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Determination of Hydroxyl Radical Photoproduction Rates in Natural Waters

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The photochemical formation rates of hydroxyl radicals (OH radicals) in river water and seawater were determined by a simple, rapid and sensitive benzene probe method, in which phenol formed by the reaction between benzene and photochemically-generated OH radicals was analyzed by on-line preconcentration HPLC. The OH radical formation rates from well-known OH radical sources, such as nitrate, nitrite and hydrogen peroxide, were in good agreement with those reported previously. River water samples containing high concentrations of nitrate and nitrite were found to show high OH radical formation rates. Ten to 80% of the OH radical formation in river water and seawater was due to the photolysis of nitrate and nitrite, but OH radical formation from hydrogen peroxide was negligible. The OH radical formation from unknown sources other than nitrate, nitrite and hydrogen peroxide was strongly correlated to the amount of fluorescent matter.

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Introduction

Short-lived, reactive peroxides and free radicals, such as hydrogen peroxide, superoxide anions and hydroxyl radicals (OH radicals), are photochemically produced in natural water.[1,2,10] These species are reactive and play important roles in chemical and biological processes in aquatic environments, such as photochemical degradation of natural organic matter and organic pollutants, redox reactions and biological reactions. The OH radical, which is one of the most reactive free radicals in the environment, is generated in natural water by the photolysis of nitrate, nitrite and hydrogen peroxide. Photo-Fenton reactions are also important sources of OH radicals in water containing sufficiently high iron concentrations. Mopper and Zhou reported that the total OH radical formation rate in seawater is significantly larger than expected from the sum of these processes.[3,4] They suggested that OH radicals are also generated by the photolysis of dissolved organic matter (DOM),[3,4] especially chromophoric and/or colored dissolved organic matter (CDOM) that is defined as dissolved organic matter having absorption in the UV region (280 – 400 nm).

Due to the high reactivity and short lifetime of OH radicals, the steady-state concentrations of OH radicals are generally very low. The photochemical formation rates of OH radicals have been determined by indirect methods using probe compounds. Some methods for determining OH radicals in natural water have been proposed. Zhou and Mopper used two different methods: one method was based on hydrogen atom abstraction from methanol, and the other was based on the addition of an OH radical to the aromatic ring of benzoic acid.[3,4] A reaction between OH radicals and dimethyl sulfoxide was used by Vaughan and Blough.[5] The rate of OH radical formation was also determined by using the degradation rate of butyl chloride.[6] Arakaki *et al*. reported a simple method using a benzene probe to determine the OH radical formation rate in rain, dew and cloud water. In this method, phenol formed from the reaction of benzene with OH radicals was determined by isocratic HPLC.[7,8] However, the OH radical formation rates for seawater were from 10 to 100 times lower than those for rain, dew and cloud water.

In the present study, a simple, rapid and highly sensitive on-line preconcentration HPLC system was applied to the determination of OH radical formation rates in river water and seawater samples. The system employed in this study was sensitive enough to detect OH radical formation in seawater and river water. The OH radical formation rates for river water and seawater were determined, and the contributions from well-known OH radical sources (nitrate, nitrite and hydrogen peroxide) were estimated. The OH radical formation rate from unknown sources (*i.e.* sources other than nitrate, nitrite and hydrogen peroxide) was also estimated, and the sources of OH radicals in natural water are discussed.

Experimental

Reagents

All chemicals and solvents used were of reagent grade and without further purification. Deionized water of specific

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resistance greater than 18 × 10^6 ohm cm was from a Milli-Q Plus water purification system.

Photochemical experiments

Photochemical experiments were carried out by using a 150 W ozone-free Xe lamp (Ushio, UXL-159H) with a low cut filter (Asahi Techno Glass, UV-31, cut-off wavelength 310 nm). The light intensity of the Xe lamp was determined by measuring the photochemical degradation rate of 2-nitrobenzaldehyde (2-NB). The degradation rate of a 8 μM 2-NB solution in a quartz photochemical reaction cell (7 cm diameter and 2 cm length) was analyzed by simple isocratic HPLC. The degradation rate of 2-NB for the Xe lamp employed in this study was 0.00075 s^{-1}. The degradation rate of 2-NB by sunlight on September 30, 1999 at Higashi-Hiroshima (at noon under clear sky conditions) was 0.00854 s^{-1}, suggesting that the Xe lamp employed in this study was about 11 times less powerful than sunlight. In this study, the OH radical formation rates were normalized to a 2-NB degradation rate of 0.00854 s^{-1}.

