Doctoral Thesis

Measurement and Photochemical Dynamics of Reactive Oxygen Species and Chromophoric Dissolved Organic Matter in Japanese Rivers

(Summary)

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Chapter one introduces this study in a concise manner. Just as their name depicts, reactive oxygen species are very reactive in whatever environment they are found, whether in the human body, plant tissues, or natural environments ranging from soils to natural waters like rivers, lakes, coastal waters, seas, and oceans. The atmosphere is not left out as the impacts of reactive oxygen species could result in the greenhouse effect which affects the whole world. The present study is into natural water and river to be specific. Three reactive oxygen species (ROS) comprising hydroxyl radical (•OH), nitric oxide radical (NO•), and singlet oxygen ($^1O_2$) across rivers in Japan were investigated. In addition, the optical properties of the rivers including chromophoric dissolved organic matter (CDOM) and fluorescent dissolved organic matter (FDOM) were elucidated.

Chapter two discusses the concurrent measurement of the photoformation rates, steady-state concentrations, and scavenging rates of the ROS across rivers ranging from small to large rivers and relatively clean to polluted rivers. Nine rivers comprising of sixty-five stations located along the west to the east axis of Japan were investigated. The absorption coefficient at 300 nm (a_{300}, m $^{-1}$), which ranged from 2.44 to 36.2 m $^{-1}$, was used to investigate the chromophoric dissolved organic matter (CDOM) properties of the rivers. The photoformation rate ranges were (13.9–944) × 10 $^{-12}$ M s $^{-1}$ for •OH, (2.76–2610) × 10 $^{-12}$ M s $^{-1}$ for NO•, and (9.48–133) × 10 $^{-9}$ M s $^{-1}$ for $^1O_2$. The steady-state concentration ranges were (1.53–16) × 10 $^{-16}$ M for •OH, (10.2–1520) × 10 $^{-12}$ M for NO•, and (3.79–53.4) × 10 $^{-14}$ M for $^1O_2$. The results showed that nitrite (NO_2^-) was a major source for both •OH and NO•, and CDOM was a major source for $^1O_2$ across all the rivers. According to significant relationships with these sources, models were generated to predict the formation rates of the ROS (in M s $^{-1}$) from known concentrations of source compounds using the equations $R_{\bullet OH}\,(10^{-12}) = 19.2\,[NO_2^-]\_{\mu M} + 36.9$, $R_{NO\bullet}\,(10^{-12}) = 41.4\,[NO_2^-]\_{\mu M} + 44$, and $R_{^1O_2}(10^{-9}) = 3.52\,(a_{300})\_{m}^{-1} + 1.61$. Dissolved organic matter (DOM), escape to the atmosphere, and water molecules were the major sinks for river •OH, NO•, and $^1O_2$, respectively. A general scavenging rate constant of •OH as a function of the dissolved organic carbon (DOC) concentration was obtained [$k_{C,\,OH} = [(7.5 \pm 6.8) \times 10^8$ L (mol C) $^{-1}$ s $^{-1}$]. These models would allow for easy prediction of ROS concentrations on a large scale.

In Chapter Three, the optical properties of DOM in five rivers, including Ohta, Kurose, Yodo, Yamato, and Kokubu, were investigated. In addition to this, their contributions to the photogeneration of ROS were elucidated. The average DOC concentrations across the rivers were the lowest (0.95 mg C L $^{-1}$) in the Ohta, and the highest (2.85 mg C L $^{-1}$) in the Yamato and were correlated with some optical parameters. Absorption ratios such as the E_2:E_3, the A_{280}/A_{350}, and the spectra slope, $S_{275\text{–}295}$ showed that the Yodo and the Kokubu rivers had the lowest and highest DOM molecular weights, respectively. PARAFAC modelling combined with the excitation-emission matrices of the DOM in the rivers was used to characterize their sources and fates. The PARAFAC analysis showed that the major components of DOM across the rivers were the terrestrial humic-like (TH-L) and tryptophan-like (TP-L) substances. Conversely, the Kokubu River contained other components like the fluorescent whitening agent, autochthonous humic-like, and extracellular polymeric substances (EPS). The significant relationships between the DOC versus the TH-L, TP-L components, and EPS suggested that they were significant contributors to the total DOM in the rivers. On investigating the ROS-generating abilities of these fluorescent components, TH-L and TP-L components contributed significantly to ROS photoformation, whereas the Kokubu River components seemingly had no contribution, probably due to the few observations of such components as reported in this study. The CDOM was observed to play a dual role in both generating and scavenging the ROS. Comprehensive models for estimating the photoformation rates of each ROS (in M s^{-1}) were deduced by integrating contributions from their respective major and minor sources. They include: $R_{\bullet\mathrm{OH}}$ $(10^{-12}) = 21.0\ [\mathrm{NO_2^-}]\_{}_{\mu\mathrm{M}} + 0.460\ [\mathrm{TH\text{-}L}]\_{}_{\mathrm{QSU}} + 10.9$; $R_{\mathrm{NO}\bullet}$ $(10^{-12}) = 67.9\ [\mathrm{NO_2^-}]\_{}_{\mu\mathrm{M}} + 35.2\ [a_{300}]\_{}_{\mathrm{m}}^{-1} - 2.51\ [\mathrm{TH\text{-}L}]\_{}_{\mathrm{QSU}} - 0.765\ [\mathrm{TP\text{-}L}]\_{}_{\mathrm{QSU}} - 8.14$; and $R_{{}^1\mathrm{O}_2}$ $(10^{-9}) = 3.81\ [a_{300}]\_{}_{\mathrm{m}}^{-1} - 0.101\ [\mathrm{TP\text{-}L}]\_{}_{\mathrm{QSU}} + 11.1$.

Finally, Chapter four discusses the major findings, conclusions, and possible recommendations for future studies.