

Hydroxyl Radical Mediated Degradation of Diuron in River Water

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Abstract: Hydroxyl radicals ($\bullet\text{OH}$) mediated degradation of diuron in river water was evaluated by measuring the steady state concentrations of $\bullet\text{OH}$ in surface river water collected from the Kurose River, Japan. Photo-production rates of $\bullet\text{OH}$ in the river water samples ranged from $0.1 \times 10^{-10} \text{ Ms}^{-1}$ to $12 \times 10^{-10} \text{ Ms}^{-1}$ and scavenging rate constants were $0.47 \times 10^5 \text{ s}^{-1}$ to $21 \times 10^5 \text{ s}^{-1}$. The steady state concentrations of $\bullet\text{OH}$ in river water, which were calculated from the photo-production rates and scavenging rate constants were in the range $1.9 \times 10^{-16} \text{ M}$ to $10.4 \times 10^{-16} \text{ M}$. In this study, the consumption of $\bullet\text{OH}$ by anions (Cl^- , NO_2^- , NO_3^- , and SO_4^{2-}) accounted for less than 30 %, suggesting that over 70 % of the photo-formed $\bullet\text{OH}$ reacts directly with other constituents of the river water including the dissolved organic matter. Besides, from the results of the filtered and unfiltered samples, particulate matters do not appear to be a major source or sink of OH radicals in river water. The reaction rate constant of hydroxyl radicals with diuron determined by competition kinetics was $(9.45 \pm 0.12) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Using this rate constant and the $\bullet\text{OH}$ steady state concentrations determined in this study, half-lives of diuron due to the reaction with $\bullet\text{OH}$ in the river were in the range 0.82 – 4.47 days. Undoubtedly, the reaction of OH radical with diuron could be a significant pathway for its degradation and may be an important process for controlling the fate of diuron in Kurose River.

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1. Introduction

Hydroxyl radical ($\bullet\text{OH}$) is a potent oxidant that controls the lifetimes of recalcitrant xenobiotics and other natural organic compounds that are resistant to degradation by other processes (Arakaki et al., 2010; Mopper and Zhou, 1990; Zepp et al., 1987, 1992). They are produced photo-chemically in sunlit surface waters via photolysis of NO_3^- , NO_2^- , H_2O_2 , and HNO_2 ; Fenton reaction and photo-Fenton; and photochemical reactions of some organic compounds (Zhou and Mopper., 1990; Arakaki et al., 2010; Takeda et al., 2004). The steady state concentration of $\bullet\text{OH}$ in the surface layer of many aquifers lies in the range $\sim 10^{-17}$ – 10^{-15} M , with the whole water column values being 1–2 orders of magnitude lower, depending on the column depth and the thickness of the photic zone (Zepp et al., 1987; Brezonik and Fulkerson 1988). Diuron (3-[3, 4-dichlorophenyl]-1,1-dimethylurea) is an herbicide derived from urea that is considered to be a priority hazardous substance by the European commission (Malato et al., 2002). This compound has been detected in the estuarine, coastal, lake, and river waters since 1992 (Okamura et al., 1999; Dahl and Blanck, 1996). Accordingly, countries including the UK, Sweden, Denmark and France have restricted the use of Diuron in antifouling paints. In Japan, Diuron has

long been used in agricultural and other activities, and a large amount of Diuron discharged into river water has been transported into the Seto Inland Sea with little or no degradation (Sakugawa et al., 2010). It is well known that diuron is a source of pollution in aquatic environment because of its use as antifouling paint biocide. In Japanese aquatic environment, 86% of samples studied showed a $3.05 \mu\text{g/L}$ concentration of diuron (Okamura et al., 2003). In Dutch coastal and marinas waters, a higher level than the permitted maximum of 430 ng/l was detected (Lamoree et al., 2002). Many other studies also reported water contamination by diuron contained in antifouling paint (Boxall et al., 2000; Thomas et al., 2001; Okamura et al., 2002; Okamura et al., 2003). Recently, it was reported that diuron has been detected in the bottom sediments and planktons (Sarangeraja et al, 2012). However, diuron showed no biodegradation over 42 days in seawater at 15°C in laboratory (Thomas et al 2002) and the half-life time of diuron by biodegradation in river waters has been determined to be 602–814 days (Sakugawa et al. 2010). To the best of our knowledge, hydroxyl radical mediated degradation of diuron in river water has not been reported. Therefore, the aim of this study is to determine the steady state concentrations of hydroxyl radicals in river water (ii) determine the

reaction rate constant of hydroxyl radicals with diuron and (iii) estimate the half-life of diuron mediated by hydroxyl radicals in river water.