Filtered natural water samples with 1.2 mM benzene were illuminated at room temperature by the Xe lamp in the same quartz photochemical reaction cell that was used for determining of the 2-NB degradation rate mentioned above. Photochemically formed OH radicals were quantitatively trapped by benzene, and phenol was formed as a result. The phenol concentration was determined by on-line preconcentration HPLC, as described below. The concentration of phenol in a sample with 1.2 mM benzene increased linearly with increasing illumination time up to 180 min, and no photochemical formation of phenol without benzene was observed. The photochemical formation of phenol in Milli-Q water with 1.2 mM benzene was not detected under the experimental conditions employed in this study. The concentrations of benzene and OH radical sources were essentially unchanged before and after the photochemical experiments.

Determination of phenol

The phenol concentrations were determined by an HPLC system equipped with an on-line preconcentration column and a fluorescence detector. A C18 reverse-phase column (Supelco, LC-18 5 μm 4.6 mm i.d. × 250 mm length or Kanto Kagaku, RP-18GP 5 μm 4.6 mm i.d. × 150 mm length) was used for separation. The mobile phase was $CH_3CN:H_2O = 50:50$ (v/v) for the Supelco column and $CH_3CN:H_2O = 40:60$ (v/v) for the Kanto Kagaku column. The flow rate of the mobile phase was 1.0 ml min^{-1}. A preconcentration column (Nomura Kagaku, Develosil PhA 10 μm, 4.0 mm i.d. × 33 mm length) was used instead of a sample loop at the sample injection valve.[8] A 0.5 ml portion of the sample was injected with a 1.0 ml gas-tight syringe. The fluorescence detector was operated at 270 nm for excitation and 297 nm for emission. The calibration curves for phenol were linear up to 200 nM, and were essentially unaffected by co-existing sea salt. The detection limit of phenol was defined here as the equivalent concentration of three times the standard deviation on the five blank measurements, which was 0.14 nM. Zhou and Mopper reported a sensitive method to detect the photochemically produced OH radical, in which formaldehyde formed from OH radicals and methanol was determined as a 2,4-dinitrophenyl hydrazone derivative by HPLC with UV detection.[4] The detection limit in the present study was better than that for their method (1 – 2 nM).

Determination of other species

Fluorescent matter (FM) in river water and seawater samples was determined at an excitation wavelength of 320 nm and an emission wavelength of 420 nm. An acidic solution of quinine sulfate (analytical grade from Nacalai Tesque, Inc.) was used as the standard for FM, in which the fluorescence intensity given by 2.8 μg L^{-1} quinine sulfate dihydrate solution (pH = 2.0) was taken as 25 fluoresce units (flu).[10]

The concentration of dissolved organic carbon (DOC) was determined by using a Shimadzu TOC5000A TOC Analyzer. Nitrate and nitrite in river water were measured by suppressor-type ion chromatography (Yokogawa Analytical Systems, IC-7000II and Dionex, DX-500). Nitrate and nitrite in seawater were determined spectrophotometrically by a HITACHI K-1000 flow-injection analyzer equipped with and without a home-made copperized cadmium column.[11] Hydrogen peroxide was determined by a previously reported method.[10]

Sampling

River water samples were collected in two rivers, the Ohta river and the Kurose river. The Ohta river is one of the biggest rivers in the Hiroshima Prefecture, and it flows through Hiroshima City into Hiroshima Bay in the Seto Inland Sea. The Kurose river is a small river that flows through Higashi-Hiroshima City. Our Hiroshima University is located on the upper reach of the Kurose river. Sampling was carried out at 8 locations on each river on December 12 – 13, 1999.

