Contribution of the Photo-Fenton Reaction to Hydroxyl Radical Formation Rates in River and Rain Water Samples

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The hydroxyl radical (OH radical) formation rates from the photo-Fenton reaction in river and rain water samples were determined by using deferoxamine mesylate (DFOM), which makes a stable and strong complex with Fe(III), resulting in a suppression of the photo-Fenton reaction. The difference between the OH radical formation rates with and without added DFOM denotes the rate from the photo-Fenton reaction. The photoformation rates from the photo-Fenton reaction were in the range of $0.7 - 45.8 \times 10^{-12}$ and $2.7 - 32.3 \times 10^{-12}$ M s^{-1} in river and rain water samples, respectively. A strong positive correlation between the OH radical formation rate from the photo-Fenton reaction and the amount of fluorescent matter in river water suggests that fluorescent matter, such as humic substances, plays an important role in the photo-Fenton reaction. In rain water, direct photolysis of hydrogen peroxide was an important source of OH radicals as well as the photo-Fenton reaction. The contributions of the photo-Fenton reaction to the OH radical photoformation rates in river and rain water samples were in the ranges of $2 - 29$ and $5 - 38\%$, respectively. Taking into account the photo-Fenton reaction, $33 - 110$ (mean: 80) and $42 - 110$ (mean: 84)% of OH radical sources in river and rain water samples, respectively, collected in Hiroshima prefecture were elucidated.

Introduction

The hydroxyl radical (OH radical), which is the most oxidative reactant among the active oxygen species,[1,2] is generated as a short-lived intermediate in rain and river water by photochemical reactions under natural sunlight irradiation.[3-8] Because of its high reactivity (second-order rate constant of the OH radical with organic compounds: $10^8 - 10^{10}$ M^{-1} s^{-1}),[9] the OH radical plays an important role in the transformation of organic compounds, especially recalcitrant organic compounds, such as those resistant to chemical, biological and direct photochemical degradation in natural water.[10,11] For example, the reaction of the photo-formed OH radical with bisphenol A, a compound that is resistant to direct photochemical degradation under natural sunlight irradiation, has a significant effect on the fate of bisphenol A in river water.[7] Similarly, it has been suggested that the oxidation of polychlorinated biphenyls (PCBs), a persistent group of organic pollutants, with OH radicals can affect the fate of PCBs in natural water.[12] Furthermore, the reaction of OH radicals with inorganic compounds, such as S(IV) species in atmospheric water, has been proposed as a pathway for the generation of sulfate.[13] In order to understand the effect of the OH radical on the behavior of organic and inorganic compounds in natural water under sunlight irradiation, it is important to determine the photochemical formation rate of the OH radical and to clarify its formation mechanism.

There are several mechanisms of OH radical photoformation in natural water: direct photolysis of nitrite (NO_2^-/HNO_2), nitrate ions (NO_3^-) and hydrogen peroxide (H_2O_2).[14,15] In our previous studies, the total contribution of OH radicals from direct photolysis of NO_2^-, NO_3^- and H_2O_2 accounted for 10 to 80% of the OH radical photoformation rate in river water.[6-8] The mean contributions to OH radical production from the photolysis of NO_2^- and NO_3^- in rain water were only 7.8 and 28.4%, respectively, while almost all of the OH radicals in dew water were derived from the photolysis of NO_2^-.[5] Consequently, unknown sources of OH radical photoformation still remain in both river and rain water. Furthermore, although the OH radical photoformation rate from unknown sources was strongly correlated to the amount of fluorescent matter (FM) in river water,[6] the role of FM in OH radical photoformation is not clear.

Fe(III), which exists in the form of complexes with natural dissolved organic matter (DOM), such as humic substances in natural water, is photochemically reduced to Fe(II) under sunlight irradiation through a ligand-to-metal charge transfer (reaction 1).[16] In addition, the photodegradation of the Fe(III) monohydroxy complex also produces Fe(II) and the OH radical (reaction 2),[17] while this reaction is unlikely to be a significant production mechanism of Fe(II) and the OH radical in natural water.[18] Reduced iron can react with H_2O_2 to produce OH radicals *via* the so-called "Fenton's reaction" (reaction 3). The photo-Fenton reaction consisting of these reactions serves as a source of OH radical formation in natural water.

