学位論文の要旨

論文題目　Photochemical Generation of Reactive Species in Seawater: Analyses, Kinetic Considerations, and Environmental Implications.

（海水中での活性化学種の光化学的生成—化学分析、反応解析、環境科学的意義）

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Abstract

Perspectives on photochemically generated reactive species in the environment, with particular emphasis on the hydrosphere was presented in Chapter 1. The role of solar radiation to provide needed light energy to drive many photochemical reactions involving; geogenic, biogenic and anthropogenic chemicals from the atmosphere and land, found in natural surface waters, was emphasized. A concise definition of reactive species, and discussion of major pathways to their photogeneration were also presented in this chapter. Environmental implications of photogenerated reactive species such as; redox reaction involving ions, dissolved oxygen recycling, generation of secondary reactive species, and photo-degradation of dissolved organic pollutants in natural waters, amongst others were highlighted. Potential technological applications of photochemical generation of reactive species in gas-phase photo-oxidation and photomicrobicidal systems were also mentioned.

Chapter 2 reports about concurrent photo-generation and analyses of hydroxyl ($\cdot$OH), nitric oxide (NO$\cdot$) and superoxide ($O_2\cdot^-$) radicals in seawater samples obtained during two consecutive

summers from the Seto Inland Sea, Japan. These were done with the sole aim of using the data generated to predict the influence of interactive reactions among several photo-generated reactive species on the variety and fates of reactive species in seawater. Photo-generation rates of ·OH are [(6.98–35.27) × 10^{-12} M s^{-1}], and those of NO· are [(1.20–58.25) × 10^{-12} M s^{-1}]. Compared with these generation rates, that for $O_2\cdot^{-}$ [(4.54–18.20) × 10^{-10} M s^{-1}] was the highest, which suggests that $O_2\cdot^{-}$ is a very important photochemically generated reactive species in coastal seawater. The average steady-state concentrations of the three reactive species are ·OH (7.23 × 10^{-18} M), $O_2\cdot^{-}$ (3.79 × 10^{-12} M), and NO· (1.39 × 10^{-10} M). Based on kinetic considerations, estimated mutual consumption/sink via interactive reactions between $O_2\cdot^{-}$ and NO· radicals are five to nine orders of magnitude higher than any other radical pair considered in this study. Hence, the radical–radical reaction between photochemical $O_2\cdot^{-}$ and NO· to form peroxynitrite ($ONOO^{-}$) was predicted to dominate above those involving; ·OH/ $O_2\cdot^{-}$ and ·OH/ NO· radical pairs.

A novel fluorescence analytical method developed to measure $ONOO^{-}$ in seawater was reported in Chapter 3. Although there are existing methods for determination of other reactive species such as; $O_2\cdot^{-}$ and NO· radicals (precursors of $ONOO^{-}$ in seawater), there was no analytical method for measurement of $ONOO^{-}$ in any natural surface water system. This newly developed analytical method is based on using β-(2-oxo-2H-1-benzopyran-7-yl)-boronic acid (CBA); a boronate probe which reacts rapidly and stoichiometrically with $ONOO^{-}$ to yield fluorescent 7-hydroxycoumarin (COH). COH generation rate during irradiation of seawater with CBA probe was determined by reversed-phase isocratic high performance liquid chromatography (HPLC) with fluorescence detection at excitation and emission wavelengths of 332 nm and 475 nm, respectively. COH standards calibration plot is linear in concentration range of (0.25–100 nM) in seawater. The detection limit, defined as 3σ (3 × standard deviation) of the lowest $ONOO^{-}$ photoformation rates measured within 10 minutes' irradiation, was 1.7 × 10^{-12} M s^{-1}. This method is quite precise as coefficients of variance are; 5.2%, 3.3% and 2.2%, for triplicate measurements of COH photo-formation rates obtained by using 1 μM, 3 μM and 5 μM CBA probe concentrations, respectively. Experimental procedures were optimized to handle potential interferents in measurements. To date, this is the first report on the successful detection and measurement of photochemically generated $ONOO^-$ in any natural water system. This modest achievement has, at least, established a qualitative empirical evidence in support of a classic example of interactive radical–radical reaction involving photochemical $O_2{\cdot}^-$ and NO· in the marine environment.