Seawater samples were collected at 3 points. The samples from the Seto Inland Sea were collected on August 7, 1999, at 34˚ 07.0′ N 132˚ 18.5′ E by R/V Toyoshio Maru belonging to Hiroshima University. Open ocean water was collected at the center of the North Pacific (30˚ 00′ N 160˚ 00′ E) on June 30, 2000 by R/V Hakuho Maru, University of Tokyo. Seawater samples from the Yellow Sea (37˚ 00′ N 124˚ 00′ E), were collected on October 21, 2001, by R/V Onnuri, Korea Ocean Research and Development Institute.

Results and Discussion

Determination of OH radical formation rates

The photochemical formation rate of OH radicals (R_{OH}) was calculated by using the following equation:

$$R_{OH} = \frac{R_{phenol}}{F_{benzene\text{-}OH} Y_{phenol}}, \tag{1}$$

where R_{phenol} is the photochemical formation rate of phenol obtained experimentally, $F_{benzene\text{-}OH}$ is the fraction of OH radicals that react with benzene, as opposed to with other competing OH radical scavengers, and Y_{phenol} is the yield of phenol from the reaction with the OH radical. Y_{phenol} was reported to be 0.75.[7,8]

$F_{benzene\text{-}OH}$ for cloud water, reported by Arakaki and Faust, was at least 0.94 with 1.2 mM added benzene,[7] suggesting that most of the OH radicals formed photochemically in cloud water reacted with benzene. However, in natural water, especially in seawater, many unknown and known scavengers that react with OH radicals are present. When a natural water sample containing benzene, with or without an added OH radical source, is exposed to the light, OH radicals are photochemically produced at the rate R_{OH}; these react with natural scavenger(s) in the sample and the added benzene at rates of $R_{scavenger}$ and $R_{benzene}$, respectively. Under the steady-state condition, the OH radical formation rate is equal to the OH radical consumption rate. The relationships among the reaction rates mentioned above are summarized by the following equations:

Table 1 Rates of OH radical formation from nitrate, nitrite and hydrogen peroxide and comparison with those reported

	Radiation	Sample	NO_2^- M s^{-1} $M(NO_2^-)^{-1}$	NO_3^- M s^{-1} $M(NO_3^-)^{-1}$	H_2O_2 M s^{-1} $M(H_2O_2)^{-1}$
This study	Sunlight	Milli-Q water	2.30×10^{-5}	1.60×10^{-7}	4.02×10^{-6}
	Xe lamp	Milli-Q water	2.07×10^{-5}	1.79×10^{-7}	3.36×10^{-6}
	Xe lamp	Seawater[a]	2.24×10^{-5}	1.63×10^{-7}	2.10×10^{-6}
	Xe lamp	Seawater[b]	2.31×10^{-5}	1.54×10^{-7}	
Zepp *et al.*[12]	Sunlight	Freshwater		2.5×10^{-7}	
Mopper and Zhou[3]	Sunlight	Seawater	2.3×10^{-5}	3.0×10^{-7}	4.1×10^{-6}
Arakaki *et al.*[8]	Sunlight	Milli-Q water	2.81×10^{-5}	2.43×10^{-7}	3.52×10^{-6}

a. Seawater collected in the Seto Inland Sea. b. Seawater collected in open ocean.

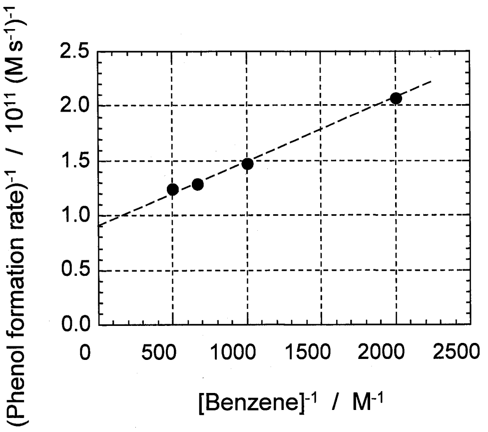

Fig. 1 Relationship between $1/R_{phenol}$ *vs.* 1/[benzene] for seawater collected in the open ocean. $F_{benzene\text{-}OH}$ calculated from the slope and intercept of the plots is estimated to be 0.66 with 1.2 mM benzene.

