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Toxicokinetic modeling of octylphenol bioconcentration in *Chlorella vulgaris* and its trophic transfer to *Daphnia magna*

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ABSTRACT

Bioconcentration of 4-*tert*-Octylphenol (OP) in freshwater algae *Chlorella vulgaris* was investigated by considering the effects of algal growth and exudate excretion. The OP uptake in algae was approximately 113 mg kg^{-1} after 24 h, and the uptake rate constant was estimated as 2.4 × 10^4 L kg^{-1} d^{-1}. The OP sorption onto exudates reduced OP bioavailability to *C. vulgaris* to 11% after 24 h, with a sorption coefficient of 9.7 × 10^3 L kg^{-1}. The elimination of OP by algae growth (0.80 d^{-1}) was dominant over real elimination (0.60 d^{-1}). The calculated bioconcentration factor of OP in *C. vulgaris* following uptake and elimination rate constants was 4.0 × 10^4 L kg^{-1}. Further, bioaccumulation of OP in *Daphnia magna* was investigated by considering both aqueous and dietary (*C. vulgaris*) exposures. Uptake and elimination rates of OP via water were 1.6 × 10^4 L kg^{-1} d^{-1} and 0.95 d^{-1}, respectively, while ingestion rate and assimilation efficiency via diet were 0.41 d^{-1} and 58%, respectively. The OP accumulation in *D. magna* predominantly occurred via water (63%) relative to diet (37%), resulting in a bioaccumulation factor of 2.7 × 10^4 L kg^{-1}. The estimated trophic transfer factor was 0.25, suggesting that OP biomagnification was unlikely in the *C. vulgaris-D. magna* trophic relationship.

1. Introduction

4-*tert*-Octylphenol (OP) is a high production volume chemical (Miyagawa et al., 2016), mainly used for manufacturing plastic additives, non-ionic surfactants, antioxidants, and fuel oil stabilizers (Nimrod and Benson, 1996; Senthil Kumaran et al., 2011; Staniszewska et al., 2014). It is a toxic substance reported to cause endocrine disruption, carcinogenicity, and growth and reproduction malfunctions in aquatic organisms (Bøgh et al., 2001; Du et al., 2008; Markey et al., 2001; Qin et al., 2013), including fish, water fleas, amphibians, and freshwater algae (Li et al., 2018; Perron and Juneau, 2011; Senthil Kumaran et al., 2011; Tatarazako and Oda, 2007; Xie et al., 2019). The highly lipophilic nature of OP (LogK_{ow} = 5.07) (Nagy et al., 2005) leads to its bioconcentration in aquatic organisms and, potentially, to trophic transfer (Correa-Reyes et al., 2007; Quiroz-Vázquez et al., 2010).

Freshwater algae, the dominant primary producers in the aquatic food chain, are lipid-rich organisms, thus making them the primary mediators of hydrophobic chemicals (Guo et al., 2017), and consequently the backbone of the trophic transfer of toxicants (Bhuvaneshwari et al., 2018). On the other hand, daphnids are preferred as a test organism in ecotoxicological studies in aquatic environment because of its short life cycle (Ebert, 2005; Im et al., 2019) and high sensitivity to toxicants (Bae et al., 2016; Guilhermino et al., 2000). Additionally, as a major food source for fish, daphnids plays an important role in transporting toxicants from producers to the secondary consumers (Dai et al., 2013; Koivisto and Ketola, 1995). Therefore, investigating the toxicokinetic behavior of OP in a model *Chlorella vulgaris-Daphnia magna* system is a prerequisite in estimating its transferability in trophic levels (Dalai et al., 2014; Ko and Baker, 1995).

Bioconcentration factor (BCF), which is the ratio of the chemical concentration in the algae to the chemical concentration in the aqueous phase (Tsui and Wang, 2004) can be used to describe the fate of hydrophobic organic chemicals (HOCs) such as OP in freshwater food chains. Because of the relatively fast growth and metabolism of algae, the growth and exudate excretion during chemical exposure to algae are generally included in the determination of BCF (Baptista et al., 2009; Guo et al., 2017; Sijm et al., 1998). Exudates are complex organic macromolecules (e.g. polysaccharides, proteins, and lipids), which can be excreted during metabolic processes of algae (Huangfu et al., 2019). Estimating BCF is also useful in assessing dietary transfer of HOCs as their bioaccumulation in higher trophic levels occurs via water ventilation and food ingestion (Goulet et al., 2007; Nielsen and Olsen, 1989; Ratier et al., 2019). In the case of *D. magna*, several studies demonstrated that aqueous uptake is dominant compared to dietary uptake because of high volume of water ventilation (Dai et al., 2013; Gomes

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et al., 2004; Opperhuizen, 1991). Moreover, bioaccumulation via dietary route greatly depends on chemical assimilation efficiency of *D. magna* (Ribeiro et al., 2017; Tsui and Wang, 2004). However, to our knowledge, the bioconcentration of OP in *C. vulgaris* and its trophic transfer to *D. magna* have not yet been assessed.

