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Relation	

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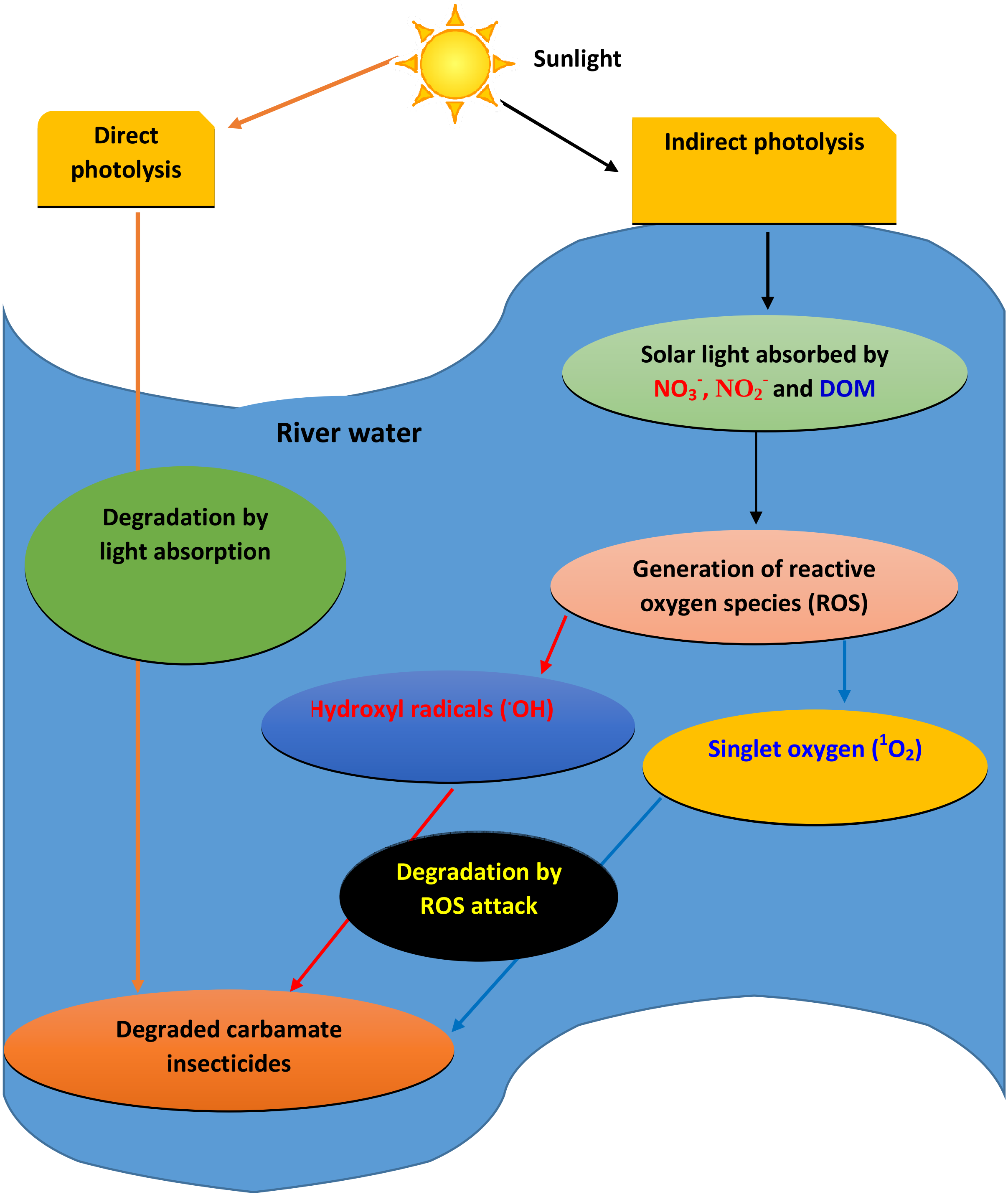
CRediT author statement

Aly Derbalah: Doing experiments, Writing, Publishing, Analysis **Michael Sunday:** Doing experiments, Writing, Reviewing **Ryota Kato:** Doing experiments**, Kazuhiko Takeda:** Sampling Supervision **Hiroshi Sakugawa:** Reviewing, Supervision



Graphical abstract

Photoformation of reactive oxygen species and their potential to degrade highly toxic carbaryl and methomyl in river water

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ABSTRACT

Reactive oxygen species (ROS) including singlet oxygen ($^1O_2$) and hydroxylradicals ($^{\bullet}OH$) photogenerated in natural waters play important roles in indirect photolysis of man-made pollutants. This study was conducted to investigate how the generation of these two ROS influences the degradation of two highly toxic insecticides (methomyl and carbaryl) in river water. To accomplish this, the reaction rate constants of $^1O_2$ and $^{\bullet}OH$ with carbaryl and methomyl were determined; the degradation rate constants of the tested insecticides in ultrapure water (direct photolysis) and in river water in the presence and absence of $^1O_2$ and $^{\bullet}OH$ scavengers were also measured. The rate constants for the reaction of $^{\bullet}OH$ with carbaryl and methomyl were found to be $(14.8 \pm 0.64) \times 10^9$ and $(4.68 \pm 0.52) \times 10^9$ M^{-1} s^{-1}, respectively. The reaction rate constant of $^1O_2$ with carbaryl (2.98 ± 0.10) × 10^5 M^{-1} s^{-1}, was much higher than that of methomyl (< 10^4 M^{-1} s^{-1}). Indirect photolysis by $^{\bullet}OH$ accounted for 63% and 62%, while $^1O_2$ accounted for 26% and 30% and direct photolysis accounted for 1.4% and 7% of methomyl and carbaryl degradation, respectively. The high degradation rate in river water demonstrated by both insecticides suggests that indirect photolysis mediated by $^{\bullet}OH$ is an important means of their degradation in river water. In addition, kinetic calculations of $^{\bullet}OH$-mediated degradation rate constants of the compounds agrees with their experimentally-determined values thereby confirming the importance of $^{\bullet}OH$ towards their degradation.