$$\text{Fe(III)-(DOM)}_m + \text{light} \longrightarrow \text{Fe(II)-DOM}_{m-1} + \text{DOM}_{ox}^+ \quad (1)$$

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$$Fe(OH)^{2+} + light \longrightarrow Fe(II) + \cdot OH \qquad (2)$$

$$Fe(II) + H_2O_2 \longrightarrow Fe(III) + \cdot OH + OH^- \qquad (3)$$
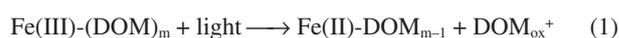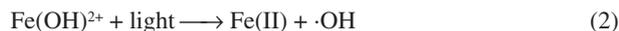
In this study, the contributions of the photo-Fenton reaction to OH radical formation in river and rain water were examined by using deferoxamine mesylate (DFOM). This compound can form a strong and stable Fe(III)-complex, resulting in suppression of the photo-Fenton reaction. However, the contributions of the photo-Fenton reaction to OH radical formation were limited in the case of highly colored, acidic and iron-rich river water.[19] In addition, it is necessary to take into account other contributions to OH radical formation, such as the direct photolysis of NO_2^-, NO_3^- and H_2O_2. Therefore, the contribution from the photo-Fenton reaction to OH radical formation was also estimated together with that from the direct photolysis of these OH radical sources. In addition, based on the relationship between the OH radical formation rate from the photo-Fenton reaction and the chemical components (H_2O_2, total iron, DOM and FM), the mechanisms of the photo-Fenton reaction in river and rain water are discussed.

Experimental

Reagents and chemicals

All chemicals and solvents used were of analytical reagent grade and were used as received. Ultra-pure water (Milli-Q water, >18 MΩ cm^{-1}, Millipore Japan) was used for the preparation of all solutions. A stock solution of DFOM ($C_{25}H_{48}N_6O_8H_4O_3S$, Sigma-Aldrich Japan) was dissolved to give a 10 mM solution. Potassium trisoxalate ferrate(III) was synthesized according to a method of Johnson.[20]

Analytical procedure for determination of OH radical photoformation rate

The photoformation rate of OH radicals was determined by a previously reported method using an automatic irradiation and injection system equipped with HPLC.[21] The added benzene in water samples transformed into phenol by photo-formed OH radicals under artificial sunlight irradiation from a Xe lamp with an optical filter. The slope of the plot of the phenol concentration against the irradiation time shows the photoformation rate of phenol in water samples (R_{phenol}). The OH radical photoformation rate (R_{OH}) was calculated by the following equation:

$$R_{OH} = \frac{R_{phenol}}{Y_{phenol} \times F_{benzene,OH}}, \qquad (4)$$

where Y_{phenol} is the yield of phenol formed per benzene oxidized by OH radicals (mean ± standard deviation = 0.75 ± 0.07) and $F_{benzene,OH}$ is the fraction of OH radicals that react with benzene.[3] Using benzene as a probe of the OH radical at 1.2 mM, most of the OH radicals formed in rain and river water samples react with benzene ($F_{benzene,OH} \cong 1.0$),[5,6,21] even if the OH radical scavengers, such as chloride ion and DOM exist in natural water samples.

The effect of DFOM at 10 μM on the suppression of OH radical formation from the photo-Fenton reaction was evaluated by using a mixing solution of 1 μM potassium trisoxalate ferrate(III) and 0.5 μM H_2O_2 at pH 5.6. The effect of the addition of a variety of different DFOM concentrations (0 – 10 μM) on the reaction of OH radicals with benzene was examined by using a solution containing 1 mM sodium nitrate as a source of OH radicals at pH 5.6.

The phenol formation rates in a water sample with and without added DFOM at 10 μM were determined and the OH radical formation rate was calculated for each solution. Then, the OH radical formation rate from the photo-Fenton reaction was obtained from the difference between the OH radical formation rates with and without added DFOM.