2. Material and Methods

2.1 Study area and sample collection

The study site was Kurose River in Hiroshima Prefecture, Japan as shown in Figure 1. The Kurose River is about 50.6 km long with a catchment area of 238.8 km². It runs urban and agricultural areas of the Kamo plateau, including Higashi-Hiroshima city and Kurose Town. The runoff from agricultural fields flows into the Kurose River. It receives the effluents from the wastewater treatment plant (WWTP) of Higashi-Hiroshima city, treating about 24.3×10^3 m³ of sewage daily by a classic activated sludge process, for about 53, 000 inhabitants of Higashi-Hiroshima city (Ogura et al., 2009; Derbalah, et al., 2004). The wastewater discharge of the Higashi-Hiroshima WWTP has been increasing because of the drastic increase in the population of Higashi-Hiroshima city during the last decade (Ogura et al., 2009). River water samples were obtained from the Kurose River, Hiroshima prefecture in June, 2009. The sampling locations are as shown in Figure 1. Water samples were collected by polyethylene buckets and were immediately transferred to clean amber 1 L glass bottles. The samples were divided into two portions. A portion of the sample was filtered through a precleaned glass fiber filter (Advantech, 0.45 μ m nominal rating) and the second portion was not filtered. All samples were stored in the dark at 4°C until analysis.

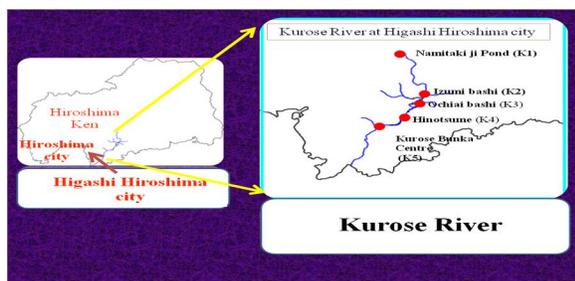


Figure1. Map showing sampling locations in Kurose River

2.2 Reagents and chemicals

All reagents were reagent grade and used as received unless otherwise stated. All solutions were prepared with ultra-pure water obtained from a Milli-Q Plus system (Millipore; ≥ 18.2 M Ω cm). Acetonitrile and benzene were purchased from Nacalai Tesque (HPLC grade > 99.5%). Commercial phenol standard stock solution (100 mg L⁻¹ of phenol) and potassium hydrogen phthalate were purchased

from Sigma-Aldrich Japan. Diuron was obtained from Kanto Chemical Co. Inc. (Tokyo, Japan). Sodium nitrite, sodium nitrate, sodium chloride, sodium sulphate, Iron (II) sulphate, sulphanilamide, were purchased from Katayama Chemical Industries (Guaranteed grade). H₂O₂ stock solution (ca.30%) was obtained from Wako Pure Chemical Industries and the concentration of the diluted stock solution was determined based on the molar extinction coefficient at 240 nm $\{\epsilon = 38.1 \text{ M}^{-1} \text{ cm}^{-1}$ (Miller and Kester, 1988)}. 2-Nitrobenzaldehyde and N-1-naphthylethelenediamine dichloride were purchased from Tokyo Kasei Kogyo.

2.3 Irradiation experiment

The solar simulator used for the irradiation experiments has been described in Olasehinde et al., 2012. However, the quartz glass reaction cell used for •OH determinations was 5 cm in diameter, 1.5 cm in length and had a 20 mL capacity. The solution inside the cell was gently stirred with a Teflon stirring bar and maintained at ca. 20 °C using a Neslab RTE 111 recirculating water bath. The J_{2NB} values for the solar simulator ranged from 0.0094 to 0.0057 s⁻¹ and all data relating to photochemical reactions were normalized to a 2-NB degradation rate of 0.0093 s⁻¹ which were determined at noon under clear sky conditions in Higashi – Hiroshima city (34° 25' N) on May 1, 1998 (Arakaki et al., 1998).