Therefore, this study examined the bioconcentration of OP in *C. vulgaris* by considering the influences of growth and exudate excretion, particularly focusing on the reduction of OP bioavailability due to sorption on exudates. Additionally, bioaccumulation of OP in *D. magna* was assessed by evaluating contributions of aqueous and dietary (*C. vulgaris*) exposures, while trophic transfer factor of OP between *C. vulgaris* and *D. magna* was assessed in the dietary exposure. We expected significant effects of algal growth and exudates on the bioconcentration of OP in *C. vulgaris*, whereas the bioaccumulation of OP in *D. magna* was hypothesized to be predominantly through aqueous exposure.

2. Materials and methods

2.1. Chemicals and test organisms

All chemicals used were of analytical grades: 4-*tert*-octylphenol (OP, Sigma Aldrich, USA, > 97%), methanol (MeOH, Sigma Aldrich, USA, 99.9%), potassium dichromate ($K_2Cr_2O_7$, Sigma Aldrich, USA, 99%), acetone (Avantor Performance Materials, USA, 99.3%), dichloromethane (CH_2Cl_2, Wako Pure Chemicals, Japan), mercury sulfate ($HgSO_4$, Sigma Aldrich, USA, ≥ 98%) oxalic acid ($H_2C_2O_4$, Showa, Japan, 99.5%), and silver sulfate (Ag_2SO_4, Junsei, Japan, 99.5%).

Freshwater algae, *C. vulgaris* were obtained from Aquanet (Republic of Korea) and cultured in sterilized BG-11 medium and maintained at 16/8 h light/dark cycle under white fluorescent light of 36 μmol photons $m^{-2}s^{-1}$ at 25 ± 2 °C. *D. magna* were obtained from National Institute of Environmental Research (Republic of Korea), cultured in M4 medium under a photoperiod of 16/8 h light/dark cycle and controlled at a temperature of 20 ± 1 °C (Samel et al., 1999). The animals were fed daily with *C. vulgaris* (1.0×10^6 cells mL^{-1}) and the medium was changed twice a week.

2.2. C. vulgaris experiments

2.2.1. OP uptake and elimination

An OP stock solution of 10 mg mL^{-1} was prepared in methanol and spiked into the BG-11 media at 0.4% v/v methanol. Preliminary studies indicated no effect of 0.4% methanol on *C. vulgaris* and *D. magna*. At exponential growth stage, algal cells at initial concentration of 1.0×10^6 cells mL^{-1} were inoculated into the BG-11 media (2000 mL) containing 0.2 mg L^{-1} OP in Erlenmeyer flasks (n = 3), and cultured in conditions as described earlier. They were sparged continuously with filtered air during culture and 1.5 mL of samples were collected at 0, 0.5, 1, 3, 12, and 24 h. The pH of test solutions was 7.1 ± 0.1 throughout the experiments, and 50% of test solutions were renewed after 12 h to minimize decrease in OP concentration (Sijm et al., 1998; Wen et al., 2016). The concentration of OP was chosen based on no observed acute toxicity (24 h) to *C. vulgaris* (Table S1). Number of algal cells in the acute toxicity testing was measured using hemocytometer under microscope (Olympus CX33, Tokyo, Japan).

The algae samples were then centrifuged at 9160 *g* for 5 min (Avanti® J-E Centrifuge, Beckman Coulter) to obtain algal cell pellets, and the OP in the supernatant was designated as dissolved OP. The supernatant OP was extracted four times with dichloromethane through liquid-liquid extraction method for further analysis. The concentrated pellets were then suspended in 1.5 mL of 10% methanol and shaken for approximately 30 s followed by centrifugation at 9160*g* for 5 min, and the OP in the supernatant was designated as OP adsorbed on cell wall (Zhou et al., 2013). The algal pellets obtained after the 10% methanol wash were kept in a refrigerator at −20 °C overnight to break the cell wall (Zhou et al., 2013) and were subsequently extracted four times with a methanol-dichloromethane mixture (2:1 v/v) to obtain the intracellular OP. The concentration of intracellular and adsorbed OP was regarded as the OP concentration in *C. vulgaris*.

