

## 学 位 論 文 の 要 旨

論文題目 Analyses, Dynamics and Fates of Reactive Oxygen Species (ROS) in Natural Waters:  
Emphasis on Photochemical Reactions.

(天然水中の活性酸素種の測定、動態、運命——特に光化学反応に関して)

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A brief introduction of the reactive oxygen species (ROS) – hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), hydroxyl radical ( $\cdot\text{OH}$ ), nitric oxide ( $\text{NO}\cdot$ ) and superoxide radical ( $\text{O}_2\cdot^-$ ) – measured in some natural waters in this study was reported in chapter 1.  $\text{H}_2\text{O}_2$  and  $\text{O}_2\cdot^-$  mediate in redox chemistry of metals (Fe, Cu, Mn) and other chemical species in natural waters, thus making them important targets of many environmental studies. Moreover,  $\text{O}_2\cdot^-$  is a precursor of  $\text{H}_2\text{O}_2$ . Similarly,  $\cdot\text{OH}$  is a potent oxidizing agent capable of degrading recalcitrant organic pollutants in natural waters.  $\text{NO}\cdot$  is photoformed in natural waters containing nitrite and it could be a potential sink of  $\text{O}_2\cdot^-$  due to their high reaction rate. The reaction of oxygen with photo-irradiated dissolved organic matter (DOM) in natural waters produces  $\text{O}_2\cdot^-$ . However, measurement of this important ROS ( $\text{O}_2\cdot^-$ ) has been a perennial challenge due to lack of suitable analytical technique. This and other environmental issues relating to the ROS in natural waters were addressed in this study.

Chapter 2 presents a report on the monthly  $\text{NO}\cdot$  measurements in the Kurose River at Higashi-Hiroshima city. Results show that  $\text{NO}\cdot$  photoformation rate ranged from 0.01 to  $35.4 (\times 10^{-10} \text{ M s}^{-1})$  with steady-state concentrations in the range of 0.02–68.5 ( $\times 10^{-11} \text{ M}$ ). There was a strong correlation ( $r^2 = 0.95$ ) between  $\text{NO}\cdot$  photoformation rate and the nitrite concentration in the river showing  $\text{NO}_2^-$  as a major  $\text{NO}\cdot$  precursor. On the average, 98% of the photoformed  $\text{NO}\cdot$  came from river nitrite. The  $\text{NO}\cdot$  lifetime ranged from 0.05 to 1.3 s in the river and remained fairly stable in the upstream and downstream. The  $\cdot\text{OH}$  radical, which was quantified during the study, had a photoformation rate of 0.01 to  $13.4 (\times 10^{-10} \text{ M s}^{-1})$  and a steady-state concentration of 0.04 to  $119 (\times 10^{-16} \text{ M})$  with a lifetime that ranged from 0.3 to 23  $\mu\text{s}$ .  $\cdot\text{OH}$  only accounted for  $\leq 0.0011\%$  of the total  $\text{NO}\cdot$  scavenged, showing that it was not a major sink for river  $\text{NO}\cdot$ .

In chapter 3, monthly measurements of  $\text{H}_2\text{O}_2$  and  $\cdot\text{OH}$  in rainwater and the Kurose River were carried out in 2013.  $\text{H}_2\text{O}_2$  concentrations in the rainwater and river were highly season-dependent.  $\text{H}_2\text{O}_2$  concentrations in the rainwater varied from the lowest 0.03  $\mu\text{M}$  in winter to the highest 14.3  $\mu\text{M}$  in spring. In the year, estimated wet deposition of  $\text{H}_2\text{O}_2$  in Higashi-Hiroshima city was 7.5  $\text{mmol m}^{-2} \text{ y}^{-1}$ . In the Kurose River,  $\text{H}_2\text{O}_2$  concentrations of 0.06–0.37  $\mu\text{M}$  were measured. The lowest and highest concentrations were found in the winter and summer, respectively. There was good correlation between solar intensity and  $\text{H}_2\text{O}_2$  concentrations measured in the rainwater ( $r = 0.79$ ,  $p < 0.01$ ) and the river ( $r = 0.81$ ,  $p < 0.01$ ), which indicate photoproduction as one of the major  $\text{H}_2\text{O}_2$  sources in the natural waters. The  $\cdot\text{OH}$  was 1 order of magnitude photoformed in the river ( $\sim 10^{-10} \text{ M s}^{-1}$ ) than in the rainwater.  $\text{H}_2\text{O}_2$  and the unknown (which probably include photo-Fenton reaction) were predominantly  $\cdot\text{OH}$  photochemical sources in the rainwater, accounting for 0.2–48%, 43–84%, respectively. In contrast,  $\text{NO}_2^-$  was the major  $\cdot\text{OH}$  source (49–80%) in the Kurose River, while  $\text{H}_2\text{O}_2$  contribution was negligible ( $< 1\%$ ).