Chapter 4 reports on the application of this novel analytical method to measure photogenerated $ONOO^-$ in 13 surface seawater samples from the Seto Inland Sea, Japan. Existing analytical methods were used to concurrently measure photochemically generated NO· and $O_2{\cdot}^-$, as well as, NO_2^-, DOC, CDOM and pH in these samples. The average $ONOO^-$ photoformation rate, steady state concentration and lifetime in those samples were; (9.0 × 10^{-10} M s^{-1}), (2.26 × 10^{-12} M), and (0.07 secs), respectively. The highest photochemical generation rates and steady-state concentrations of $ONOO^-$; (28.74 × 10^{-10} M s^{-1}) and (6.11 × 10^{-12} M), respectively were measured in Osaka Bay. On the other hand, the Kii channel region of the Seto Inland Sea has one of the lowest $ONOO^-$ photo-formation rates (2.4 × 10^{-10} M s^{-1}), and steady-state concentrations (1.58 × 10^{-12} M). Comparative evaluation of the three reactive species' data suggests that existence of detectable photochemically generated $ONOO^-$ in seawater depends to a large extent on, and is in the limit of, photoformed NO· radical. There is good correlation between chemical stability of photoformed $ONOO^-$ and alkalinity of seawater. Correlation coefficients of salinity versus photoformation rates and lifetimes of $ONOO^-$ are; ($r = -0.455$; $P > 0.05$) and ($r = 0.403$; $P > 0.05$), respectively. These values suggest that seawater salinity or ionic strength has no effect on the photoformation rate and lifetime of $ONOO^-$ in seawater. Consideration of both empirical evidences and kinetic estimates reveal that less than 10% of photoformed $O_2^{\cdot-}$ and NO· radicals are involved in $ONOO^-$ photoformation, suggesting that interactive radical-radical reaction between $O_2^{\cdot-}$ and NO· radicals is not a major sink of photoformed NO· radical in seawater. Due to the relatively longer lifetime, lower reactivity and lower aqueous solubility of NO· radical, these results lend credence to the sea–to–air NO· efflux phenomenon, which has been predicted as a major sink of photoformed NO· radical in seawater. Hence, this evidence–based inference on bulk diffusion of NO· radical from seawater can be proposed as a non-anthropogenic contributor to daytime atmospheric NO_x concentrations, and this suggests that dynamics of atmosphere–hydrosphere interactions do have significant environmental and health implications.

In Chapter 5, it was reported that catechin–glycerol impregnated filters illuminated by a 350 lumens LED light source can be used to photogenerate $O_2^{\cdot-}$ at a rate of 4.35×10^{-11} M $s^{-1}cm^{-2}$, in the gas-phase with an oxygen gas stream maintained at a flow rate of 1 L min^{-1} for 1 hour. The fact that the experimental conditions for this photogeneration are relatively inexpensive and easy to achieve suggest that this system can be further optimized for technological applications where milder, biologically tolerant photo-oxidation or photomicrobicidal disinfection might be required.