The OH radical formation rates from the direct photolysis of NO_3^-, NO_2^- and H_2O_2 were calculated by multiplying the concentration of each source in the water samples by their rate constants for OH radical formation. The rate constants used for OH radical formation from NO_3^-, NO_2^- and H_2O_2 were 2.76×10^{-5}, 2.56×10^{-7} and 2.76×10^{-6} s^{-1}, respectively.[21] The percentage contribution from each source to the OH radical formation rate determined was then estimated.[6]

The light intensity of the irradiation system was determined by using the chemical actinometry of 2-nitrobenzaldehyde (2-NB) and the same reaction cell as that for the determination of OH radicals.[21] The degradation rates of 2-NB ($J_{2\text{-NB}}$) obtained in the present study ranged from 0.0090 to 0.0093 s^{-1}. In this study, the OH radical photoformation rates were normalized to $J_{2\text{-NB}} = 0.0093$ s^{-1}, which was determined at noon, under clear-sky conditions in Higashi-Hiroshima city (34°N) on Oct. 7, 2002.[8] It must be recognized that the photochemical reaction depends on both the light intensity and the wavelength of the light source. However, this normalization enables a comparison to be made between data, and a quantitative discussion on the contribution from each OH radical source.

Other determinations

The concentrations of anions (Cl$^-$, NO_3^- and SO_4^{2-}) and the pH were determined by ion chromatography (Dionex, DX-500) and a glass-electrode pH meter (TOA, HM30S), respectively. The nitrite ion concentration was determined by a colorimetric method, the diazotization reaction using *N*-1-naphthyl-ethylenediamine dihydrochloride and sulfanilamide. Dissolved organic carbon (DOC) was determined by using a TOC-5000 (Shimadzu Co.). FM was determined by using a fluorescence spectrophotometer (Hitachi Ltd., F-4500) at an excitation wavelength of 320 nm and an emission wavelength of 420 nm. A 2.8 μg L^{-1} quinine sulfate dehydrate solution (analytical grade from Nacalai Tesque, Inc.) acidified by sulfuric acid at pH 2.0 was used as the standard for FM, in which the fluorescence intensity was taken as 25 fluorescence units (flu.).[22] The total dissolved iron was determined by using inductively coupled plasma atomic emission spectrometry (Optima 3000, Perkin Elmer). The H_2O_2 concentration was determined by a method of Sakugawa *et al.*[23]

Sampling

River-water samples were collected from the Kurose, Ohta, Seno, Ashida and Oze Rivers of Hiroshima prefecture, western Japan. Sampling was carried out from Oct. 2004 to Oct. 2005. For river-water samples collected in 2004, measurements of FM were not performed. Rain-water samples were collected on the roof of Hiroshima University from June 2005 to Nov. 2005. A polyethylene funnel with an opening of diameter 24 cm and a 1-L PE bottle were set out before a precipitation event, and then immediately transported to the laboratory after the event. River and rain water samples were filtered through a pre-combusted glass fiber filter (Advantec, 0.45 μm nominal rating) and a nuclepore polycarbonate filter (Whatman, 0.2 μm pore size). Filtered water samples were stored in the dark at 4°C until analysis. The chemical compositions of river and rain water samples collected are summarized in Table 1.

Table 1   Summary of the chemical compositions of river and rain water samples collected in Hiroshima prefecture

	Unit	River			Rain		
		n	Mean	Min. – Max.	n	Mean	Min. – Max.
pH		20	7.5	6.7 – 9.0	5	5.0	4.2 – 5.9
Cl^-	μM	29	341	123 – 1551	9	8.7	0.2 – 31.0
NO_3^-	μM	33	51.2	2.0 – 197	9	24.2	7.2 – 96.5
SO_4^{2-}	μM	29	81.0	22.0 – 400	9	17.2	0.3 – 63.1
NO_2^-	μM	33	1.20	N.D. – 16.7	9	0.31	N.D. – 1.47
DOC	mgC L^{-1}	33	1.20	0.35 – 3.26	9	1.01	0.48 – 2.60
FM^a	Flu.	21	86.8	0.02 – 217	8	9.54	5.17 – 25.6
Total iron	μM	31	1.04	0.05 – 7.36	9	0.52	N.D. – 3.12
H_2O_2	μM	33	0.03	N.D. – 0.08	9	7.49	0.77 – 13.9

a. Excitation/emission wavelength = 320/420 nm.
N.D., Not detected.

