Fe}^{2+}$ -DOM upon light exposure via  $\text{O}_2^-$ .

Moreover, to clarify the effect of riverine DOM compositions on the photo-Fenton reaction, it was revealed that dissolved

organic carbon (DOC) concentration was not correlated with  $\text{H}_2\text{O}_2$  concentration in diurnal water samples (Fig. 3a), but fluorescence intensity (FI) of peak C of downstream DOM is negatively correlated with  $\text{H}_2\text{O}_2$  (Fig. 3b). Note that upstream DOM is composed of mostly fulvic acid of forested mountain origin, while the downstream DOM was composed of both fulvic acid and fluorescent whitening agents or household detergents including distyryl biphenyl and diaminostilbene type of anthropogenic origin, mostly from the untreated sewerage effluents from the nearby Higashi-Hiroshima City in the middle of the Kurose River (Mostofa et al., 2005). Correspondingly,  $\text{H}_2\text{O}_2$  concentration was significantly correlated with DOC concentration ( $R = 0.22$ ,  $p < 0.05$ ,  $n = 76$ ; Fig. 4a) and FI of peak C of DOM ( $R = 0.21$ ,  $p < 0.05$ ,  $n = 86$ ; Fig. 4b) for the monthly samples collected from two rivers (the Kurose and Ohta). Additionally, such a correlation is very effective in the water of the Ohta River alone ( $R = 0.64$ ,  $p < 0.001$ ,  $n = 31$ ; Fig. 4c), possibly due to the predominant presence of fulvic acid. In addition, river water is free of anthropogenic contamination. These results suggest that DOM compositions, particularly fulvic acid, might play an important role in  $\text{H}_2\text{O}_2$  photoproduction that is subsequently linked with the photo-Fenton reaction. Moreover, the differences in the DOM effect on the  $\text{H}_2\text{O}_2$  production from diurnal and monthly samples are primarily initiated by the diurnal light effects, showing characteristic changes in the  $\text{H}_2\text{O}_2$  photoproduction from two sampling pathways. Monthly samples were usually collected from 10:00 am to 15:00 pm (JST), often during the same time-range for a specific sampling site, thereby offering the constant light effect on DOM. However, the effect of DOM, mostly fulvic acid, on the photo-Fenton reaction is apparently visible for the monthly samples considering the constant light effect on the river water, but DOM compositions on the photo-Fenton reaction are vital in rivers.

Finally, the simultaneous generation of  $\text{Fe}^{2+}$  and  $\text{H}_2\text{O}_2$  as well as the fact that they reach their maximum levels as a function of solar intensity (Fig. 1) could, therefore, be a useful indicator for the occurrence of the photo-Fenton reaction. These findings will assist in a further understanding of the importance of Fe-DOM complexation, forming a  $\pi$ -electron bonding system that is susceptible to a rapid excitation upon light exposure and its concomitant photo-Fenton reaction system.

## Acknowledgments

The authors acknowledge with thanks the Japan Society for the Promotion of Science for the financial support through a Grant-in-Aid for Scientific Research (B) (No. 18310010). This work was also partly supported by the Key Construction Program of the National “985” Project, Tianjin University, China.

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