$$R_{OH} = R_{scavenger} + R_{benzene}, \tag{2}$$

$$R_{scavenger} = k_{scavenger}[\text{scavenger}][\text{OH}]_{ss} = k'_{scavenger}[\text{OH}]_{ss}, \tag{3}$$

$$R_{benzene} = k_{benzene}[\text{benzene}][\text{OH}]_{ss}, \tag{4}$$

where $k_{scavenger}$ is the reaction rate constant of OH radicals with natural scavengers in the sample solution, $k'_{scavenger}$ is the apparent OH radical scavenging rate constant of natural scavengers, $k_{benzene}$ is the reaction rate constant of OH radicals with benzene, and $[\text{OH}]_{ss}$ is the steady-state OH radical concentration. In solutions containing a high concentration of benzene with no other scavengers, most of the OH radicals formed photochemically react with benzene ($R_{benzene} \gg R_{scavenger}$).

The fraction of OH radicals that react with benzene ($F_{benzene\text{-}OH}$) in Eq. (1) can be described as follows:

$$F_{benzene\text{-}OH} = \frac{R_{benzene}}{R_{benzene} + R_{scavenger}} = \frac{[\text{benzene}]}{[\text{benzene}] + k'_{scavenger}/k_{benzene}}. \tag{5}$$

From Eqs. (1) – (5), thus, the phenol formation rate (R_{phenol}) can be described as follows:

$$\frac{1}{R_{phenol}} = \frac{1}{R_{OH}\,Y_{phenol}} + \frac{k'_{scavenger}}{R_{OH}\,Y_{phenol}\,k_{benzene}\,[\text{benzene}]}. \tag{6}$$

Equation (6) indicates that a plot of $1/R_{phenol}$ *vs.* 1/[benzene] should be a straight line and that $k'_{scavenger}/k_{benzene}$ can be calculated from the slope and intercept of the plots. $F_{benzene\text{-}OH}$ is calculated from $k'_{scavenger}/k_{benzene}$ and the concentration of benzene (1.2 mM) by Eq. (5)

In water samples collected from the Kurose and Ohta rivers, the $F_{benzene\text{-}OH}$ values calculated from plots of $1/R_{phenol}$ *vs.* 1/[benzene] were 0.92 and 0.99, respectively. These results indicate that most of the photochemically formed OH radicals reacted with benzene in river water in a similar manner to their reactions in cloud water and Milli-Q water. Figure 1 shows a plot of $1/R_{phenol}$ *vs.* 1/[benzene] for seawater collected in the open ocean. The plot shows a single straight line, and $F_{benzene\text{-}OH}$ calculated from the slope and intercept of the plot is 0.66 with 1.2 mM benzene. $F_{benzene\text{-}OH}$ in Seto Inland Sea seawater estimated in the same way was 0.68. These results suggest that 32 – 34% of photochemically formed OH radicals react with OH radical scavengers other than benzene in seawater samples. Many OH radical sinks in seawater have been reported together with their scavenging rates.[1,2,12] Mopper and Zhou estimated that scavenging by Br^- consumes about 93% of the OH radicals formed photochemically in seawater.[3] The difference between the $F_{benzene\text{-}OH}$ of river water and seawater may be due to the scavenging process by Br^- ions.

Rates of OH radical formation from nitrate, nitrite and hydrogen peroxide

The concentration of photochemically formed phenol increased linearly with an increase in the concentrations of nitrate, nitrite and hydrogen peroxide up to 600 μM, 8 μM and 40 μM, respectively. The rates of OH radical formation are summarized in Table 1. The OH radical formation rates were normalized to the 2-NB degradation rate of 0.00854 s^{-1} (clear sky condition at noon on September 30, 1999 at Higashi-Hiroshima).

The previously reported OH radical production rates are also summarized in Table 1. The results cited in Table 1 were obtained at middle latitudes and noon time under a clear sky; those OH radical production rates and our results should be comparable with each other. The formation rates determined in this study are in good agreement with those reported previously, although our formation rates from nitrate are slightly lower than those reported previously.