Results and Discussion

Validity of the methods used to determine the OH radical formation rate from the photo-Fenton reaction using DFOM

The photoformation of phenol in a mixing solution of 1 μM potassium trisoxalate ferrate(III) and 0.5 μM H_2O_2, which we call the photo-Fenton solution, with and without DFOM at 10 μM, is shown in Fig. 1. In the solution without DFOM, Fe(II) is produced photochemically from Fe(III) oxalate complexes, resulting in the formation of OH radicals by the reaction of Fe(II) and H_2O_2.[24] The slope of the plot of the phenol concentration against the irradiation time for the solution with DFOM was much smaller than that for the solution without DFOM. The OH radical formation rates in photo-Fenton solution with and without DFOM, and 0.5 μM H_2O_2 solution were (193 ± 3.3), (7.2 ± 0.6) and (5.8 ± 0.6)× 10^{-12} M s^{-1} (n = 3), respectively. The OH radical photoformation rate in the solution with DFOM was similar to that in a 0.5 μM H_2O_2 solution. These results indicate that the photo-Fenton reaction was suppressed by the addition of DFOM to the solution. Therefore, the difference between the photoformation rates of OH radicals with and without the addition of DFOM represents the OH radical formation rate derived from the photo-Fenton reaction. Furthermore, the pH value was essentially unchanged by the addition of DFOM.

Since the determination of OH radicals is based on competition kinetics, it is possible that a large amount of DFOM induced the consumption of OH radicals by DFOM, resulting in an underestimation of the OH radical photoformation rate. The effect of the addition of a variety of different DFOM concentrations (0 – 10 μM) to a solution containing 1 mM sodium nitrate as a source of OH radicals on the reaction of OH radicals with benzene was examined. Up to 10 μM of DFOM showed no effect on the reaction of OH radicals with 1.2 mM benzene (Fig. 2). It has been reported that the reaction rate constant of the OH radical with DFOM ($k_{DFOM,OH}$) is 1.3×10^{10} M^{-1} s^{-1}.[25] Using this rate constant, the first-order scavenging rate constant of DFOM ($k_{DFOM,OH} \times$[DFOM]) at 10 μM was calculated to be 1.3×10^4 s^{-1}. This calculated value was three orders of magnitude smaller than that of benzene at 1.2 mM (1.56×10^7 s^{-1}) used in this study. Therefore, it is also demonstrated theoretically that the effect of 10 μM added DFOM on the reaction of OH radicals with benzene is negligible.

Using the rain and river-water samples, the effect of the reaction time of DFOM with Fe(III) and that of the DFOM
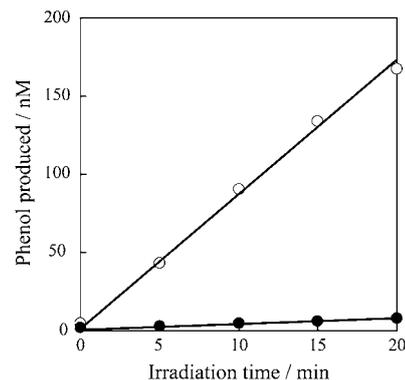
Fig. 1   Photoformation of the OH radical in a photo-Fenton solution (1 μM potassium trioxalate ferrate(III) and 0.5 μM hydrogen peroxide) with (●) and without (○) adding DFOM at 10 μM.
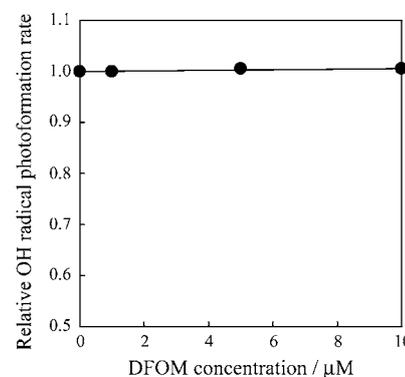
Fig. 2   Effect of the DFOM concentration on the OH radical photoformation rate in a solution containing of 1 mM $NaNO_3$ as a source of the OH radical.
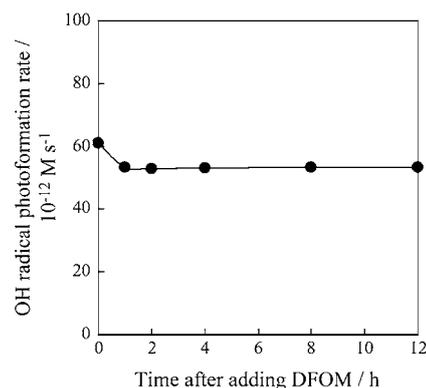
Fig. 3   Time-course studies showing the effect of 10 μM DFOM on the OH radical formation rate in a river-water sample.