Keywords: Hydroxyl radicals; Singlet oxygen; Methomyl; Carbaryl; Photolysis; Water

1. Introduction

Pesticides have been used intensively worldwide to protect crops from pests and diseases in order to maintain adequate productivity so that food is more affordable. Pesticides will continue to be used as an effective means of controlling pests and increasing agricultural production (**Alhousari, 2011**). Methomyl and carbaryl (Fig. 1S) are a carbamate compounds widely used to control several insects in many different types of crops (**Tomlin, 2003; EPA, 2004**) and considered very toxic to humans, aquatic organisms, and other beneficial organisms such as bees and birds (**Street, 1981; Barcelo et al., 1996; McDuffie, 2001; Drea et al., 2012; Bazrafshan et al., 2017**). Due to their extensive use, methomyl and carbaryl have been detected in surface and ground water at various concentrations (**Chowdhury et al., 2012**; **Chattoraj et al., 2014; Struger et al., 2016).**

In the aquatic environment, pesticides are transformed by photo- and biodegradation (**Derbalah et al., 2013, 2014, 2016**; **Katagi 2018**). However, photodegradation (direct and indirect) is one of the most important abiotic transformations for pesticides in the aquatic environment (**Katagi, 2018**). Several reactive species, including hydroxyl radicals ($^{\bullet}OH$), singlet oxygen ($^1O_2$), triplet oxygen, chromophoric organic matter in the triplet state, superoxide ions and hydroperoxyl radicals ($O_2^{\bullet -}/HO_2\bullet$), and carbonate radicals ($\bullet CO_3^-$), can be produced upon sunlight irradiation of components such as dissolved organic matter (DOM), nitrate, nitrite, and Fe(III) present in natural waters (**Zepp et al., 1981; Draper and Crosby, 1984; Haag and Hoigné, 1986; Richard and Canonica, 2005; Vione et al., 2009**). These species play important roles in the chemical breakdown of organic pollutants such as pesticides in water (**Street, 1981; Haag and Hoigné, 1986; McDuffie, 2001; Vermilyea and Voelker, 2009; Arakaki et al., 2010).**

Among these species, $^{\bullet}OH$ and $^1O_2$ contribute significantly to the indirect photodegradation of a wide range of organic pollutants. $^{\bullet}OH$ is perhaps the most reactive oxygen specie, exhibiting high reaction rate constants with a wide range of organic and inorganic pollutants in natural waters (**Buxton et al., 1988**). Its high reaction rate constants of approximately 10^9 M^{-1} s^{-1} (**Vermilyea and Voelker, 2009)** with organic pollutants enables it to contribute to the breakdown of organic pollutants such as pesticides that are considered relatively stable and cannot be destroyed by biological processes or direct photolysis (**Mabury and Crosby, 1996; Armbrust, 2000; AlHousari et al., 2010; Dell'Arciprete et al., 2010; Arakaki et al., 2010**).

$^1O_2$ is formed by energy transfer from the triplet excited states of DOM to dissolved molecular oxygen (**Zepp et al., 1981; Haag and Hoigné, 1986; Richard and Canonica, 2005**). The reactivity of $^1O_2$ with organic compounds, including pesticides, is relatively lower compared to the reactivity of $^{\bullet}OH$. Nevertheless, its higher steady-state concentration in the aquatic environment, which can be three to four orders of magnitude greater than that of $^{\bullet}OH$, gives it a competitive advantage to participate in pesticides degradation. Therefore, this may also represent an important degradation pathway for pesticides.

An understanding of the fates of pesticides is essential for rational decision-making regarding their authorization. Furthermore, information regarding the possible pathways and scenarios for pesticide degradation in aquatic environments is crucial; ensuring that the period for which they persist in the environment and the potential risks they pose to humans and aquatic organisms can be safely predicted (**Alhousari, 2011**). Due to the high toxicity and frequent detection of both carbaryl and methomyl in water (**Street, 1981; Barcelo et al., 1996; McDuffie, 2001; Wilsont and Foos, 2006; Chowdhury et al., 2012; Chattoraj et al., 2014; Struger et al., 2016**), there is a need to investigate their photodegradation in river water and also unravel the contributions of direct photolysis and/or indirect photolysis (mediated by ROS) under environmentally-relevant irradiation conditions. To the best of our knowledge, such investigation has not been conducted before now. Hence, this study was conducted to evaluate the photodegradation of methomyl and carbaryl, as well as to obtain their half-lives under environmentally relevant irradiation conditions in river water. The contributions of $^{\cdot}OH$ and $^1O_2$ to the degradation of the two compounds in river water were also determined.

2. Materials and methods

2.1. Reagents and chemicals

Acetonitrile and benzene were purchased from Nacalai Tesque, Kyoto, Japan (HPLC grade > 99.5%). Phenol methomyl (99.9%), carbaryl (99.9%), and potassium hydrogen phthalate were obtained from Sigma-Aldrich (Japan). Sodium nitrite, sodium nitrate, sodium chloride, sodium sulfate, iron(II) sulfate, sulfanilamide, rose bengal (RB), and furfuryl alcohol (FFA) were purchased from Katayama Chemical Industries (guaranteed grade) (Japan). Hydrogen peroxide (ca. 30%) was obtained from Wako Pure Chemical Industries (Japan). The 2-nitrobenzaldehyde (2-NB) and *N*-1-naphthyl ethylenediamine dichloride were purchased from Tokyo Kasei Kogyo (Japan). Disodium terephthalate (TP) and 2-hydroxyterephthalic acid (HTP) were obtained from Tokyo Chemical Industry Co. Ltd. (Japan). Stock and working solutions of the examined insecticides were prepared in ultrapure water only, without solvents.

2.2. Water samples

Surface river water samples were collected in June 2018 from Izumi Station on the Kurose River (chemical composition shown in Table 1S in Higashi-Hiroshima, Japan. Samples were collected into clean glass one-liter capacity bottles, then filtered through fiberglass filters (Advantech, Tokyo, Japan, 0.45 μm nominal rating) for further treatment. Samples were stored in brown borosilicate bottles at 4°C to prevent biological degradation until analysis (within a week).

2.3. ROS determination

Determination of $^{\cdot}OH$ and $^1O_2$ generated during irradiation of water samples was done using chemical probes. For these determinations, irradiation was done using a solar simulator consisting of a lamp housing (WACOM Co., Saitama, Japan HX-500) equipped with a 500 W Xe lamp (WACOM Co., KXL-500F) and an optical filter (HOYA Co.,Tokyo, Japan ultraviolet (UV)-31) with a transmission wavelength limit of 310 nm. A detailed description of the solar simulator has been reported elsewhere (**Nakatani et al., 2007**). The photoformation rates and steady-state concentrations of $^{\cdot}OH$ and $^1O_2$ were normalized to 2-NB degradation rate of 0.0093 s^{-1} as previously described (**Takeda et al., 2014**).

The amount of photoformed $^{\cdot}$OH in the river water sample was determined using benzene as a chemical probe (**Takeda et al., 2004**). Benzene reacts with $^{\cdot}$OH at a high bimolecular reaction rate constant of 7.8×10^9 M^{-1} s^{-1} to produce phenol (**Buxton et al., 1988**). A sample containing 1.2 mM benzene was irradiated for 40 min while aliquots were withdrawn at 10 min intervals and analyzed for phenol using high-performance liquid chromatography (HPLC). The photoformation rate, scavenging rate constant, and steady-state concentration of $^{\cdot}$OH were determined and are detailed in the supplementary information (SI), section S1.