OH radical formation rates in natural water

The OH radical photoproduction rates for river water and seawater samples are summarized in Tables 2 and 3. The concentrations of nitrate, nitrite, hydrogen peroxide, FM and DOC are also listed. The OH radical formation rates in the samples from the Kurose river were high, because the Kurose river contains high concentrations of nitrate and nitrite.

Table 2 The OH radical formation rates in river water samples, concentration of OH radical sources, percent contributions from different sources and OH radical formation rate from unknown sources other than nitrate, nitrite and hydrogen peroxide

	OH radical formation rate/ $\times 10^{-12}$ M s^{-1}	Concentration					f_i				OH radical formation rate from unknown sources[b]/ $\times 10^{-12}$ M s^{-1}
		NO_2^-/ μM	NO_3^-/ μM	H_2O_2/ nM	FM/ flu	DOC, ppmC	NO_2^-, %	NO_3^-, %	H_2O_2, %	Unknown[a], %	
Ohta river											
1 (Upstream)	10.1	0.05	0.9	22	48	1.5	10.2	1.6	0.7	87.5	8.88
2	10.8	0.05	9.7	20	55	0.7	9.5	16.1	0.6	73.8	7.98
3	5.6	0.05	14.8	20	63	0.6	18.3	46.8	1.2	33.7	1.90
4	7.9	0.05	21.6	46	73	0.5	13.1	49.0	1.9	36.0	2.84
5	10.2	0.05	20.4	20	53	0.5	10.1	35.5	0.7	53.7	5.51
6	12.6	0.05	19.0	24	84	0.7	8.2	26.9	0.6	64.2	8.10
7	26.4	0.1	24.8	20	97	0.6	8.5	16.8	0.3	74.5	19.66
8 (Downstream)	25.9	0.3	33.2	26	141	0.9	25.6	23.0	0.3	51.1	13.22
Kurose river											
1 (Upstream)	17.5	0.05	18.7	20	125	0.6	5.9	19.1	0.4	74.7	13.10
2	171.8	5.5	77.9	20	709	3.1	66.7	8.1	0.0	25.2	43.21
3	239.9	5.9	90.4	26	712	3.4	50.6	6.7	0.0	42.6	102.17
4	890.4	34.4	101.8	43	944	3.4	79.8	2.0	0.0	18.2	161.84
5	377.7	12.6	172.1	32	599	2.3	68.7	8.1	0.0	23.1	87.24
6	194.4	5.3	175.9	23	379	1.9	56.0	16.2	0.0	27.8	53.96
7	179.8	5.0	159.6	23	356	1.9	57.5	15.9	0.0	26.5	47.74
8 (Downstream)	146.3	3.4	152.7	33	316	0.7	47.6	18.7	0.1	33.7	49.29

a. $f_{unknown} = 100 - (f_{NO_3^-} + f_{NO_2^-} + f_{H_2H_2})$ (%). b. OH radical formation rate from unknown sources = (OH radical formation rate) × $f_{unknown}$/100.

Table 3 The OH radical formation rates for seawater, concentration of OH radical sources, percent contributions from different sources and OH radical formation rate from unknown sources other than nitrate, nitrite and hydrogen peroxide