For elimination experiments, *C. vulgaris* (1.0×10^6 cells mL^{-1}) were inoculated into a culture medium containing 0.2 mg L^{-1} OP and incubated for 24 h. After centrifugation at 9160*g* for 5 min, algal cell pellets were transferred into fresh BG-11 medium without OP and cultured under the same conditions as the uptake test. Samples (n = 3) were collected at a similar time span as the uptake experiment and used to analyze the OP concentration in *C. vulgaris* as described earlier.

2.2.2. Cell growth and exudate measurements

The growth of *C. vulgaris* was assessed using a first order nonlinear kinetic model as (Ji et al., 2014):

$$N_t = N_0(e^{-\mu t}) \quad (1)$$

where N_t and N_0 are the dry weight concentration of *C. vulgaris* (kg L^{-1}) at time t and 0, respectively, and μ is the growth rate constant (d^{-1}). The dry weight concentration of *C. vulgaris* was measured based on the optical density at 680 nm using a UV–Vis spectrophotometer (OPTIZEN POP; Mecasys, Republic of Korea) as (Greenberg et al., 1998; Ji et al., 2014):

$$\text{Dry weight(DW, kg } L^{-1}) = 0.3065 \times OD_{680} - 0.0097 \ (R^2 = 0.9958) \quad (2)$$

Exudate concentration was determined using a chemical oxygen demand surrogate according to Sijm et al. (1995). At exponential growth stage, algal cells at initial concentration of 1.0×10^6 cells mL^{-1} were inoculated into the BG-11 media (400 mL) in 1 L Erlenmeyer flasks (n = 3) and cultured in conditions as described earlier. Aliquots of 10 mL were withdrawn regularly and a glass microfiber filter (Whatman®, 1.2 μm pore size) was used to obtain the exudate water. The samples were added to solutions containing 5 mL 0.15 M $K_2Cr_2O_7$, 0.2 g $HgSO_4$, and 15 mL of Ag_2SO_4 (20 g Ag_2SO_4 in 1 L of 12 M H_2SO_4), and then heated in a pre-heated heat block for 1 h. After cooling, the absorbance was determined using a UV–Vis spectrophotometer (OPTIZEN POP) at 610 nm. Oxalic acid ($H_2C_2O_4$) was used as the external standard and results were expressed in kg L^{-1}.

Concentrations of OP adsorbed onto the exudates were determined according to Baptista et al. (2009) and Sijm et al. (1998). Exponential growth stage algal cells at initial concentration of 1.0×10^6 cells mL^{-1} were inoculated into the BG-11 media (400 mL) in 1 L Erlenmeyer flasks (n = 3) and cultured in conditions as described earlier. Aliquots of 50 mL were sampled regularly and filtered through a glass microfiber filter (Whatman®, 1.2 μm pore size) to obtain the exudate water. Exudate water samples and deionized water (control) were spiked with 0.2 mg L^{-1} OP and incubated for 1 h under the same conditions as the uptake experiment. The 1 h interval was assumed to be the sorption equilibrium time of OP on *C. vulgaris* dead cells (Peng et al., 2009). The solid-phase microextraction (SPME) method was applied to measure the freely dissolved OP using 1 cm long manual SPME fibers (Supelco No. 57302) coated with 7-μm polydimethylsiloxane (Sijm et al., 1998). The fibers were directly immersed into magnetically stirred samples for approximately 30 min, which is the steady state adsorption time of OP on the fiber according to preliminary tests, for OP extraction (Daimon and Pawliszyn, 1997; Liu et al., 2010). The fibers were then immersed into stirring methanol-dichloromethane mixture (2:1 v/v) for 15 h to desorb OP (Liu et al., 2010) before analysis in high performance liquid chromatograph (HPLC). It was assumed that SPME only adsorbs freely dissolved chemical in a medium (Buchholz and Pawliszyn, 1993; Wang et al., 2002) and aqueous concentration of freely dissolved OP would remain constant during sorption to the small fiber volumes (Spietelun et al., 2010; Vaes et al., 1996). The concentrations of OP adsorbed on the exudates were obtained by calculating the difference between OP concentrations in the control and the ones adsorbed on the fiber.

2.3. D. magna experiments

2.3.1. OP uptake and elimination in aqueous exposure

Fifteen-day-old adult *D. magna* with similar body sizes were used in order to achieve an adequate amount of biomass for better analytical measurements of OP accumulation (Preuss et al., 2008). A 0.1 mg L^{-1} OP solution, equivalent to the dissolved OP concentration at equilibrium in the *C. vulgaris* experiment, was prepared in M4 medium for the uptake test. One hundred and twenty *D. magna* individuals were first placed in a clean M4 medium for 2 h to clear their guts and were then introduced into 2000 mL of OP solution (n = 3). The exposure lasted for 9 h during which 20 *D. magna* individuals and 5 mL aliquot of solution were sampled at every 1.5 h. Test solutions were renewed at each sampling time to minimize decrease in OP concentration and the ratio of animals to medium volume was maintained constant throughout the process (Tsui and Wang, 2004). This study assumed little or no disturbance caused to *D. magna* during solutions renewal. Food was not added throughout this process to avoid possible effect of OP sorption on algae. The pH of test solutions was 7.0 ± 0.1 throughout the experiments.