$^1O_2$ photogenerated in the irradiated samples was measured using FFA as a probe. It reacts with $^1O_2$ and degrades following first-order degradation kinetics, (**Haag and Hoigné, 1986**). Samples were spiked with FFA (final concentration, 100 μM) and irradiated under the solar simulator, during this time aliquots of the reaction mixture were obtained and analyzed for FFA using HPLC. The detailed procedure is available under S1. The $^1O_2$ steady-state concentration ($[^1O_2]_{ss}$) was determined by dividing the observed first-order degradation rate constant (k) of FFA in the irradiated sample by the reaction rate constant of FFA with $^1O_2$ ($k_{FFA,^1O_2}$), which was given as 1.09×10^8 $M^{-1}s^{-1}$ (**Haag et al., 1984**). By considering water as the main scavenger of $^1O_2$ in natural waters, with a k_d of 2.5×10^5 s^{-1} (**Rodgers and Snowden, 1982**), the photoformation rate of $^1O_2$ ($R_{^1O_2}$) was obtained as a product of the $[^1O_2]$ss and k_d.

2.4. Reaction rate constant of target insecticides with $^{\bullet}$OH

The reaction rate constants between the tested insecticides and $^{\cdot}$OH were determined based on competition kinetics with TP as the $^{\cdot}$OH probe (**Yang and Guo, 2001; Louit et al., 2009; Charbouillot et al., 2011; Bekdeser et al., 2012; Takeda et al., 2017 a and b**). The $^{\cdot}$OH was generated using a high-power 365 nm UV-light-emitting diode (LED) (NS365L-6SMG, Nitride

Semiconductors, Naruto, Japan) and 0.1 µM nitrite aqueous solution (**Takeda et al., 2018**), and was detected with 0.05 mM TP as shown in equation 5.

$$NO_2^- \ (\lambda max{\sim}355 \text{ nm}) + H_2O + hv \longrightarrow {}^{\bullet}OH + NO + OH^- \quad (5)$$

In the irradiated sample solution containing TP, nitrite, and insecticide, the generated $^{\bullet}OH$ competitively reacted with the TP and insecticides. The TP reacted with $^{\bullet}OH$ quantitatively to generate a strongly fluorescent product, HTP (**Yang and Guo, 2001; Louit et al., 2009; Charbouillot et al., 2011; Bekdeser et al., 2012; Takeda et al., 2017a**). The reaction rate constant was calculated by equation 6:

$$\frac{F_0}{F} = 1 + \frac{k_{X,OH}\,[C]}{k_{TP,OH}\,[TP]} \quad (6)$$

where $k_{TP,OH}$ and [TP] are the reaction rate constant and concentration of TP, respectively, and $k_{X,OH}$ and [C] are the reaction rate constant and concentration of the insecticide, respectively. Additionally, F is the fluorescence signal of HTP in the presence of the insecticide while F_0 is the fluorescence signal of HTP without insecticide, i.e., [C] = 0. Equation 6 indicates that a plot of F_0/F against [C] at constant [TP] should give a straight line with a y-intercept of 1 and a slope of $k_{X,OH}/(k_{TP,OH}\,[TP])$. The reaction rate constant of the insecticides with $^{\bullet}OH$ ($k_{X,OH}$) can then be simply calculated from the slope of this plot and the values of $k_{TP,OH}$ and [TP]. We selected a $k_{TP,OH}$ of 4.0×10^9 M^{-1} s^{-1} (**Charbouillot et al., 2011)** to calculate the rate constants of the target insecticides.

To determine the reaction rate constants, a quartz photochemical reaction cell (20 mm in diameter and 12 mm thick (optical path)) was used. The UV-LED was placed 10 mm above the top surface of the reaction cell, after which the sample solution was irradiated for 10 min. The HTP formed was analyzed using HPLC as described by **Takeda et al. (2018).**

2.5. Reaction rate constant of target insecticides with $^1O_2$

The reaction rate constants of $^1O_2$ with carbaryl and methomyl were determined by monitoring the degradation rates of methomyl and carbaryl as they react with photogenerated $^1O_2$, using RB as a sensitizer (equations 7 and 8) (**Vione et al., 2011; Ruggeri et al., 2013**). The reaction rates of the insecticides with $^1O_2$ were then determined as shown in equation 9:

$$RB + hv + O_2 \longrightarrow RB + {}^1O_2 \qquad (7)$$

$$\text{Insecticides} + {}^1O_2 \longrightarrow \text{Products (insecticides-}{}^1O_2\text{)} \quad (8)$$

$$\text{Rate of target insecticides degradation } (R_{deg}) = k_{\text{insecticides},1O2}\,[\text{insecticides}]\,[{}^1O_2] \ (9)$$

where $k_{\text{insecticides},1O2}$ is the reaction rate constant of insecticides with $^1O_2$. At constant $[^1O_2]$, R_{deg} is directly proportional to the insecticide concentration. Therefore, as the insecticide concentration increases, R_{deg} is expected to increase. Moreover, when insecticides react with $^1O_2$, R_{deg} can also be expressed as the product of the rate of $^1O_2$ generation ($R_{^1O2}$) and the fraction (F) of $^1O_2$ that reacts with the insecticides. This is expressed in equations 10 – 13 below.

$$R_{deg} = R_{^1O_2} \text{ x } (F) \qquad (10)$$

$$F = \frac{k_{insecticides,^1O_2}\,[insecticides]}{k_d + k_{insecticides,^1O_2}\,[insecticides]} \qquad (11)$$

where k_d is the dissociation rate constant of $^1O_2$ in water = 2.5×10^5 s^{-1} as reported previously (**Rodgers and Snowden, 1982**).

$$R_{deg} = R_{^1O_2}\ x\ \frac{k_{insecticides,^1O_2}\,[insecticides]}{k_d + k_{insecticides,^1O_2}\,[insecticides]} \qquad (12)$$

At low concentrations of insecticides (µM range), $k_{\text{insecticides},1O2}$ [insecticides] << k_d, giving rise to equation 13:

$$R_{deg} = R_{^1O_2}\ k_d^{-1}\ k_{insecticides,^1O_2}\,[insecticides] \quad (13)$$

From equation 13, a plot of R_{deg} against [insecticides] at a constant $^1O_2$ generation ($R_{^1O_2}$) can be generated that gives a slope = $R_{^1O_2}\ k_d^{-1}\ k_{insecticides-^1O_2}$. Because k_d is known, $R_{^1O_2}$ can be obtained using FFA under the same experimental conditions.