Depth/ m	OH radical formation rate/ $\times 10^{-12}$ M s^{-1}	Concentration					f_i				OH radical formation rate from unknown sources[b]/ $\times 10^{-12}$ M s^{-1}
		NO_2^-/ μM	NO_3^-/ μM	H_2O_2/ nM	FM/ flu	DOC, ppmC	NO_2^-, %	NO_3^-, %	H_2O_2, %	Unknown[a], %	
Yellow Sea											
0	3.9	0.020	0.28		50	1.3	10.5	1.3		88.2	3.45
20	3.6	0.020	0.15		32	1.2	11.3	0.7		87.9	3.20
30	4.9	0.034	0.12		60	1.1	14.3	0.4		85.2	4.18
40	8.2	0.054	3.14		70	1.1	13.5	6.8		79.7	6.57
50	7.3	0.034	3.09		71	1.2	9.7	7.6		82.7	6.00
60	7.2	0.153	2.69		61	1.1	44.2	6.7		49.1	3.51
Seto Inland Sea											
0	15.3	0.05	0.09	23	75	1.7	6.8	0.1	0.5	92.6	14.14
5	5.7	0.06	0.05	20	65	1.4	20.4	0.2	1.2	78.2	4.49
10	9.1	0.09	0.05	20	61	1.3	20.0	0.1	0.7	79.1	7.21
15	10.2	0.05	0.18	20	59	1.2	10.1	0.3	0.7	88.9	9.05
20	23.5	0.74	0.99	20	56	1.2	64.8	0.8	0.3	34.2	8.04
30	49.5	1.78	3.25	20	61	1.3	74.5	1.2	0.1	24.2	11.99

a. $f_{unknown} = 100 - (f_{NO_3^-} + f_{NO_2^-} + f_{H_2H_2})$ (%). b. OH radical formation rate from unknown sources = (OH radical formation rate) × $f_{unknown}$/100.

In order to discuss the sources of OH radicals, we estimated the contributions of various sources to OH radical photoproduction. The percent contributions from well-known OH radical sources, such as nitrate, nitrite and hydrogen peroxide, to total OH radical formation (f_i (i = NO_2^-, NO_3^- and H_2O_2)) can be calculated by

$$f_i = \frac{k_i[C_i]}{R_{total}} \times 100\ (\%) \quad (i = NO_2^-, NO_3^- \text{ and } H_2O_2), \tag{7}$$

where k_i is the rate of OH radical formation from nitrite, nitrate and hydrogen peroxide shown in Table 1, $[C_i]$ is the concentration of each species and R_{total} is the OH radical photoproduction rate determined experimentally for the sample. The f_i (i = NO_2^-, NO_3^- and H_2O_2) values are summarized in Tables 2 and 3. In the river water samples, nitrate and nitrite were important OH radical sources, and about 50 – 80% of photochemically formed OH radicals in the Kurose river samples were due to nitrite.

Hydrogen peroxide was a less important source of OH radicals. Fujiwara *et al.* reported that the concentration of hydrogen peroxide in coastal seawater was proportional to the intensity of solar radiation. The maximum concentration of

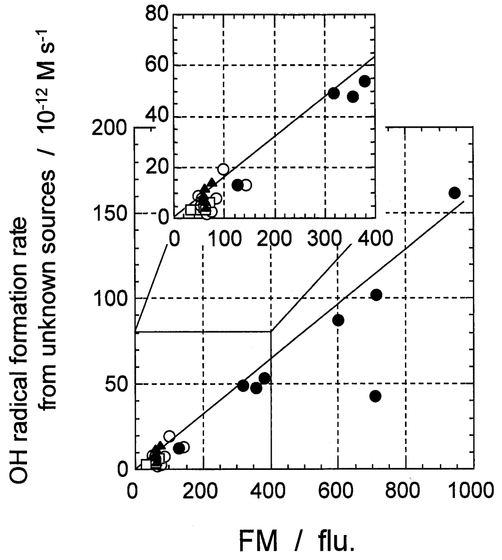

Fig. 2 OH radical formation rates from unknown sources other than nitrate, nitrite and hydrogen peroxide against FM as an index of CDOM. ●, Kurose river; ○, Ohta river; ▲, Seto Inland Sea; □, Yellow Sea.