The animals were collected using a 300 μm mesh and washed gently twice with M4 medium and once with deionized water to remove OP present in the carapace. Animals were then dried at an OP non-destructive temperature of 60 °C for 12 h (Zhou et al., 2013). The OP concentration in *D. magna* was extracted using the organic solvent extraction approach (Morrison et al., 1996). Briefly, the samples were homogenized in 1.5 mL methanol/acetone (1:1 v/v) and then centrifuged at 16,000 *g* and 4 °C for 15 min (Micro High Speed Centrifuge-MICRO 17 TR, Hanil Science Industrial) to obtain a supernatant. The supernatant containing OP was then extracted four times using a methanol-dichloromethane mixture (2:1 v/v) (Zhou et al., 2013). Additionally, the OP in aliquot was extracted four times with dichloromethane through liquid-liquid extraction method for further analysis.

Elimination test was performed following the exposure of 120 *D. magna* individuals to OP as described in the uptake procedure. We assumed that OP was well assimilated during the exposure while the unassimilated OP was removed from the guts (Maes et al., 2014). The animals were taken and rinsed gently with fresh M4 medium and then re-suspended into fresh M4 medium containing uncontaminated *C. vulgaris* (1.0×10^6 cells mL^{-1}), and the elimination lasted for 32 h (n = 3). This longer duration was to ensure adequate time for OP elimination by *D. magna* (Maes et al., 2014). Fifteen animals and 5 mL aliquots were collected after every 4 h for retained and depurated OP analysis, respectively, as described earlier. Test solutions were renewed at each sampling time and the ratio of animals to medium volume was maintained constant throughout the process (Tsui and Wang, 2004). We assumed little or no disturbance caused to *D. magna* during solutions renewal. Any feces and neonates were collected using 40 μm mesh and 1.5 mL dropping pipette, respectively.

2.3.2. OP uptake and elimination in dietary exposure

C. vulgaris was treated with the initial concentration of 0.2 mg L^{-1} OP for 24 h. The OP contaminated algae (100 ± 13 mg kg^{-1}) were obtained through centrifugation at 9860*g* for 5 min (Avanti® J-E Centrifuge, Beckman Coulter) and then washed twice with BG-11 medium and once with M4 medium prior to *D. magna* feeding at a concentration of 1.0×10^6 cells mL^{-1}. In the uptake phase, 20 fifteen-day-old adult *D. magna* were fed with the contaminated algae in a 450 mL medium in dark for 30 min at 20 ± 2 °C (n = 3) to analyze algae ingestion rate. The dry weight concentration of *C. vulgaris* was measured at the beginning and end of experiment. Exposure in darkness was chosen to avoid algal growth while the 30 min interval was chosen because it is shorter than the gut passage time in *D. magna* (Caspers, 1972; Maes et al., 2014), which minimizes the removal of OP via defecation. The animals were then collected using a 300 μm mesh and gently rinsed twice with fresh M4 medium and once with deionized water to measure OP concentration in *D. magna*.

In the elimination phase, 160 fifteen-day-old adult *D. magna* in 2000 mL medium (n = 3) were fed with contaminated algae under similar conditions as the uptake phase. The animals were then collected and gently rinsed twice with fresh M4 medium and re-suspended in a fresh M4 medium containing uncontaminated *C. vulgaris* (1.0×10^6 cells mL^{-1}) for OP elimination. The elimination period lasted for 32 h during which 20 animals and 5 mL aliquots were sampled after every 4 h for the analysis of the OP concentration retained in *D. magna* to determine assimilation efficiency. The medium and food were totally renewed at each sampling time and the ratio of animals to medium volume and food concentration were maintained constant throughout the test period. Any feces and neonates were collected using 40 μm mesh and 1.5 mL dropping pipette, respectively.

2.4. Chemical analysis of OP

The concentration of OP was analyzed in an HPLC apparatus (Waters, Massachusetts, USA) fitted with; Waters 515 HPLC pump, Waters 2475 Multi λ Fluorescence and 2996 Photodiode Array Detectors, and Waters 717 plus Autosampler. Thermo Scientific ODS HYPERSIL C18 column (150 mm × 4.6 mm, particle size 5 μm) was used and the HPLC conditions were set as described by Zhou et al. (2013). Briefly, mobile phases consisted of water and acetonitrile (3:7 v/v) at a flow rate of 1 mL min^{-1} and wavelength at 305 nm. The injection volume was 50 μL while the retention time was 10 min.

