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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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## ABSTRACT

The photo-Fenton reaction is a key source of the highly reactive hydroxyl radical (HO) 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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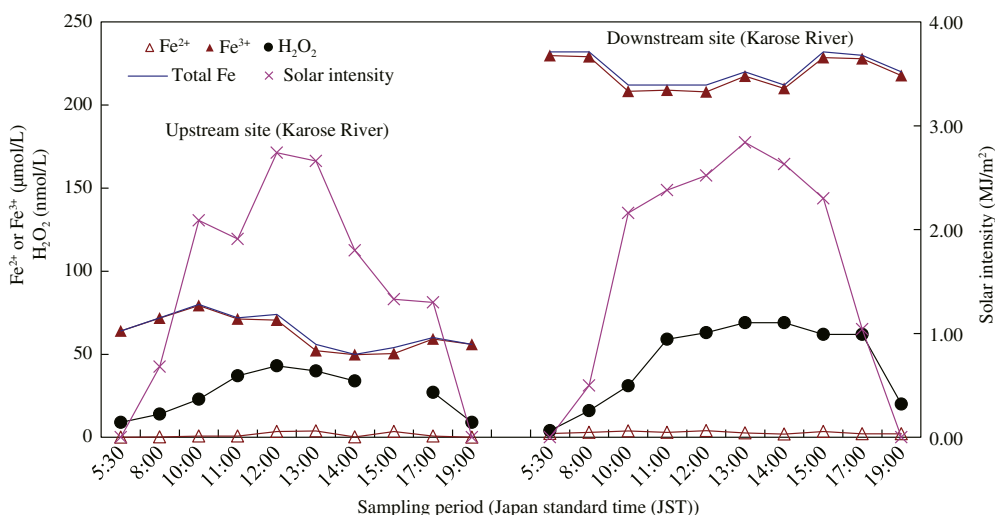
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## Introduction

The photo-Fenton reaction, an advanced oxidation technology, is one of the key processes for the production of hydroxyl radicals (HO) 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 HO $\cdot$  production in Satilla River water (White et al., 2003). This process is expected to be the main contributor to 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.

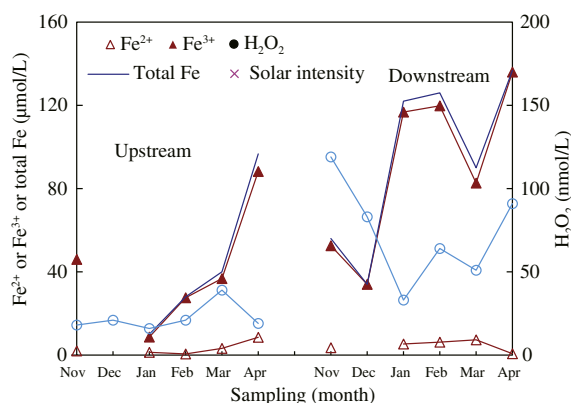
(fulvic and humic acids), which can form complexes with dissolved  $\text{Fe}^{2+}$  (Hopwood et al., 2015; Mostofa et al., 2013; White et al., 2003). Note that over 99% of dissolved Fe is strongly complexed with the functional groups of DOM in marine waters (Kondo et al., 2012; Su et al., 2015). The 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  $\log K_{\text{Fe(II)-DOM}} = 7-8$  (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).

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