concentration on the suppression of the photo-Fenton reaction were examined. The OH radical photoformation rate of a river-water sample at 1, 2, 4, 8 and 12 h after the addition of DFOM at a concentration of 10 μM is shown in Fig. 3. One hour after the addition of DFOM to the river-water sample, the OH radical photoformation rate was fairly constant and remained this way over a time period of 12 h. Therefore, the reaction time after the addition of DFOM to water samples was set at 1 h. The OH radical photoformation rates at different DFOM concentrations

Table 2   Summary of the OH radical photoformation rates and the calculated rates from each OH radical source in river and rain water samples

	n		Measured/ 10^{-12} M s^{-1}	Calculated from individual OH radical sources/10^{-12} M s^{-1}			
				Photo-Fenton	NO$_3^-$	NO$_2^-$	H$_2$O$_2$
River	33	Mean	56.1	7.0	13.0	29.5	< 0.1
		Range	7.8 – 525.4	0.7 – 45.8	0.5 – 50.5	< 0.1 – 460.9	
Rain	9	Mean	57.9	11.4	6.2	8.6	20.7
		Range	25.0 – 118.0	2.7 – 32.3	1.8 – 24.7	0.5 – 40.5	2.1 – 38.4
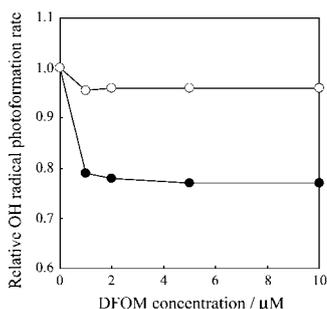
Fig. 4   OH radical photoformation rate from the photo-Fenton reaction as a function of the DFOM concentration in river (○) and rain (●) water samples.

(0 – 10 μM) were determined in river and rain water samples. Representative results of the OH radical photoformation rates as a function of a variable DFOM concentration in river and rain water samples are shown in Fig. 4. The OH radical photoformation rates were constant at DFOM concentrations above 5 μM. In addition, the concentration of dissolved total iron in almost all of the rain and river water samples used in this study was less than 5 μM. Since DFOM can form a strong complex with Fe(III) at a 1:1 molar ratio, these results suggest that a DFOM concentration of 10 μM is sufficient for suppressing OH radical formation from the photo-Fenton reaction in the river and rain water samples used in this study.

OH radical photoformation rates from photo-Fenton reactions in river and rain water

The photoformation rates of OH radicals in river and rain water samples are summarized in Table 2, which also gives the calculated photoformation rates of OH radicals from individual OH radical sources, such as the photo-Fenton reaction and the photolysis of nitrite ions, nitrate ions and hydrogen peroxide. The total photoformation rates measured were the same as those observed in our previous reports for river (5.6 – 890.4 × 10^{-12} M s^{-1})[6] and rain (range: < 0.5 – 330.3 × 10^{-12} M s^{-1})[5] water samples.

In river water, the OH radical photoformation rates from the photo-Fenton reaction determined by the difference between the OH radical formation rates with and without added DFOM were in the range of 0.7 – 45.8 × 10^{-12} M s^{-1}. In order to clarify the mechanism inducing the photo-Fenton reaction, the relationships between the OH radical formation rate from the photo-Fenton reaction and various chemical components (DOC, H$_2$O$_2$, total-iron and FM) were examined. There was a strong positive correlation between the OH radical formation rate from the photo-Fenton reaction and the content of FM ($r = 0.753$) and DOC ($r = 0.587$) (Fig. 5). The content of FM also exhibited a significantly positive correlation with the DOC concentration

($r = 0.819$, $p < 0.001$). In our previous study, a strong positive correlation between OH radical formation from unknown sources (other than the direct photolysis of nitrite, nitrate and H$_2$O$_2$) and FM was observed in river water.[6] The fluorescence intensity at an excitation wavelength of 320 nm and an emission wavelength of 420 nm, as used in this study, can be used as a rough index of the amount of humic substances in river water samples collected in Hiroshima prefecture.[26] Fukushima and Tatsumi reported that the photoreduction of Fe(III) is enhanced by addition of humic acids.[27] Therefore, the positive correlation between the OH radical formation rate from the photo-Fenton reaction and FM suggests that the FM, such as humic substances, plays an important role in the photo-Fenton reaction in river water, while the detailed mechanism is not yet clear. In support of this view, Southworth and Voelker reported that OH radical formation was high in a synthesis solution of Suwanee River fulvic acid and Fe(III) and that DFOM eliminated OH radical formation.[28]