In chapter 4, daytime flux of  $\text{NO}\cdot$  at the Seto Inland Sea-atmosphere boundary was measured in

September, 2013 and June, 2014. The average daytime  $\text{NO}\cdot$  concentration measured in the sea surface was  $1.9 \times 10^{-11} \text{ mol L}^{-1}$  ( $\sim 9.87 \times 10^{-9} \text{ atm}$ ), while that measured over the sea was  $5.2 \times 10^{-10} \text{ atm}$ . Using an average wind speed of  $3.2 \text{ m s}^{-1}$  measured over the Seto Inland Sea during the cruise, a daytime  $\text{NO}\cdot$  efflux of  $0.22 \text{ pmol m}^{-2} \text{ s}^{-1}$  from the sea to the atmosphere was estimated. Assuming 8 h of solar intensity per day, about  $1.54 \times 10^6 \text{ g NO y}^{-1}$  efflux of  $\text{NO}\cdot$  from the 23,000  $\text{km}^2$  Seto inland Sea surface was determined.

In chapter 5, a method was developed for the measurement of  $\text{O}_2\cdot^-$  in sunlit seawater using a fluorogenic probe – 3',6'-(diphenylphosphinyl)fluorescein (PF-1). Reaction of the photoformed  $\text{O}_2\cdot^-$  with PF-1 produced fluorescein, which was separated by isocratic HPLC and measured using a fluorescence detector at 490/513 nm (excitation/emission wavelength). The reaction rate constant of the probe with  $\text{O}_2\cdot^-$  was pH-dependent:  $(3.2\text{--}23.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at  $\text{pH}_{\text{TOT}} 7.65\text{--}8.50$ . The detection limit of  $\text{O}_2\cdot^-$  photoformation rate was  $1.78 \text{ pM s}^{-1}$ . The method produced results that were consistent with those obtained in literatures when applied to ten (10) seawater samples from the Seto Inland Sea. The  $\text{O}_2\cdot^-$  photoformation rates were  $3.1\text{--}8.5 \text{ nM s}^{-1}$ , with steady-state concentrations ranging  $(0.06\text{--}0.3) \times 10^{-10} \text{ M}$ . The method requires no technical sample preparation and can analyze large number of samples.

In chapter 6,  $\text{O}_2\cdot^-$ ,  $\cdot\text{OH}$ ,  $\text{NO}\cdot$ , and  $\text{H}_2\text{O}_2$ , in surface seawater obtained from the Seto Inland Sea were determined by concerted photochemical measurements.  $\text{O}_2\cdot^-$  was photoformed at rates (range of  $10^{-10} \text{ M s}^{-1}$ ) 1–2 orders of magnitude higher than  $\cdot\text{OH}$  and  $\text{NO}\cdot$ . About 27% of the  $\text{O}_2\cdot^-$  was transformed to  $\text{H}_2\text{O}_2$ . About 3% of the  $\text{O}_2\cdot^-$  photoformed was consumed by  $\text{NO}\cdot$ , while 15–21% of the  $\text{NO}\cdot$  was consumed by the  $\text{O}_2\cdot^-$ . Therefore,  $\text{O}_2\cdot^-$  could be a major sink for  $\text{NO}\cdot$  in the sea. Estimated consumptions of  $\text{O}_2\cdot^-$  by the  $\cdot\text{OH}$  and due to bimolecular dismutation were negligible. In the seawater, (+)-catechin- and humic-like fluorescent dissolved organic matter contributed 3.2–4.1% and 3.6–4.8% of the  $\text{O}_2\cdot^-$  photoformation rates, respectively.

Chapter 7 gives a general discussion and major conclusions of this study. The four ROS in this study are ubiquitous in sunlit natural waters. Nitrite is a major photochemical source of  $\text{NO}\cdot$  and  $\cdot\text{OH}$  in natural waters. The  $\text{O}_2\cdot^-$  concentration ( $\sim 10^{-11} \text{ M}$ ) in the Seto Inland Sea would be sufficient for speciation of the resident metals and other redox-active compounds.