$R_{^1O_2}$ was determined from the initial degradation rate of FFA (R_{FFA}) as shown in equation 14 below.

$$R_{FFA} = R_{^1O_2}\ x\ \frac{k_{FFA,^1O_2}\,[FFA]}{k_d + k_{FFA,^1O_2}\,[FFA]} \quad (14)$$

where $k_{FFA,1O2}$ is the reaction rate constant between FFA and $^1O_2$, which is 1.09×10^8 M^{-1} s^{-1} (**Haag and Hoigné, 1984**). A detailed experimental procedure for the determination of R_{deg} and $R_{^1O_2}$ is provided in SI S2.

2.6. Photodegradation of carbaryl and methomyl in ultrapure water and river water

Carbaryl and methomyl solutions (1mg/L) in ultrapure water were irradiated under the solar simulator using a Pyrex filter to investigate the contributions of direct photolysis to their degradations at a buffered pH value of 6.8. Dark controls without light were performed to account for the degradation under dark conditions. The degradation under dark conditions was negligible and the data are not shown. Photochemical experiments for direct degradation rates were conducted with a solar simulator as described by **Takeda et al. (2014)**.

Photodegradation studies of carbaryl and methomyl (1mg/L) in river water in the absence and presence of 1% methanol ($^{\bullet}OH$ scavenger) (**Motohashi and Saito, 1993**) and 1 mM NaN_3 ($^1O_2$ scavenger) (**Miskoski and Garcia, 1993**) were conducted using a solar simulator that consisted of a lamp housing (WACOM Co., HX-500) equipped with a 500 W Xe lamp (WACOM Co., KXL-500F) and an optical filter (HOYA Co., UV- 31) with a transmission wavelength limit of 310 nm (**Dell'Arciprete et al., 2010**). Samples were withdrawn at intervals and analyzed by HPLC (described above) to monitor the degradation of the insecticides. The degradation rate constant (k) was obtained as the slope of the plot of the natural logarithm of concentration (Ln C_t/C_o) against irradiation time, where C_t was the concentration of the compound at time (t) and C_o was the initial concentration of the compound. The obtained k values were normalized to a 2-NB degradation rate of 0.0093 s^{-1} as previously described (**Arakaki et al., 1999**). This experiment was conducted in triplicate. The contribution of each ROS ($^{\bullet}$OH and $^1O_2$) in the degradation of the tested insecticides in water was estimated by equation 15:

$$\text{ROS contribution} = (\text{Jriver} - \text{Jscavenger})/\text{Jriver} \times 100 \qquad (15)$$

where ROS contribution represents the contribution (%) of $^{\bullet}$OH and $^1O_2$ in the degradation of each insecticide, Jriver is the degradation rate of each insecticide in river water and Jscavenger is the degradation rate of each insecticide in the presence of $^{\cdot}$OH or $^1O_2$ scavengers. The contribution (%) of direct photolysis in the degradation of each insecticide was estimated by equation 16:

$$\text{Direct photolysis} = (\text{Jwater}/\text{Jriver}) \times 100 \qquad (16)$$

where Jwater is the degradation rate of each insecticide in ultrapure water.

2.7. Calculation of photochemical half-lifetimes

The photochemical half-lives for the tested insecticides as mediated by each ROS were calculated using equation 17 (**Nakatani, 2004)**:

$$t_{1/2} = \frac{Ln\ 2}{F_{solar}\ x\ (k_{direct} + k_{insecticide,ROS}\ x[ROS]_{ss})} \qquad (17)$$

where k_{direct} is the direct photolysis rate constant in Milli-Q water, $k_{insecticide,ROS}$ is the reaction rate constant of each insecticide with ROS ($^{\bullet}OH$ or $^{1}O_2$), and [ROS]ss is the steady-state concentration of the ROS. Additionally, F_{solar} is a light intensity factor (taken as 0.1) to account for the diurnal and seasonal changes in the solar radiation intensity. F_{solar} was obtained as a product of 0.3 (a factor used to indicate eight hours of daily sunlight exposure) and 1/3 (based on winter sunlight intensity being approximately one-third that of summer according to the solar actinic flux at the Earth's surface) (**Trapp and Matthies, 1995; Diamond et al., 2001; Takeda et al., 2014**; **Kaonga et al., 2016**).

2.8. Data analysis

For analysis of variance (ANOVA) of obtained data, XLSTAT PRO statistical analysis software (Addinsoft) was used. Fisher's least significant difference (LSD) test was used to separate the mean of each treatment. All analyses were performed at a significance value of $P \leq 0.05$.

3. Results and discussion

3.1. ˙OH and $^{1}O_2$ generation in river water

The generation of $^{\bullet}OH$ and $^{1}O_2$ in river water was investigated using benzene and FFA, respectively, as selective probes. As shown in Table 1, the photoformation rate ($R^{1}O_2$) and steady-state concentration $[^{1}O_2]_{ss}$ in the river water were 7.9×10^{-8} M s^{-1} and 3.1×10^{-13} M, respectively. These values were two orders higher than those of the $^{\bullet}OH$ photoformation rate (R_{OH}) and steady-state concentration $[^{\bullet}OH]_{ss}$ of 1.76×10^{-10} M s^{-1} and 1.2×10^{-15} M, respectively. The reported values were normalized against natural sunlight intensity using 2-NB as a chemical actinometer.

In this study, the formation rate of the $^{\cdot}$OH radicals in Kurose River water was on the same order as that reported by **Takeda et al. (2004)**. The photoproduced $^{\cdot}$OH in water from the Kurose River was large due to the concentrations of nitrate and nitrite (**Takeda et al., 2004**). The [$^1O_2$]ss values obtained in this study agree with the typical values (10^{-13} M) reported in river water samples (**Peterson et al., 2012**). The steady-state concentration of ROS is a ratio of the photoformation rate and the scavenging rate constant (SRC). The SRC of $^{\cdot}$OH in this study (1.47×10^5 s^{-1}) is on the same order as the k_d of $^1O_2$ in water (2.5×10^5 s^{-1}) (**Rodgers and Snowden, 1982**). Therefore, the higher steady-state concentration of $^1O_2$ than that of $^{\cdot}$OH in river water is because of the higher photoproduction rate of $^1O_2$. Moreover, the high reactivity and short lifetime of $^{\cdot}$OH cause its steady-state concentrations in natural waters to be generally low (**Takeda et al., 2004**). In addition, $^{\cdot}$OH is efficiently consumed by natural DOM, which limits its steady-state concentration in water illuminated by sunlight (**Richard and Canonica, 2005**). Unlike $^{\cdot}$OH, which has more than one source (NO_3^-, NO_2^-, DOM, H_2O_2) and sink (DOM, Br$^-$, Cl$^-$) (**Takeda et al., 2004**), the main source of $^1O_2$ in natural waters is chromophoric DOM (**Peterson et al., 2012**), while its primary sink is deactivation by water molecules.