Preliminary tests indicated that percentage recovery of OP from deionized water, BG-11 and M4 media were 98 ± 1%, 97 ± 2%, and 98 ± 1%, respectively. For the SPME fiber experiments, recovery of OP in the control (deionized water) was 96 ± 3% while the relative standard deviation of OP in the fiber was 4.5%. This is expected due to negligible influence of abiotic processes in the removal of OP (Baptista et al., 2009). In contrast, the calculated OP percentage recovery from *C. vulgaris* and *D. magna* were 82 ± 2% and 91 ± 5%, respectively. The unrecovered large fractions of OP from algae may be attributed to loss by biodegradation (Liu et al., 2010; Zhou et al., 2013). Pedersen and Hill (2000) reported OP metabolites such as 4-(1′,1′,3′,3′-tetramethylbutyl)phenoxy-β-glucuronide and 4-(2′-hydroxy-1′,1′,3′,3′-tetramethylbutyl)phenol. Additionally, OP can be conjugated in the algal cells making it difficult to be eliminated or extracted (Guo et al., 2017).

2.5. Modeling bioconcentration of OP in C. vulgaris

Bioconcentration of OP in *C. vulgaris* was assessed by the method proposed by Sijm et al. (1998) using a one-compartment first-order toxicokinetic model. Considering *C. vulgaris* growth dilution effect on OP, uptake and elimination can be described as:

$$\frac{dC_{cv}}{dt} = k_1 C_w - (k_2 + \mu) C_{cv} \quad (3)$$

where C_{cv} is OP concentration in *C. vulgaris* (mg kg^{-1} $_{DW}$) at time t (d), k_1 is the uptake rate constant (L kg^{-1} d^{-1}), C_w is the freely dissolved concentration of OP in water (mg L^{-1}), k_2 is the elimination rate constant (d^{-1}) and μ is the growth rate constant (d^{-1}). The uptake and elimination rate constants were determined using nonlinear square fit in R (v. 3.6.1) following Eq. (4) as (Maes et al., 2014):

$$\frac{C_{cv}}{C_w} = \frac{k_1}{k_2 + \mu}\left(1 - e^{-(k_2+\mu)t}\right) \quad (4)$$

Assuming a steady-state, bioconcentration factor (BCF, L kg^{-1}) can be derived from Eq. (4), giving:

$$BCF = \frac{C_{cv}}{C_w} = \frac{k_1}{k_2} \quad (5)$$

Sorption of OP on exudates reduces the freely dissolved

concentration in water. Therefore, apparent OP concentration in water (C_w^*, mg L^{-1}) is obtained by summing freely dissolved (C_w) and exudate-bound (C_{exd}, mg kg^{-1}) concentrations as (Schrap et al., 1994):

$$C_w^* = C_w + C_{exd}s \tag{6}$$

where s is the exudate concentration in water (kg L^{-1}). Additionally, the reduction in OP bioavailability due to sorption on exudates can be assessed by assuming a linear partitioning of OP to exudates (Sijm et al., 1998):

$$\frac{C_w}{C_w^*} = \frac{C_w}{C_w + C_{exd}s} = \frac{C_w}{C_w + C_wK_ps} = \frac{1}{1 + K_ps} \tag{7}$$

where K_p is the exudate-water sorption coefficient of OP (L kg^{-1}).

2.6. Modeling bioaccumulation of OP in D. magna

For *D. magna* OP exposure, a one compartment kinetic model was applied for micropollutant accumulation in aquatic invertebrates based on chemical uptake from food and water and elimination, which was originally developed by Thomann (1981). Firstly, OP uptake via water is calculated as:

$$\frac{dC_{dm}}{dt} = k_{up}C_w - k_{el}C_{dm} \tag{8}$$

where C_{dm} is OP concentration in *D. magna* (mg kg^{-1} $_{DW}$) at time t (d), k_{up} is the uptake rate constant (L kg^{-1} d^{-1}), C_w is freely dissolved OP concentration in water (mg L^{-1}) and k_{el} is the elimination rate constant (d^{-1}). The uptake and elimination rate constants were determined using nonlinear square fit in R (v. 3.6.1) following Eq. (9) (Gross-Sorokin et al., 2003):

$$\frac{C_{dm}}{C_w} = \frac{k_{up}}{k_{el}}\left(1 - e^{-k_{el}t}\right) \tag{9}$$