2.4 Procedures for the determination of OH radicals in river waters

The detailed procedure for the determination of OH radicals in natural water has been described elsewhere (Arakaki and Faust, 1998). Briefly, •OH photo-formation rates were determined by irradiating river water samples with 1.2 mM benzene in a 20-mL quartz glass cell that was used for the determination of 2-NB degradation rate. The irradiated samples with the probe were withdrawn at regular intervals for HPLC analysis. The phenol formed due to the reaction of the photo-formed •OH with benzene was analyzed by reversed-phase HPLC system equipped with RP-18 GP column (150 × 4.6 mm I.D., 5 μ m) column. The fluorescence detector was operated at excitation and emission wavelengths of 270 and 298 nm, respectively. The mobile phase was CH₃CN:H₂O = 40:60 (v/v), with a flow rate of 1 mL min⁻¹. The photo-formation rate of phenol (R_p) was determined from the slope of the plots of total concentration of phenol versus cumulative irradiation time using a linear regression fit. Thus, the •OH photoformation rate (R_{OH}) was calculated by:

$$R_{OH} = R_p / (F_b \times Y_p) \quad (1)$$

where R_p is the photoformation rate of phenol in water samples (M s⁻¹), Y_p the yield of phenol formed per benzene oxidized •OH (Mean \pm standard deviation = 0.75 ± 0.07 (Arakaki and Faust, 1998),

and F_b the fraction of $\bullet\text{OH}$ that reacts with benzene. F_b river water was reported to be in the range 0.92–0.99 (Takeda et al., 2004). For the purpose of calculating R_{OH} in Eq. 1, F_b was assumed as to be 1.

For the determination of the scavenging rate constants ($\sum(k_{s,\text{OH}}[S])$), aliquots of benzene stock solution were added to different aliquots of the river water samples to give initial benzene concentrations from 5 to 200 μM . The solutions were irradiated for a total period of 60 min and analyzed for phenol at regular intervals. A Plot of $1/R_{\text{phenol}}$ against $1/[\text{benzene}]$ yields a straight line (Figure 2). From the results of the least square regression line for the relationship between $1/R_{\text{phenol}}$ and $1/[\text{benzene}]$, $\sum(k_{s,\text{OH}}[S])$ in the water samples was calculated by using the y-intercept, slope and the rate constant of benzene for the reaction with $\bullet\text{OH}$ ($k_{b,\text{OH}}$: $7.8 \times 10^9 \text{M}^{-1}\text{s}^{-1}$ (Buxton et al., 1988) as follows:

$$\sum(k_{s,\text{OH}}[S]) = \text{slope} \times k_{b,\text{OH}} / \text{y-intercept} \quad (2)$$

and steady-state concentrations of OH radicals were estimated by using Eq. 3.

$$[\bullet\text{OH}]_{\text{ss}} = R_{\text{OH}} / \sum(k_{s,\text{OH}}[S]) \quad (3)$$

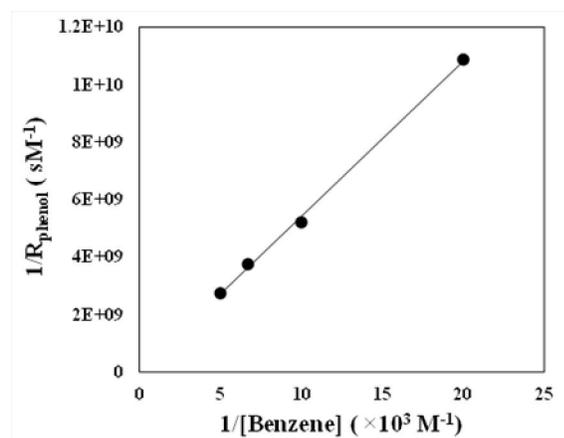


Figure 2: Relationship between $1/R_{\text{phenol}}$ and $1/[\text{benzene}]$ in river water. The values for the y-intercept and slope are $2. \times 10^7 \text{sM}^{-1}$ and $5.3 \times 10^5 \text{s}$, respectively. Correlation coefficient (r^2) = 0.998

2.5 Ancillary measurements

Concentrations of the anions (NO_2^- , NO_3^- , SO_4^{2-} and Cl^-) and the pH of the river water samples were determined by ion chromatography (DX-500, Dionex) and a compact pH meter (B-212 Horiba). H_2O_2 was determined by the method described by Olasehinde *et al.*, 2008. Dissolved organic carbon (DOC) in the water samples was determined by a total organic carbon (TOC) analyzer (TOC-5000A, Shimadzu). A summary of the anions, H_2O_2 and the DOC concentrations is presented in Table 1.