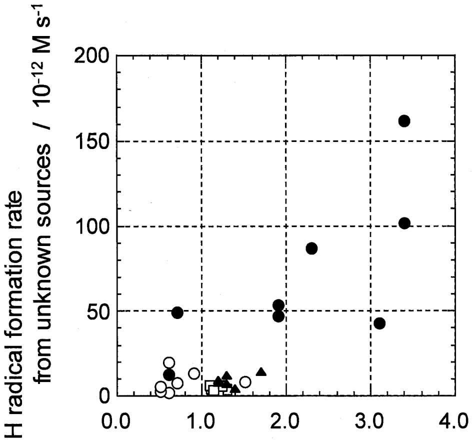

Fig. 3 OH radical formation rates from unknown sources other than nitrate, nitrite and hydrogen peroxide against DOC. ●, Kurose river; ○, Ohta river; ▲, Seto Inland Sea; □, Yellow Sea.

hydrogen peroxide reported was about 400 nM, at midday in the summer. The OH radical formation from 400 nM hydrogen peroxide was calculated to occur at a rate of 0.84×10^{-12} M s^{-1}, suggesting that OH radical formation from photochemically formed hydrogen peroxide is also negligible compared to the OH radical formation rates in seawater.

The formation percentages and OH radical formation rates from unknown sources were also estimated, and the results are given in Tables 2 and 3. Twenty to 90% of the OH radicals were photochemically formed from unknown sources other than nitrite, nitrate and hydrogen peroxide. In the surface-to-mid-layer seawater, more than 80% of the OH radicals were formed from unknown sources. A plot of OH radical formation from unknown sources against FM as an index of CDOM is shown in Fig. 2. The relationship between the OH radical formation from unknown sources and DOC is also shown in Fig. 3. FM was strongly correlated with the rate of OH radical formation from unknown sources, although the relationship between OH radicals from unknown sources and DOC was not clear. The fluorescence of natural water samples in the UV region is appreciated to be an indicator of CDOM. Many successful correlations between the UV absorbance and fluorescence have been reported for seawater. These results indicate that OH radical formation from unknown sources can be explained by the photolysis of CDOM; FM is a better indicator for the photochemical formation of OH radicals from CDOM than DOC.

Nitrate and nitrite ions, however, have weak absorption bands in the UV region; the absorption coefficients are 7 M^{-1} cm^{-1} at 300 nm for nitrate and 25 M^{-1} cm^{-1} at 360 nm for nitrite, respectively. The absorbances of 100 μM nitrate at 300 nm and 10 μM nitrite at 360 nm are estimated to be 0.7×10^{-3} cm^{-1} and 0.25×10^{-3} cm^{-1}, respectively. Typical absorbances measured at 350 nm for the Kurose river water samples were $3 - 10 \times 10^{-3}$ cm^{-1}. These estimations indicate that the absorbance in the UV region used as an index of CDOM content for river water containing 100 μM nitrate and 10 μM nitrite contains 10 – 30% inorganic nitrogen absorption. Consequently, in the river water samples that contain high concentrations of nitrate and nitrite, inorganic nitrogen absorption may cause an overestimation of CDOM, as determined by the UV absorption.

Conclusion

The photochemical formation rates of OH radicals in river water and seawater were determined by a simple, rapid and sensitive benzene probe method. The on-line preconcentration HPLC system employed in this study provided sufficient sensitivity to detect OH radical formation in seawater and river water. The OH radical formation rates determined from well-known OH radical sources, such as nitrate, nitrite and hydrogen peroxide, were in good agreement with those reported in previous studies. The river water samples containing high concentrations of nitrate and nitrite showed a high OH radical formation rate, and the photolysis of nitrate and nitrite were important sources of OH radicals. In oligotrophic seawater samples from the surface-to-midlayer, more than 80% of OH radicals were formed from unknown sources (*i.e.* from sources other than nitrate, nitrite and hydrogen peroxide). The hydrogen peroxide contribution to OH radical formation was negligible in both river water and seawater.

Based on the correlation between the OH radical formation from unknown sources and FM as an index of CDOM, the OH radical formation from unknown sources can be explained by the photolysis of CDOM. Fluorescence is available for an index of the photochemical formation of OH radicals from CDOM in natural water. In the river water samples collected in the midstream of Kurose river, the OH radical formation rates from CDOM were high, although the formation percentages from CDOM value were small. CDOM is a major source for the photochemical formation of OH radicals in seawater samples from the surface-to-midlayer. It is concluded that the photolysis of CDOM is a significant OH radical source in the river water and seawater samples from the surface-to-midlayer, which are the most important regions of water for the photochemistry of natural water.

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