By assuming that elimination rates of OP from water and food exposures are similar and can be described by a single rate constant (k_{el}) (Reinfelder et al., 1998), OP bioaccumulation through water and food can be described as (Wang and Fisher, 1999):

$$\frac{dC_{dm}}{dt} = [(k_{up}\cdot C_w) + (AE\cdot IR\cdot C_{cv})] - k_{el}C_{dm} \tag{10}$$

where AE is OP assimilation efficiency via food digestion (%), IR is the food ingestion rate (kg kg^{-1} d^{-1}) and C_{cv} is OP concentration in food (*C. vulgaris*, mg kg^{-1} $_{DW}$). At steady-state, the bioaccumulation factor of OP in *D.* magna (BAF_{dm}, L kg^{-1}) can be derived from Eq. (10):

$$BAF_{dm} = \frac{C_{dm}}{C_w} = \frac{(k_{up}) + (AE\cdot IR\cdot BCF)}{k_{el}} \tag{11}$$

By assuming that the ingestion rate of *D. magna* is not affected by changes in algal biomass concentration during the 30 min feeding time (Peters, 1984), IR was determined as (Kukkonen and Landrum, 1995; Wang and Fisher, 1999):

$$IR = \frac{V\cdot(N_o - N_{30})}{t\cdot M_{dm}} \tag{12}$$

where V is media volume (L), N_0 and N_{30} are the initial and final dry weight concentration of *C. vulgaris* (kg L^{-1}) during the feeding period (t = 0.021 d^{-1}), respectively, and M_{dm} is the dry biomass (kg) of *D. magna*.

Additionally, by assuming that *D. magna* completed algae digestion within 12 h (Lam and Wang, 2006; Maes et al., 2014) and given that OP elimination via other routes such as feces was negligible (Wang and Fisher, 1999), the AE of OP was computed using the y-intercept (curve stripping) method described by Riggs (1963)):

$$A_t = A_0(e^{-kt}) \tag{13}$$

where A_t is the percentage of ingested OP that is retained in *D. magna* during physiological loss (12–32 h), A_0 is the AE and k is the physiological turnover rate constant representing OP loss through metabolism (physiological loss).

Given the BCF of *C. vulgaris*, the fraction of OP accumulated in *D. magna* via aqueous exposure (C_{fr}) was calculated as (Tsui and Wang, 2004):

$$C_{fr} = \frac{k_{up}}{(AE\cdot IR\cdot BCF) + k_{up}} \tag{14}$$

and the fraction accumulated via dietary exposure was calculated as 1 - C_{fr}.

The trophic transfer factor (TTF), which is a simplified definition of biomagnification factor, can be used to describe the ratio of OP concentration in *D. magna* to that in *C. vulgaris* as (Tsui and Wang, 2004):

$$TTF = \frac{AE\cdot IR}{k_{el}} \tag{15}$$

3. Results and discussion

3.1. Bioconcentration of OP in C. vulgaris

The uptake of OP by *C. vulgaris* consisted of an initial rapid phase within 3 h, with no significant ($p > 0.05$) change afterwards (Fig. 1), a trend that is comparable to nonylphenol (NP) uptake in *Isochrysis galbana* (Correa-Reyes et al., 2007). The bioconcentration of OP in *C. vulgaris* was approximately 117 ± 8 mg kg^{-1} $_{DW}$ after 3 h. The slight decline in uptake beyond 3 h was possibly due to an increase in algal biomass and decrease in concentration of freely dissolved OP (Staniszewska et al., 2015; Wang et al., 2019). The elimination of OP was rapid at the beginning (0–0.5 h) followed by a short transition between 0.5 and 2 h, after which elimination presented a fairly regular pattern (Fig. 1). The initial rapid elimination was possibly due to desorption of the cell wall bound OP (Koelmans et al., 1993).

By assuming negligible uptake of the released OP, a first-order kinetic model was well fitted (R^2 = 0.93) to the elimination data (described in Fig. S1), and the apparent elimination rate constant ($k_2 + \mu$) was estimated to be 1.40 d^{-1} (Table 1). Additionally, an over doubleday growth rate (mean = 2.6) of *C. vulgaris* was observed within 24 h regardless of OP presence (Fig. 2). The growth rate constant (μ) was estimated to be 0.80 d^{-1} using the first-order model (Eq. (1)) fitting to the experimental data (Fig. S2). This indicated that dilution effect of