3.2. Reaction rate constants of the tested insecticides with $^{\cdot}$OH and $^1O_2$

To examine the capacity of $^{\cdot}$OH and $^1O_2$ to degrade the examined insecticides, the reaction rate constants of methomyl and carbaryl with the two ROS were measured. The reaction rate constants of $^{\cdot}$OH with the insecticides were determined by the competition kinetics method using TP as a reference compound as described by **Takeda et al. (2017a)**. As shown in Table 2, the reaction rate constant of $^{\cdot}$OH with carbaryl (14.8×10^9 M^{-1} s^{-1}) was approximately three times higher than that of methomyl (4.68×10^9 M^{-1} s^{-1}). The electron-rich aromatic rings present in carbaryl would be the most likely primary site for addition reactions with hydroxyl radicals.

Hydrogen abstraction could also contribute to the reactivity (**Scully and Hoigné, 1987**). According to equation 6, a plot of F_0/F against insecticide concentrations [X] with an intercept of one is required to determine the reaction rate constant. Fig. 2S shows a plot of F_0/F against the insecticide concentrations [X] that were used to determine the reaction rate constants of the insecticides with $^{\cdot}OH$. An intercept of approximately one as expected from equation 6 was obtained.

The reaction rate constants of $^1O_2$ with the insecticides were determined by monitoring the degradation of the insecticides at varying concentrations in the presence of high $[^1O_2]_{ss}$ generated using RB as a sensitizer (**Vione et al., 2011; Ruggeri et al., 2013**). A plot of the R_{deg} of carbaryl as a function of its concentration is shown in Fig. 3S. According to equation 13, a plot of R_{deg} against [insecticide] gives a slope = $R_{^1O_2}\ k_d^{-1}\ k_{insecticides,^1O_2}$. The slope obtained for the carbaryl detection experiment (Fig. 3S) was 2.11×10^{-5} M^{-1} s^{-1}. The R_{1O2} obtained using FFA in the experiment instead of carbaryl was 1.78×10^{-5} M^{-1} s^{-1}, while the k_d was taken to be 2.5×10^5 s^{-1} (**Rodgers and Snowden, 1982)**. Based on these values, the reaction rate constant of $^1O_2$ with carbaryl was determined to be 2.98×10^5 M^{-1} s^{-1}. However, the reaction rate constant of $^1O_2$ with methomyl was very low (< 10^4 M^{-1} s^{-1}). This was because methomyl at varying concentrations did not undergo any significant degradation in the presence of high concentrations of $^1O_2$. Analysis of methomyl did not reveal enough degradation to enable calculation of its reaction rate constant with $^1O_2$. This suggests that the methomyl rate constant with $^1O_2$ is much lower than that of $^1O_2$ with carbaryl. $^1O_2$ is reactive towards electron-rich compounds (**Scully and Hoigné, 1987**), and the absence of such electron-rich functional groups in methomyl explains why it showed a very minimal reaction with $^1O_2$. The aromatic rings present in carbaryl may be responsible for its better reactivity with $^1O_2$ compared with methomyl.

Our results showed that the reaction rate constant of carbaryl with $^1O_2$ was approximately five orders of magnitude lower than its rate constant with $^{\cdot}OH$. Similarly, the reaction rate constant of methomyl with $^1O_2$ (which is much lower than that of carbaryl with $^1O_2$) will also be several orders lower than its rate constant with $^{\cdot}OH$. This great difference in the rate constants of the insecticides with the two ROS suggests the importance of $^{\cdot}OH$ in the photodegradation of the two compounds in the environment. The steady-state concentration of $^1O_2$ in river water is usually higher (two orders in this study) than that of $^{\cdot}OH$. Nevertheless, the rate constants of the insecticides with $^{\cdot}OH$ are far higher than those with $^1O_2$. These higher rate constants are enough to offset the potential contribution associated with the higher steady-state concentration of $^1O_2$.

3.3. Photodegradation of methomyl and carbaryl in ultrapure and river water

The direct photolysis of the tested insecticides (methomyl and carbaryl) in ultrapure water normalized to the intensity of natural sunlight is shown in Table 3. The data showed that the degradation rate of carbaryl (4.62×10^{-6} s^{-1}) was much higher than that of methomyl (6.27×10^{-7} s^{-1}). This suggests that methomyl is more stable than carbaryl when subjected to direct photolysis. Photolytic transformations of the tested insecticides are caused by the absorption of energy (photons) from light. By absorbing light energy, these pesticides are transformed through a number of chemical reactions including cleavage of chemical bonds, oxidation, and hydrolysis (**Zepp and Cline, 1977; Clark, 1994; Larson et al., 1997**).

The degradation rates of the target insecticides in river water, 6.5×10^{-5} s^{-1} (for carbaryl) and 4.47×10^{-5} s^{-1} (for methomyl), were generally higher than that of the degradation rate in ultrapure water (direct photolysis). This suggests the significant contribution of indirect photolysis mediated by ROS in the degradation of the target insecticides in river water. Hence, the contribution of $^{\cdot}OH$ and $^1O_2$ to the photolysis of the target insecticides in river water was investigated by scavenger experiments. As shown in Fig. 1 and Table 3, the degradation rate of carbaryl in the absence of scavengers (6.5×10^{-5} s^{-1}) was higher than in the presence of 1% methanol (2.03×10^{-5} s^{-1}) and 1 mM NaN_3 (3.66×10^{-5} s^{-1}) as $^{\cdot}OH$ and $^1O_2$ scavengers, respectively. Similarly, the degradation rate of methomyl in the absence of scavengers (4.47×10^{-5} s^{-1}) was higher than in the presence scavengers of $^{\cdot}OH$ (1.62×10^{-5} s^{-1}) and $^1O_2$ (3.25×10^{-5} s^{-1}) as shown in Table 3 and Fig. 2. As shown in Fig. 3, photodegradation studies in the presence of scavengers revealed that $^{\cdot}OH$ accounted for 63 and 62% of the degradation of methomyl and carbaryl, respectively, while $^1O_2$ accounted for 26 and 30% and direct photolysis accounted for 1.4 and 7.1%, respectively. The residual degradation percentage of methomyl (9.3%) and carbaryl (1%) may be because of the generation of other photosensitizers such as chloride and sulfate radicals (**Lian et al., 2017**). These findings demonstrate that indirect photolysis mediated by $^{\bullet}OH$ is an important means of degradation of the two insecticides in river water. **Muller and Chin (2002)** also reported that NOM and nitrate in conjunction acted as photosensitizers that resulted in the indirect photolytic degradation of carbaryl in wetland surface waters. Additionally, they suspected that the principal pathway occurs through the generation of ROS, which in turn are capable of reacting with the target pesticide.