In rain water, the OH radical photoformation rates from the photo-Fenton reaction determined by the difference between the OH radical formation rates with and without added DFOM were in the range of 2.7 – 32.3 × 10^{-12} M s^{-1}. The relationship between the OH radical formation rate from the photo-Fenton reaction and the amount of FM in rain water was slightly positive ($p < 0.01$, $r = 0.725$) (Fig. 6). The small fluorescence intensity in rain water, as compared to that in river water, indicated that the amount of FM, such as humic substances in rain water, is smaller than that in river water. In addition, the model calculation predicted that, in rain water, half of the dissolved Fe(III) forms a complex with humic substances and the rest of the Fe(III) is present as oxalate or hydroxide complexes, which are sources of photoproduced Fe(II).[18] Therefore, it suggests that OH radical formation from the photo-Fenton reaction in rain water might be induced by the photochemical reduction of various Fe(III) complexes.

In our HPLC analysis of OH radical formation rates, the phenol concentrations in all river and rain water samples with and without added DFOM increased linearly with the irradiation time, suggesting that the photoformation of H$_2$O$_2$ during light irradiation has a insignificant effect on OH radical formation.[3,29] In addition, there was no significant correlation between the OH radical formation rate from the photo-Fenton reaction and the pH value in river and rain water samples, while it is generally believed that the pH value of a solution affects the OH radical formation rate from the photo-Fenton reaction.[24]

The percentage contributions of the OH radical photoformation rate from the photo-Fenton reaction account for 2 – 29 (mean: 15)% of the total OH radical photoformation rate in river water (Table 3). Taking into account the photo-Fenton reaction, 33 – 110 (mean: 80)% of OH radical sources in river-water samples were elucidated. It is expected that the percentage contributions over 100% observed in several
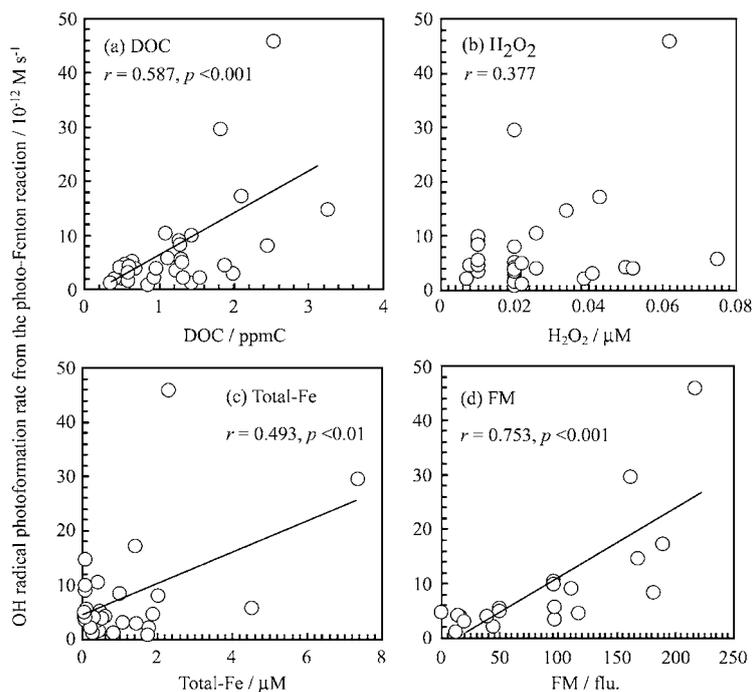
Fig. 5   Correlation between the OH radical formation rates from the photo-Fenton reaction and (a) DOC concentration, (b) H_2O_2 concentration, (c) total Fe concentration and (d) FM in the river water.
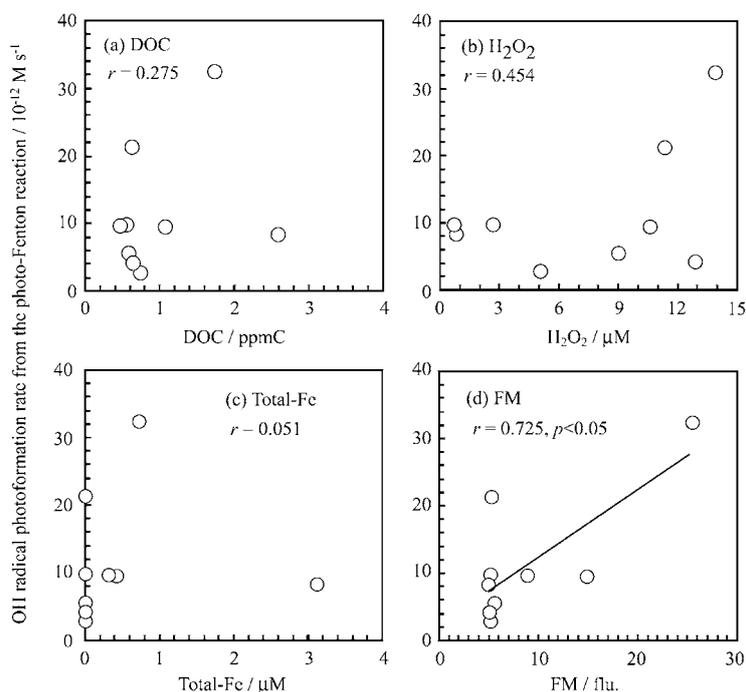
Fig. 6   Correlation between the OH radical formation rates from the photo-Fenton reaction and (a) DOC concentration, (b) H_2O_2 concentration, (c) total Fe concentration and (d) FM in the rain water.