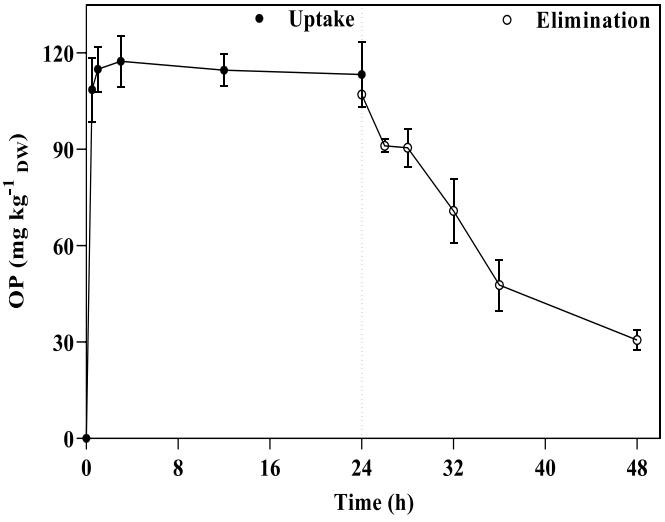

Fig. 1. Uptake and elimination of 4-*tert*-octylphenol (OP) in *Chlorella vulgaris* following 24 h exposure to 0.2 mg L^{-1} OP. Concentrations are based on dry weight of *C. vulgaris*. Values are presented as mean ± standard deviation (n = 3).

Table 1
Toxicokinetic model parameters for 4-*tert*-octylphenol (OP) in *Chlorella vulgaris* and *Daphnia magna*.

Parameter	Unit	Value *	R^2
C. vulgaris			
k_1	L kg^{-1} d^{-1}	2.4 ± 0.6 × 10^4	0.90
k_2	d^{-1}	0.60 ± 0.03	0.98
BCF	L kg^{-1}	4.0 ± 0.1 × 10^4	
K_p	L kg^{-1}	9.7 ± 0.1 × 10^3	0.99
μ	d^{-1}	0.80 ± 0.06	0.95
D. magna			
k_{up}	L kg^{-1} d^{-1}	1.6 ± 0.01 × 10^4	0.94
k_{el}	d^{-1}	0.95 ± 0.05	0.96
IR	d^{-1}	0.41 ± 0.05	
AE	%	58 ± 2	0.95
k	d^{-1}	0.010 ± 0.006	0.95
BAF_{dm}	L kg^{-1}	2.7 ± 0.1 × 10^4	
C_{fr}		0.63 ± 0.07	
TTF		0.25 ± 0.04	

* mean ± standard deviation (n = 3).
k_1= uptake rate constant; k_2 = elimination rate constant; *BCF*=bioconcentration factor; K_p = exudate-water sorption coefficient; μ = algal growth rate constant; k_{up} = uptake rate constant; k_{el} = elimination rate constant; AE = assimilation efficiency; k = physiological turnover rate constant; IR = ingestion rate; BAF_{dm} = bioaccumulation factor; C_{fr} = aqueous exposure fraction; TTF = trophic transfer factor.

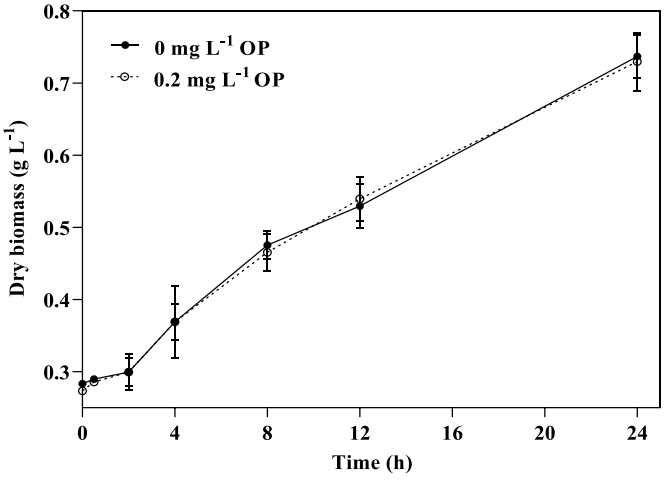

Fig. 2. Cell growth of *Chlorella vulgaris* for 24 h in the presence (0.2 mg L^{-1}) and absence (0 mg L^{-1}) of 4-*tert*-octylphenol (OP). Values are presented as mean ± standard deviation (n = 3).

algal growth accounted for approximately 57% of the observed OP elimination for 24 h. Lipophilic chemicals, including OP, once accumulated in lipid rich organisms such as *C. vulgaris*, remain strongly bound to the algae cells (Bhuvaneshwari et al., 2018). Therefore, OP can be predominantly eliminated through algal growth dilution rather than aqueous elimination (Larisch and Goss, 2018). Similar observations were reported for bisphenol A and 17α-Ethinylestradiol in *Chlorella pyrenoidosa* and *Desmodesmus subspicatus,* respectively (Guo et al., 2017; Maes et al., 2014).