Table 1: Chemical compositions and the pH in the river water

Site	pH	Cl ⁻ (μM)	SO ₄ ²⁻ (μM)	NO ₂ ⁻ (μM)	NO ₃ ⁻ (μM)	DOC (mgL^{-1})	H ₂ O ₂ (μM)
Namitakiji	7.4	196	34.4	bd	0.9	1.23	28
Izumibachi	7.5	565	456	17.6	110	4.7	42
Ochiabachi	7.7	344	287	8.3	124	4.5	38
Kurose Bunka Center	7.7	498	302	7.9	133	4.4	41
Hinostume	7.8	800	412	34.1	185	5.2	45

3. Results and Discussion

3.1 Photo-formation rate of $\bullet\text{OH}$ in river water

As shown in Table 2, the $\bullet\text{OH}$ photo-formation rates in the river water samples were in the range $0.1 - 12 \times 10^{-10} \text{Ms}^{-1}$. Photo-formation rate of $\bullet\text{OH}$ was highest in water samples collected from Hinostume site ($12 \times 10^{-10} \text{Ms}^{-1}$) probably due to the high concentrations of nitrite and nitrate ions in these samples. In a study by Derbalah *et al.* (2004), the concentrations of NO_2^- and NO_3^- in Hinostume site were in the range 9.6–240 μM and 75–143 μM , respectively. The author attributed the exceptionally high concentrations of NO_2^- and NO_3^- in this site to the contamination by the run-off from the agricultural fields.

Further, previous investigators showed that the mean photoformation rates of $\bullet\text{OH}$ in dew and rain water samples were 3.5×10^{-10} and $1.0 \times 10^{-10} \text{Ms}^{-1}$, respectively (Arakaki *et al.*, 1998). Similarly, Haag and Hoigne *et al.* (1985) reported that the $\bullet\text{OH}$ production rates in Greifensee lake water were about 10^{-11}Ms^{-1} . Therefore, the $\bullet\text{OH}$ formation rates obtained in this study are similar to those previously reported for rain, dew and lake water samples. However, the $\bullet\text{OH}$ formation rates in the studied samples were one to two orders of magnitude higher than those reported by Mopper and Zhou (1990) for open ocean ($2.8 - 15.9 \times 10^{-12} \text{Ms}^{-1}$) and Zhou and Mopper (1990) for coastal water ($9.7 - 30 \times 10^{-12} \text{Ms}^{-1}$).

Table 2: R_{OH} and the percent contribution from the photolysis of NO_3^- , NO_2^- and H_2O_2 in river water

Site	R_{OH} (10^{-10}M s^{-1})	% contribution ^b			
		NO ₃ ⁻	NO ₂ ⁻	H ₂ O ₂	Unknown
Namitakiji	0.1	2.4	—	1.28	96.3
Izumibachi	6.6	3.9	71.3	0.02	24.6
Ochiabachi	4.3	6.8	50.7	0.03	42.4
Kurose Bunka	2.9	11.0	72.7	0.06	16.2
Hinostume	12.0	3.7	75.8	0.01	20.4

3.2 The percent contribution by •OH radical sources to the observed •OH formation rates

The percent contribution of OH radical sources to the observed •OH photo-formation rates are shown in Table 2. The formation rates of •OH from nitrate, nitrite and H₂O₂ photolysis were estimated based on their photolysis rate constants as reported by the previous investigators (Olasehinde, et al., 2012; Takeda et al., 2004). The percent contributions from the photolysis of NO₃⁻ and H₂O₂ to the observed •OH photo-formation rates were less than 11 and 2%, respectively. However, NO₂⁻ photolysis appears to be the major source of •OH photo-formation rate in the water samples, accounting for more than 75% of the observed •OH photo-formation rates. It should be noted that in spite of the high concentrations of nitrate in the river water samples compared to nitrite, the direct photolysis of NO₃⁻ could be regarded as an insignificant source of OH radicals because of the low •OH photo-formation rate constant from NO₃⁻ (~ 10⁻⁷ s⁻¹) which is about two orders of magnitude lower than that of the nitrite ion (~ 10⁻⁵ s⁻¹).