Finally, Chapter 6 is a discussion of major findings, conclusions and recommendations for future studies. The chapter highlights the fact that successful detection and measurement of $ONOO^-$ by using the novel boronate-based fluorescence analytical method validates the prediction that photogenerated NO· and $O_2^{\cdot-}$ would react together to yield $ONOO^-$ in the seawater milieu. Consideration of kinetic estimates with experimental values obtained in this study, led to the conclusion that photoformation of $ONOO^-$ is not a major sink for both photochemical NO· and $O_2^{\cdot-}$ in seawater. However, the current study lends credence to earlier predictions, and recent findings that bulk diffusion of $NO\cdot$ from sea to atmosphere would be a major sink of photoformed $NO\cdot$ in seawater. Therefore, photoformed $NO\cdot$ radical in surface waters is being proposed as a non-anthropogenic contributor to daytime atmospheric NO_x concentrations, and this illustrates the significance of atmosphere–hydrosphere interaction dynamics on human health and the environment. Earlier investigators have predicted that reaction of $ONOO^-$ with CO_2 can generate up to 10 – 15% of total carbonate radicals ($CO_3^{-\cdot}$) in seawater. Thus, $ONOO^-$ photogeneration can enhance to pollutant degradation by $CO_3^{-\cdot}$ in sunlit seawater because the latter can react with electron-rich substrates such as anilines, phenols and organic sulfur compounds which are ubiquitous in natural surface water. Therefore, recommendation for further studies include; concurrent measurement of photoformed $O_2\cdot^-$, $NO\cdot$, $ONOO^-$ and $CO_3^{\cdot-}$, in addition, to other relevant seawater parameters. This future research effort is expected to account for the fate and roles of photochemical $ONOO^-$ sunlit seawater. Optimization of the newly developed gas-phase $O_2\cdot^-$ generation system, and its deployment in relevant technological applications was also recommended.

Japanese Abstract

海洋表層に太陽光が入射すると，さまざまな活性化学種が短時間に発生し，溶存有機物の無機化や金属類の酸化還元反応に関与することが知られている。代表的な物質としてスーパーオキシド（O_2^-）やヒドロキシルラジカル（OH）などの活性酸素種や，一酸化窒素（NO）などの活性窒素種が存在する。本論文では，これらの活性化学種の測定，動態解析，役割解明に関する研究を行った。

第1章は序論であり，研究の背景，意義，目的について述べている。

第2章は，瀬戸内海における海水中の O_2^-，OH，NO の測定結果およびこれらの化学種の相互作用を解析している。瀬戸内海海水中の O_2^-，OH，NO の光化学的生成速度はそれぞれ 10^{-10}，10^{-12}，10^{-12} Ms^{-1} レベルであった。また，定常状態濃度はそれぞれ 10^{-12}，10^{-18}，10^{-10} M レベルであった。これら3つの化学種の消失反応過程を解析した結果，O_2^-と NO との直接反応によりペルオキシナイトライト（$ONOO^-$）が生成することが予想された。

第3章は，海水中の ONOO-の測定法開発に関する研究である。O_2^-と NO の反応から生成した $ONOO^-$を β-(2-oxo-2H-1-benzopyran-7-yl)-boronic acid と反応させ，反応物（7-hydroxycoumarin）を高速液体クロマトグラフィー蛍光検出法で測定した。その結果，海水中 $ONOO^-$を高感度で測定することが可能になった。

第4章は，前章の方法を用いて瀬戸内海海水中の $ONOO^-$を測定した結果を示す。$ONOO^-$の光化学的生成速度および定常状態濃度は，それぞれ 10^{-10}～10^{-9} Ms^{-1} および 10^{-12} M であった。光化学的生成速度および定常状態濃度の両方が大阪湾で最も高く，紀伊水道で最も低かった。海水中の NO が $ONOO^-$の生成に寄与する割合は10%以下と低く，大部分の NO は NO ガスとして海水から大気に移行することが示唆された。

第5章は，本研究の目的から二次的に派生した研究を述べている。光化学的に生成するO_2^-の有機物に対する酸化能力は高いことが知られている。これを利用して大気中悪臭成分の分解除去に応用する研究を行った。カテキンを塗布したフィルターに可視光 LED を照射することにより，フィルター1cm^2当たり約4×10^{-11} M s^{-1}のO_2^-を効率的，簡便，安価で発生することに成功した。この方法は，空気中の悪臭物質の除去への適用が期待できる。

第6章は，総合討論であり，研究の総括および今後の課題を述べている。