3.4. Validation of ROS contributions from kinetic calculations

The involvement of the two ROS in the degradation of the insecticides was further investigated by comparing the experimentally-determined degradation rate constants of the insecticide, as mediated by each ROS, with the calculated degradation rate constants. The experimental values were obtained by deducting the degradation rate constants in the presence of a scavenger from the degradation rate constants obtained in the absence of the scavenger during irradiation of insecticide-spiked river water sample. The degradation rates due to direct photolysis were also deducted. The calculated degradation rate constants were obtained as a product of $k_{insecticide, ROS}$ and $[ROS]_{ss}$ for corresponding ROS - insecticide pair. Details have been provided in supplementary information (S3). The results (Table 2S) showed that, for $^{\cdot}OH$-mediated degradation of carbaryl, there was an agreement between the experimental degradation rate constants (4 x 10^{-5} s^{-1}) and the calculated rate constants (1.8 x 10^{-5} s^{-1}). Similarly, there was a considerable agreement between the experimental (2.0 x 10^{-5} s^{-1}) and calculated (0.56 x 10^{-5} s^{-1}) degradation rate constants for $^{\cdot}OH$-mediated degradation of methomyl. However, for $^1O_2$-mediated degradation of the insecticides, agreements between the calculated and the experimentally-determined degradation rate constants could not be established (Table 2S). This disagreement could be due to the microheterogeneous distribution of $^1O_2$ between the DOM phase and bulk aqueous phase. It has been reported that $^1O_2$ in the DOM microenvironment could be several orders (up to three orders) of magnitude larger than in the aqueous phase (**Latch and McNeil, 2006; Grandbois et al., 2008**). The hydrophobic nature of carbaryl, as evidenced by its very low water solubility (4 mg/100 mL), suggests it may bind to DOM in river water. The binding of carbaryl to DOM may expose it to $[^1O_2]$ in the DOM microenvironment which is several orders of magnitude higher than the $[^1O_2]$ in the bulk aqueous environment. Under such circumstances, the $^1O_2$-mediated degradation of the insecticide may proceed largely in the DOM region. Hence, the experimentally-determined degradation rate constants will differ significantly from the calculated values which are based on aqueous phase $[^1O_2]$. Regardless of the discrepancy between the calculated and experimental $^1O_2$ degradation rate constants, the agreement between the experimental and calculated degradation rate constants for $^{\cdot}OH$-mediated degradation of these insecticides confirms the role of $^{\cdot}OH$ as the primary ROS responsible for their degradation in river water.

3.5. Half-lives in river water

The half-lives of the insecticides as mediated by each ROS ($^{\bullet}OH$ and $^1O_2$) in river water were determined using equation 16. The determined half-lives were normalized to an irradiation condition (F_{solar}) of approximately eight hours (0.3 d) of daily sunlight and a 1/3 variation in yearly light intensity based on light intensity in winter being 1/3 that of summer. As shown in Table 4, the calculated half-lives of carbaryl (3.6 d) in river water with $^{\bullet}OH$ were shorter than that of the half-life with $^1O_2$ (17.06 d). Furthermore, the calculated half-life of methomyl in river water with $^{\bullet}OH$ (13.3 d) was much lower than that with $^1O_2$ (> 186 d). The shorter photochemical half-life of carbaryl could be attributed to its higher reactivity with $^{\bullet}OH$ and $^1O_2$ and higher direct photolysis compared with methomyl. This higher reactivity of carbaryl may be because of its aromatic structure compared with the aliphatic structure of methomyl, which makes $^{\bullet}OH$ more reactive with electron-rich aromatic organic compounds because of its electrophilicity and non-selective nature towards C-H bonds (**Zepp et al., 1985; Buxton et al., 1988; Mabury and Crosby, 1996**).

Overall, the results indicate that $^{\bullet}OH$ specie play an important and major role in the breakdown of pollutants in water, including the insecticides investigated in this study, because of their high reaction rate constants toward a very wide range of organic and inorganic compounds (**Bazrafshan et al., 2017**). Because of their high reactivity with organic compounds, $^{\bullet}OH$ species provide effective solutions to the breakdown of organic compounds with high stability and resistance to chemical, biological, and direct photochemical degradation (**Walse et al., 2004; Richard and Canonica, 2005; Takeda et al., 2017a**).

Finally, inspite of Kurose river water flow into Seto Inland sea, it is very difficult to discuss how much the methomyl and carbaryl are photodegraded when these insecticides in river water flow into seawater using the calculated half-lives. This is because the [ROS] in River water is completely different from [ROS] in seawater. In addition, the sample matrix of seawater is completely different from that of river water. Therefore, it might be misleading to use the calculated half-lives in river water to provide explanation for seawater. Therefore, for clarity sake, we focused only on river water study.

4. Conclusions

This study has reported the photodegradation of two carbamate insecticides, carbaryl and methomyl, in river water under environmentally-relevant conditions. To the best of our search, this is the first report to do so. Indirect photolysis mediated by $^{\bullet}OH$ was primarily responsible for their degradation. Photodegradation studies in the presence and absence of scavengers of $^{\bullet}OH$ and $^1O_2$ showed that $^{\bullet}OH$ accounted for 63% and 62% degradation of methomyl and carbaryl, respectively. The involvement of $^1O_2$ was generally lower (about 30%) in the degradation of both compounds. Neither compound showed significant degradation under direct photolysis in ultrapure water. The reaction rate constants for the reactions of carbaryl and methomyl with $^{\bullet}OH$, determined in this study, were approximately five orders higher than those of their reactions with $^1O_2$. Such preferentially high reaction rate constants with $^{\bullet}OH$ supports the role of $^{\bullet}OH$ as the primary ROS mediating the degradation of these compounds in river water. Furthermore, kinetic estimations of degradation rate constants, calculated from reaction rate constants and ROS steady-state concentrations, agrees with experimentally-determined degradation rate constants for $^{\bullet}OH$-mediated degradation. This validates the experimental observation and confirms the importance of $^{\bullet}OH$ in the degradation of the compounds in river water. The degradation half-lives of the insecticides as mediated by $^{\bullet}OH$ were 3.6 and 13.3 days for carbaryl and methomyl, respectively.

Conflict of interest

The authors declare that there is no conflict of interest regarding this publication

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Figure captions

Fig. 1 Degradation rate constants of carbaryl in river water in the presence and absence of $^1O_2$ (NaN_3) and $^{\cdot}OH$ (methanol) as scavengers.