Table 3: $\sum(k_{s,OH}[S])$ and the percent contribution of •OH scavenging (%) from Cl⁻, SO₄²⁻, NO₃⁻, and NO₂⁻

Site	$\sum(k_{s,OH}[S])$ $\times 10^5 \text{ s}^{-1}$	% contribution				
		Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻	NO ₂ ⁻	Unknown
Namitakiji	0.47	8.3	0.1	<0.001	—	91.6
Izumibachi	21.0	0.5	0.03	<0.001	8.3	91.2
Ochiabachi	5.1	1.9	0.08	0.01	16.1	82.6
Kurose Bunka	7.3	1.4	0.06	<0.001	10.0	88.6
Hinostume	11.5	1.4	0.05	<0.001	29.2	69.6

$$\% = k_{i-OH} \times [i] / (\sum(k_{s,OH}[S]) \times 100)$$

where k_{i-OH} is the reaction rate constant of •OH with [i]; [i] is the concentration of the anions (NO₃⁻, NO₂⁻, Cl⁻, SO₄²⁻); $\sum(k_{s,OH}[S])$ is the overall scavenging rate constant of •OH

3.4 Hydroxyl radical steady-state concentrations

The steady-state concentrations of hydroxyl radicals ([•OH]_{ss}) in the river water samples are shown in Table 4. Based on the photochemical formation rates and the scavenging rate constant, the estimated [•OH]_{ss} ranged from 1.9–10.4 × 10⁻¹⁶ M. From this study, it was observed that the steady state concentration of OH radicals was highest at Hinostume site. This is plausible because the concentrations of OH radical sources are highest at this sampling site probably due to the contamination by the run-off from the agricultural fields. The values

obtained in this study are about one to two orders of magnitude higher than those reported for seawater (Mopper and Zhou, 1990), but were similar to the values reported for river water (Brezonik and Fulkerson-Brekken, 1998; Nakatani et al, 2004).

Table 4: R_{OH} , ($\sum(k_{s,OH}[S])$) and [•OH]_{ss} in river water

Site	R_{OH} (10 ⁻¹⁰ M s ⁻¹)	$\sum(k_{s,OH}[S])$ (10 ⁵ s ⁻¹)	[•OH] _{ss} (10 ⁻¹⁶ M)
Namitakiji	0.1	0.47	1.9
Izumibachi	6.6	21.0	3.2
Ochiabachi	4.3	5.0	8.6
Kurose Bunka	2.9	7.3	4.0
Hinostume	12.0	11.5	10.4

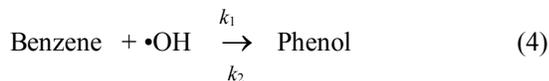
3.5 Effect of particulate matter on hydroxyl radical concentrations

The effect of particulate matter on •OH concentrations was investigated on the river water samples collected from Ochia-bachi site. The water samples were divided into two portions. A portion of the sample was filtered through a pre-cleaned glass fiber filter (Advantech, 0.45 μm nominal rating) to remove the particulate matter greater than 0.45 μm and the second portion was not filtered. Based on calculation, the measured •OH concentrations in filtered and unfiltered samples were remarkably comparable, with the filtered samples having ~ 4.5 % higher than the unfiltered samples. However, the difference was within the experimental error. The results suggest that particulate matter (> 0.45 μm) do not appear to be a major photochemical source or sink of •OH in the samples studied. These results are in good agreement with the conclusions of (Arakaki et al., 2010; Arakaki and Faust, 1998), who found that red soil particles and particulate matters are not a major photochemical source or sink of OH in seawater and cloud waters, respectively.

3.6 Determination of second order reaction rate constant of Diuron with hydroxyl radicals

Standard competition kinetics method was employed to determine the reaction rate constant of diuron with •OH in air-saturated aqueous solution. Hydroxyl radical was generated by irradiating 1mM NO₃⁻ in a 20-mL quartz cell. Benzene reacts with •OH in air-saturated solution yielding phenol, with a second order reaction rate of 7.8 × 10⁹ M⁻¹ s⁻¹ (Buxton et al., 1988). In experimental solution containing benzene without any other •OH scavenger, all •OH formed reacts with benzene to produce phenol. The total amount of phenol formed under this condition is denoted as [phenol]₀. However, if diuron is present in the experimental solution with benzene, both

reactants compete for the $\bullet\text{OH}$ produced which leads to the attenuation of the signal intensity of phenol compared to the reaction of benzene with $\bullet\text{OH}$ in the absence of diuron. In this system, the amount of phenol formed is a fraction of the total $\bullet\text{OH}$ generated which is denoted as phenol '.