river-water samples are attributable to measurement errors in both the observed and calculated values. The percentage contributions of the OH radical photoformation rates from the photo-Fenton reaction account for 5 – 38 (mean: 21)% of the total formation rates in rain water (Table 3). In addition to the photo-Fenton reaction, the contribution from the direct photolysis of H_2O_2, which is mainly derived from the dissolution of gas-phase H_2O_2 into atmospheric water,[30] was an important source of OH radicals in rain water, whereas this was not the case for river water. Taking into account the photo-Fenton reaction and direct photolysis of H_2O_2, 42 to 110 (mean: 84)% of OH radical sources in the rain-water samples were elucidated.

Our results presented in Table 3 suggest that there are still unknown sources of OH radical photoformation present in river

Table 3 Percentage contribution of OH radical photoformation from each OH radical source in river and rain water samples

	n		Contribution, %				
			Photo-Fenton	NO_3^-	NO_2^-	H_2O_2	Sum[a]
River	33	Mean	15	33	31	< 1	80
		Range	2 – 29	3 – 70	< 1 – 89		33 – 110
Rain	9	Mean	21	10	16	37	84
		Range	5 – 38	5 – 29	< 1 –73	3 – 74	42 – 110

a. Sum of OH radical contributions from photo-Fenton, NO_3^-, NO_2^- and H_2O_2.

and rain water samples. Direct photolysis reactions of chromophoric dissolved organic matter (CDOM), such as *p*-benzoquinone[31] and humic substances,[4] are possible sources of OH radicals in river water, though further study is needed to confirm this.

Conclusions

The rates of OH radical formation from the photo-Fenton reaction in river and rain water samples were determined by using DFOM, which can form a stable and strong complex with Fe(III), resulting in an inhibition of the photochemical reduction of Fe(III). The photo-Fenton reaction was suppressed by the addition of DFOM to water samples without interfering with the reaction of OH radicals with benzene and without affecting other photochemical reactions. The measurement results showed that the photo-Fenton reaction is one of the primary sources of OH radical photoformation in both river and rain water. Based on the correlation between the OH radical formation rate from the photo-Fenton reaction and FM in river water, it is suggested that FM, such as humic substances, plays an important role in photo-Fenton reaction. In contrast, it is expected that the photochemical reactions of various Fe(III) complexes induce the photo-Fenton reaction in rain water. In addition to the photo-Fenton reaction, the direct photolysis of H_2O_2 is an important process for OH radical formation in rain water. Taking into account the contribution of OH radical formation from the photo-Fenton reaction, more than 80% of OH radical sources in the river and rain water samples from Hiroshima prefecture were elucidated. It is speculated that one as yet unconfirmed source of OH radical photoformation present in both river and rain water samples is the direct photolysis of CDOM.

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