Fig. 2 Degradation rate constants of methomyl in river water in the presence and absence of $^1O_2$ (NaN_3) and $^{\cdot}OH$ (methanol) as scavengers.

Fig. 3 Contribution of each ROS ($^1O_2$ and $^{\cdot}OH$) and the direct photolysis to degradation of the tested insecticides in water. *Other oxidants (i.e., chloride and sulfate radicals, Lian et al., 2017).

Table 1

Steady-state concentration and photoformation rate of ROS in water from the Kurose River

Reactive oxygen species	Steady-state concentration (M)	Photoformation rate (Ms^{-1})	Scavenging rate (s^{-1})
$^{\cdot}$OH	(1.2 ±0.01^{a}) x 10^{-15}	(1.76 ±0.01^{a}) x 10^{-10}	(1.47± 0.01^{a}) x 10^{5}
$^{1}O_2$	(3.1± 0.02^{b}) x 10^{-13}	(7.9± 0.03^{b}) x 10^{-8}	(*2.5 ±0.02^{b}) x 10^{5}

*Deactivation rate constant of $^{1}O_2$ by water as reported by Rodgers and Snowden (1982).

*Statistical comparisons were made among treatments within a single column.

*The different letters represent significant differences using Fisher's LSD test at *P≤0.05*.

*Each mean value came from three replicates

Table 2

Reaction rate constants of the tested insecticides with $^{\cdot}OH$ and $^1O_2$

ROS	Reaction rate constants (M^{-1} s^{-1})	
	Methomyl	Carbaryl
$^{\cdot}OH$	$(4.68 \pm 0.25) \times 10^9$	$(14.8 \pm 0.12^a) \times 10^9$
$^1O_2$	$< 10^4$	$(2.98 \pm 0.10^b) \times 10^5$

*Statistical comparisons were made among treatments within a single column.

*The different letters represent significant differences using Fisher's LSD test at *P≤0.05*.

*Each mean value came from three replicates

Table 3

Degradation rate constants of the tested insecticides in different water matrixes

Water type	Degradation rate constant, k (s^{-1})	
	Methomyl	Carbaryl
Ultrapure water (direct photolysis)	(6.27 ± 0.31^{a}) x10^{-7}	(4.62 ± 0.22^{a}) x10^{-6}
River water (direct + indirect photolysis)	(4.47 ± 0.27^{b}) x10^{-5}	(6.50 ± 0.34^{b}) x10^{-5}
River water + NaN_3 ($^1O_2$ scavenger)	(3.25 ± 0.17^{c}) x10^{-5}	(4.10 ± 0.15^{b}) x10^{-5}
River water + methanol ($^{\cdot}OH$ scavenger)	(1.62 ± 0.10^{d}) x10^{-5}	(2.03 ± 0.10^{c}) x10^{-5}

*Statistical comparisons were made among treatments within a single column.

*The different letters represent significant differences using Fisher's LSD test at $P\leq0.05$.

*Each mean value came from three replicates

Table 4

Calculated photochemical half-lives of the tested insecticides as mediated by $^{\bullet}$OH and $^1O_2$ in river water

Insecticides	Half-lifetimes (d^{-1})	
	$^{\cdot}$OH	$^1O_2$
Methomyl	13.30±0.24[a]	> 186[a]
Carbaryl	3.60±0.14[b]	17.0±0.34[b]

*Statistical comparisons were made among treatments within a single column.

*The different letters represent significant differences using Fisher's LSD test at *P≤0.05*.

*Each mean value came from three replicates

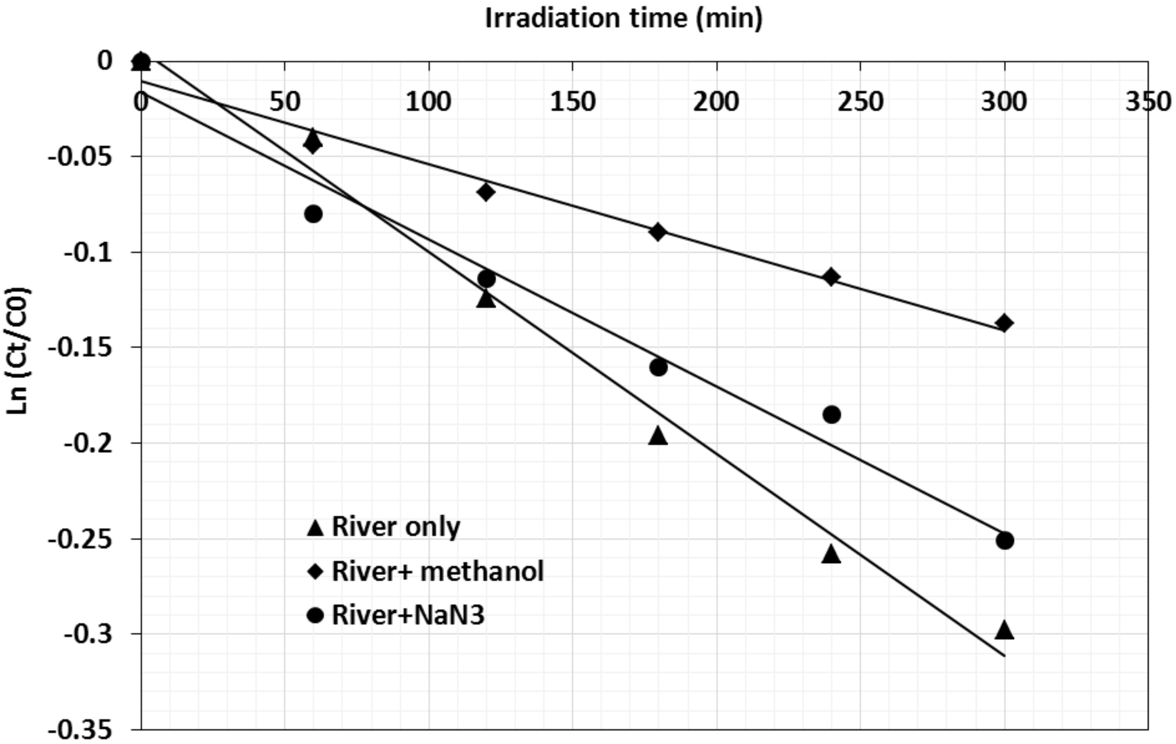
Irradiation time (min)
0
50
100
150
200
250
300
350
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.35
Ln (Ct/C0)
▲ River only
◆ River+ methanol
● River+NaN3