In this study, we carried out a series of experiments by 10-min irradiation of 1mM NO_3^- with 10 μM diuron varying the concentration of benzene from (20 – 80 μM). However, to determine the concentration of the $[\text{Phenol}]_o$, a 1mM NO_3^- was irradiated with 200 μM benzene in the absence of diuron for 10 min. It has been established that 200 μM benzene is sufficient to effectively scavenge all $\bullet\text{OH}$ formed from 1mM NO_3^- (Nakatani et al., 2004). Using equation 6, A plot of $[\text{phenol}]_o / [\text{phenol}]'$ vs $[\text{diuron}] / [\text{benzene}]$ for separate experiments with solutions of varying $[\text{diuron}] / [\text{benzene}]$ ratio is shown in Figure 3, where $[\text{phenol}]'$ and $[\text{phenol}]_o$ are the concentrations of phenol produced from the reaction of benzene and $\bullet\text{OH}$ in air-saturated solutions with and without diuron respectively, $[\text{diuron}]$ is the initial concentration of diuron, $[\text{benzene}]$ is the initial concentration of benzene, k_2 is the reaction rate constant of diuron with $\bullet\text{OH}$ ($\text{M}^{-1}\text{s}^{-1}$) and k_1 is the reaction rate constant of benzene with $\bullet\text{OH}$ ($\text{M}^{-1}\text{s}^{-1}$). $[\text{Phenol}]_o / [\text{Phenol}]' = 1 + \{(k_2 [\text{diuron}]) / (k_1 [\text{Benzene}])\}$ (6)

Thus, the value of k_2 estimated from the slope of this graph based on equation 6 was $(9.45 \pm 0.12) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (mean \pm standard deviation, $n=3$).

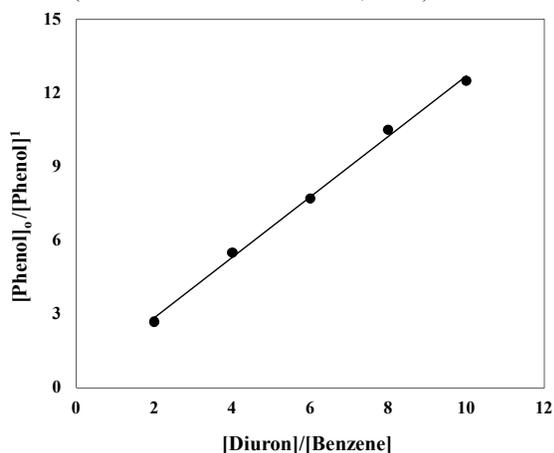


Figure 3: Graph for the reaction rate constant of Diuron with hydroxyl radical. The values for the y-intercept and slope are 0.384 and 1.23, respectively. Correlation coefficient (r^2) = 0.9971

3.7 Half-lives of diuron mediated by hydroxyl radicals in River water

The half-lives of diuron mediated by $\bullet\text{OH}$ in river water were calculated by using equation 7.

$$t_{1/2} = \frac{0.693}{k_{D-\bullet\text{OH}} \times [\bullet\text{OH}]_{\text{ss}}} \quad (7)$$

Where $k_{D-\bullet\text{OH}}$ is the reaction rate constant of $\bullet\text{OH}$ with diuron and $[\bullet\text{OH}]_{\text{ss}}$ is the steady state concentration of $\bullet\text{OH}$ in the river water. Based on calculation, the half-lives of diuron mediated by OH radical in the river was in the range 0.82 – 4.47 days. However, half-life for the biodegradation of diuron in river water was reported to be in the range 602 – 814 days (Sakugawa et al, 2010). Thus, the half-lives of diuron reported in this study are 2 to 3 orders of magnitude lower than the values reported for its biodegradation in the river water. Therefore, the reaction of OH radical with diuron in the river could be a significant process for its degradation and may be an important process controlling the fate of diuron in Kurose River.

4. Conclusion

The steady-state concentrations of OH radicals were estimated based on the photo-formation rates and the scavenging rate constants determined by irradiating water samples collected from the Kurose River. The $[\bullet\text{OH}]_{\text{ss}}$ ranged from 1.9×10^{-16} to $10.4 \times 10^{-16} \text{ M}$ in the samples studied. The reaction rate constant of diuron with $\bullet\text{OH}$ determined using competition kinetics method was $(9.45 \pm 0.12) \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. The consumption of $\bullet\text{OH}$ by anions accounted for less than 30 % in the samples, suggesting that over 70 % of the photo-formed $\bullet\text{OH}$ reacts directly with other constituents of the river water including the dissolved organic matter. As a result of the short half-lives of diuron due to the reaction with $\bullet\text{OH}$ in the river, the degradation of diuron mediated by hydroxyl radicals may be an important pathway for its loss in Kurose River.

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