Doctoral Thesis

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

(Summary)

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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 (H_2O_2), hydroxyl radical ($^{\bullet}OH$), nitric oxide ($NO^{\bullet}$) and superoxide radical ($O_2^{\bullet -}$) – measured in some natural waters in this study was reported in chapter 1. H_2O_2 and $O_2^{\bullet -}$ 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, $O_2^{\bullet -}$ is a precursor of H_2O_2. Similarly, $^{\bullet}OH$ is a potent oxidizing agent capable of degrading recalcitrant organic pollutants in natural waters. $NO^{\bullet}$ is photoformed in natural waters containing nitrite and it could be a potential sink of $O_2^{\bullet -}$ due to their high reaction rate. The reaction of oxygen with photo-irradiated dissolved organic matter (DOM) in natural waters produces $O_2^{\bullet -}$. However, measurement of this important ROS ($O_2^{\bullet -}$) 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 $NO^{\bullet}$ measurements in the Kurose River at Higashi-Hiroshima city. Results show that $NO^{\bullet}$ photoformation rate ranged from 0.01 to 35.4 (× 10^{-10} M s^{-1}) with steady-state concentrations in the range of 0.02–68.5 (× 10^{-11} M). There was a strong correlation ($r^2 = 0.95$) between $NO^{\bullet}$ photoformation rate and the nitrite concentration in the river showing NO_2^- as a major $NO^{\bullet}$ precursor. On the average, 98% of the photoformed $NO^{\bullet}$ came from river nitrite. The $NO^{\bullet}$ lifetime ranged from 0.05 to 1.3 s in the river and remained fairly stable in the upstream and downstream. The $^{\bullet}OH$ radical, which was quantified during the study, had a photoformation rate of 0.01 to 13.4 (× 10^{-10} M s^{-1}) and a steady-state concentration of 0.04 to 119 (× 10^{-16} M) with a lifetime that ranged from 0.3 to 23 μs. $^{\bullet}OH$ only accounted for ≤ 0.0011% of the total $NO^{\bullet}$ scavenged, showing that it was not a major sink for river $NO^{\bullet}$.

In chapter 3, monthly measurements of H_2O_2 and $^{\bullet}OH$ in rainwater and the Kurose River were carried out in 2013. H_2O_2 concentrations in the rainwater and river were highly season-dependent. H_2O_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_2O_2 in Higashi-Hiroshima city was 7.5 mmol m^{-2} y^{-1}. In the Kurose River, H_2O_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_2O_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_2O_2 sources in the natural waters. The $^{\bullet}OH$ was 1 order of magnitude photoformed in the river (~10^{-10} M s^{-1}) than in the rainwater. H_2O_2 and the unknown (which probably include photo-Fenton reaction) were predominantly $^{\bullet}OH$ photochemical sources in the rainwater, accounting for 0.2–48%, 43–84%, respectively. In contrast, NO_2^- was the major $^{\bullet}OH$ source (49–80%) in the Kurose River, while H_2O_2 contribution was negligible (<1%).

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

September, 2013 and June, 2014. The average daytime $NO^{\bullet}$ concentration measured in the sea surface was 1.9×10^{-11} mol L^{-1} (~9.87×10^{-9} atm), while that measured over the sea was 5.2×10^{-10} atm. Using an average wind speed of 3.2 m s^{-1} measured over the Seto Inland Sea during the cruise, a daytime $NO^{\bullet}$ 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 1.54×10^{6} g NO y^{-1} efflux of $NO^{\bullet}$ from the 23,000 km^2 Seto inland Sea surface was determined.

In chapter 5, a method was developed for the measurement of $O_2^{\bullet-}$ in sunlit seawater using a fluorogenic probe – 3′,6′-(diphenylphosphinyl)fluorescein (PF-1). Reaction of the photoformed $O_2^{\bullet-}$ 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 $O_2^{\bullet-}$ was pH-dependent: (3.2–23.5) × 10^{7} M^{-1} s^{-1} at pH_{TOT} 7.65–8.50. The detection limit of $O_2^{\bullet-}$ 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 $O_2^{\bullet-}$ 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, $O_2^{\bullet-}$, $^{\bullet}OH$, $NO^{\bullet}$, and H_2O_2, in surface seawater obtained from the Seto Inland Sea were determined by concerted photochemical measurements. $O_2^{\bullet-}$ was photoformed at rates (range of 10^{-10} M s^{-1}) 1–2 orders of magnitude higher than $^{\bullet}OH$ and $NO^{\bullet}$. About 27% of the $O_2^{\bullet-}$ was transformed to H_2O_2. About 3% of the $O_2^{\bullet-}$ photoformed was consumed by $NO^{\bullet}$, while 15–21% of the $NO^{\bullet}$ was consumed by the $O_2^{\bullet-}$. Therefore, $O_2^{\bullet-}$ could be a major sink for $NO^{\bullet}$ in the sea. Estimated consumptions of $O_2^{\bullet-}$ by the $^{\bullet}OH$ 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 $O_2^{\bullet-}$ 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 $NO^{\bullet}$ and $^{\bullet}OH$ in natural waters. The $O_2^{\bullet-}$ concentration (~10^{-11} M) in the Seto Inland Sea would be sufficient for speciation of the resident metals and other redox-active compounds.