Fig. 1

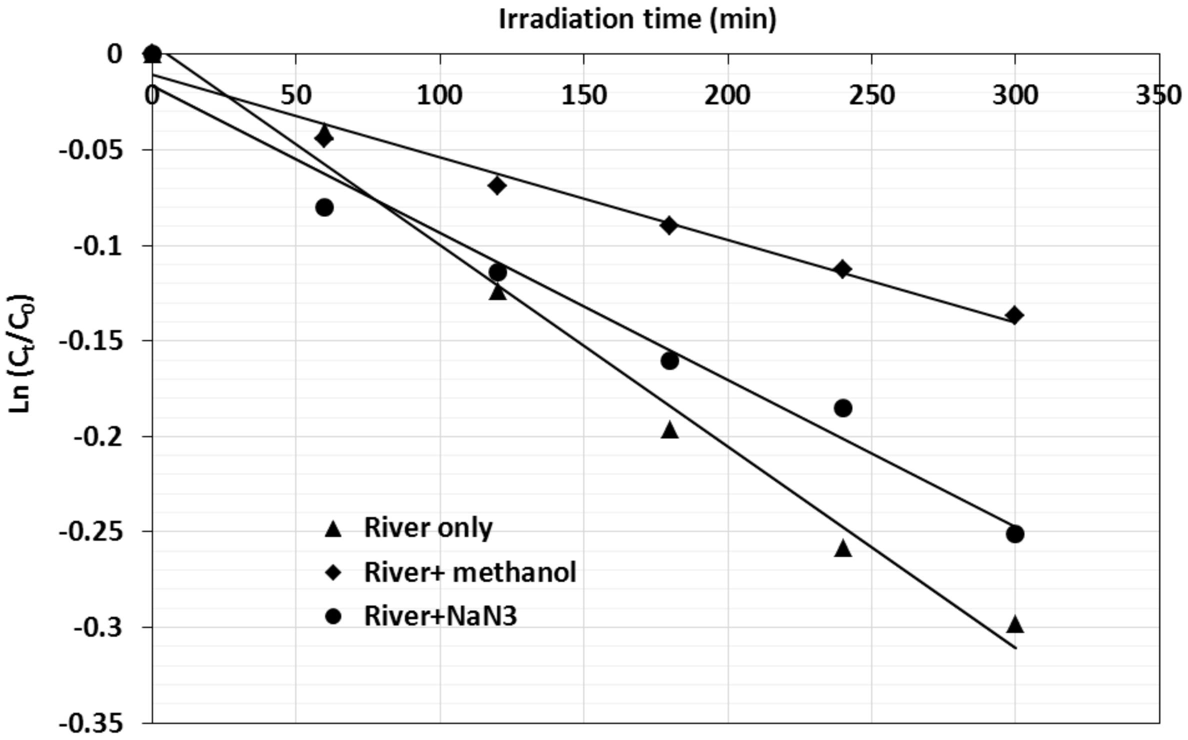
Irradiation time (min)
0
50
100
150
200
250
300
350
0
-0.05
-0.1
-0.15
-0.2
-0.25
-0.3
-0.35
Ln (C_t/C_0)
▲ River only
◆ River+ methanol
● River+NaN3

Fig. 2

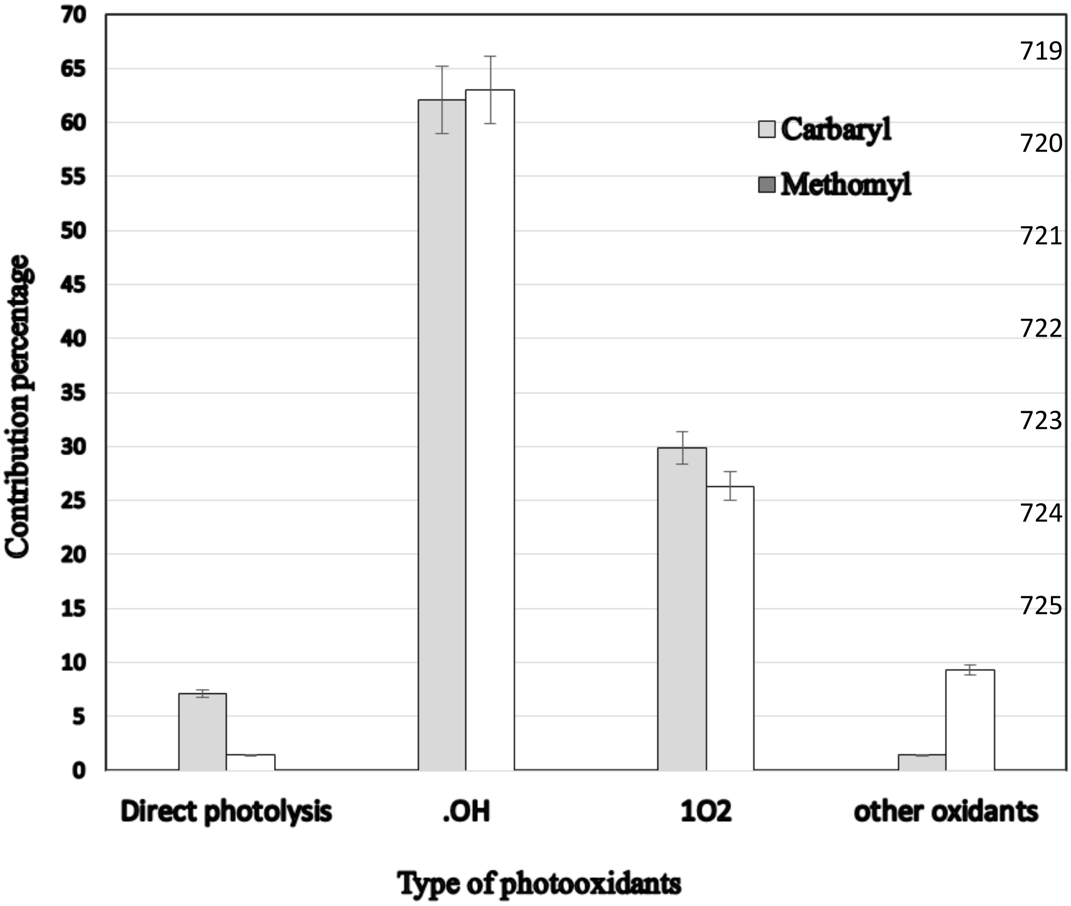
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
Contribution percentage
□ Carbaryl
■ Methomyl
Direct photolysis
.OH
1O2
other oxidants
Type of photooxidants

Fig. 3

Highlights

- Reactive oxygen species ($^1O_2$ and •OH) photogenerated in Kurose river water
- Generation rate of $^1O_2$ was higher by two order than •OH in Kurose river water.
- The reaction rate constants of carbaryl and methomyl with ·OH were several orders higher than $^1O_{2.}$
- Contribution of direct photolysis was very low compared to indirect photolysis in river water.
- •OH was the ROS largely responsible for the degradation of carbaryl and methomyl.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: