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

A brief introduction of the reactive oxygen species (ROS) – hydrogen peroxide (H$_2$O$_2$), hydroxyl radical (·OH), nitric oxide (NO•) and superoxide radical (O$_2$•−) – measured in some natural waters in this study was reported in chapter 1. H$_2$O$_2$ and O$_2$•− 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, O$_2$•− is a precursor of H$_2$O$_2$. Similarly, ·OH is a potent oxidizing agent capable of degrading recalcitrant organic pollutants in natural waters. NO• is photoformed in natural waters containing nitrite and it could be a potential sink of O$_2$•− due to their high reaction rate. The reaction of oxygen with photo-irradiated dissolved organic matter (DOM) in natural waters produces O$_2$•−. However, measurement of this important ROS (O$_2$•−) 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 NO• measurements in the Kurose River at Higashi-Hiroshima city. Results show that NO• photoformation rate ranged from 0.01 to 35.4 ($\times 10^{-10}$ M s$^{-1}$) with steady-state concentrations in the range of 0.02–68.5 ($\times 10^{-11}$ M). There was a strong correlation ($r^2 = 0.95$) between NO• photoformation rate and the nitrite concentration in the river showing NO$_2$− as a major NO• precursor. On the average, 98% of the photoformed NO• came from river nitrite. The NO• lifetime ranged from 0.05 to 1.3 s in the river and remained fairly stable in the upstream and downstream. The ·OH radical, which was quantified during the study, had a photoformation rate of 0.01 to 13.4 ($\times 10^{-10}$ M s$^{-1}$) and a steady-state concentration of 0.04 to 119 ($\times 10^{-16}$ M) with a lifetime that ranged from 0.3 to 23 µs. ·OH only accounted for ≤ 0.0011% of the total NO• scavenged, showing that it was not a major sink for river NO•.

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

In chapter 4, daytime flux of NO• at the Seto Inland Sea-atmosphere boundary was measured in
September, 2013 and June, 2014. The average daytime NO• 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 m s$^{-1}$ measured over the Seto Inland Sea during the cruise, a daytime NO• efflux of 0.22 pmol m$^{-2}$ s$^{-1}$ from the sea to the atmosphere was estimated. Assuming 8 h of solar intensity per day, about $1.54 \times 10^6$ g NO y$^{-1}$ efflux of NO• from the 23,000 km$^2$ Seto inland Sea surface was determined.

In chapter 5, a method was developed for the measurement of O$_2$•‒ in sunlit seawater using a fluorogenic probe – 3′,6′-(diphenylphosphinyl)fluorescein (PF–1). Reaction of the photoformed O$_2$•‒ 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 O$_2$•‒ was pH-dependent: $(3.2–23.5) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ at pH$_{TOT}$ 7.65–8.50. The detection limit of O$_2$•‒ photoformation rate was 1.78 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 O$_2$•‒ photoformation rates were 3.1–8.5 nM s$^{-1}$, with steady-state concentrations ranging (0.06–0.3) × $10^{-10}$ M. The method requires no technical sample preparation and can analyze large number of samples.

In chapter 6, O$_2$•‒, •OH, NO•, and H$_2$O$_2$, in surface seawater obtained from the Seto Inland Sea were determined by concerted photochemical measurements. O$_2$•‒ was photoformed at rates (range of $10^{-10}$ M s$^{-1}$) 1–2 orders of magnitude higher than •OH and NO•. About 27% of the O$_2$•‒ was transformed to H$_2$O$_2$. About 3% of the O$_2$•‒ photoformed was consumed by NO•, while 15–21% of the NO• was consumed by the O$_2$•‒. Therefore, O$_2$•‒ could be a major sink for NO• in the sea. Estimated consumptions of O$_2$•‒ by the •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 O$_2$•‒ 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 NO• and •OH in natural waters. The O$_2$•‒ concentration ($\sim 10^{-11}$ M) in the Seto Inland Sea would be sufficient for speciation of the resident metals and other redox-active compounds.