The uptake rate constant (k_1= 2.4 × 10^4 L kg^{-1} d^{-1}) was obtained by fitting Eq. (4) to the experimental data (Fig. S3). Comparable uptake rate constants for polychlorinated biphenyl (PCB) congeners in various algae species are reported by Sijm et al. (1998) and Skoglund et al. (1996) in ranges of 7.9 × 10^3–3.7 × 10^5 and 5.7 × 10^4–4.6 × 10^5 L kg^{-1} d^{-1}, respectively. However, PCBs are more hydrophobic (LogK_{ow} = 5.1 − 6.9) than OP (LogK_{ow} = 5.07) and thus higher values for PCBs can be expected (Garg and Smith, 2014; Miller et al., 2016; Skoglund et al., 1996).

Table 2
Freely (C_w) and apparently (C_w^*) dissolved concentration of 4-*tert*-octylphenol (OP) and the bioavailability of OP (C_w/C_w^*) in the uptake experiment of *Chlorella. vulgaris*.

Time (h)	C_w (mg L^{-1}) *	C_w^* (mg L^{-1}) *	C_w/C_w^* *
0	0.198 ± 0.020	0.197 ± 0.010	1.00 ± 0.000
1	0.172 ± 0.006	0.174 ± 0.021 **	0.988 ± 0.020
3	0.159 ± 0.019	0.164 ± 0.010 **	0.969 ± 0.061
12	0.148 ± 0.012	0.162 ± 0.005 **	0.913 ± 0.012
24	0.145 ± 0.002	0.162 ± 0.009 **	0.895 ± 0.090

* mean ± standard deviation (n = 3).
** significant difference from C_w at $p < 0.05$.

The BCF of OP in *C. vulgaris* was determined following the ratio k_1/k_2, resulting in 4.0 × 10^4 L kg^{-1}. This value is much higher than that of OP in *Scenedesmus obliquus* (3.2 × 10^3 L kg^{-1}) determined by Zhou et al. (2013). However, comparable BCF values (1.5–6.0 × 10^4 L kg^{-1}) for other HOCs in algae were reported (Ellison et al., 2014; Halling-Sørensen et al., 2000; Sijm et al., 1998). Differences in BCF values can be explained by the relations between HOC bioconcentration and the nature of the chemical, algae species, algal biomass and lipid content (Berglund et al., 2001; Borgå et al., 2004; Liu et al., 2010a).

The bioavailability of OP (C_w/C_w^* ratio) in the uptake period was reduced in a range of 1–11% by algal exudates (Table 2). Baptista et al. (2009) demonstrated that OP bioavailability in *Microcystis aeruginosa* may be inhibited due to OP sorption on exudates, while uptakes of ammonium chloride, and ofloxacin and ciprofloxacin were inhibited by exudates produced by *C. vulgaris* and bacteria biofilms, respectively (Li et al., 2019; Zhang et al., 2018; Zhang et al., 2018, 2018). Specifically, bioavailability of silver nanoparticles to *C. pyrenoidosa* was reduced by up to 27.3% (K. Zhou et al., 2016), while reduced bioavailability of PCB congeners (14–70%) to *C. pyrenoidosa* have also been reported, due to sorption on algal exudates (Sijm et al., 1998). Sorption coefficient (K_p=9.7 × 10^3 L kg^{-1}) of OP onto exudate was determined using Eq. (7) (Fig. S4), and suggested a linear partitioning of OP on exudates (Wen et al., 2016). Peng et al. (2009) reported a linear sorption of OP on dead biomass of *C. vulgaris* (K_p=7.3 × 10^4 L kg^{-1}). Other studies also reported similar linear sorption of NP and ciprofloxacin on humic acid and algal exudates, respectively (Zhang et al., 2015, 2018).

3.2. Bioaccumulation of OP in D. magna

Aqueous OP uptake in *D. magna* in the absence of food was rapid in the first 4.5 h but no significant change afterwards ($p > 0.05$), resulting in an OP bioconcentration of approximately 115 mg kg^{-1} $_{DW}$ (Fig. 3). Elimination of OP was remarkably rapid within the initial 24 h but seemed to slow down afterwards. Elimination rate constant (k_{el} = 0.95 d^{-1}) was obtained by a first-order nonlinear fit to the experimental data (described in Fig. S5). Given the elimination rate constant, uptake rate constant (k_{up} = 1.6 × 10^4 L kg^{-1} d^{-1}) was estimated by fitting Eq. (9) to the uptake data (Fig. S6). This k_{up} falls within the range of reported values in *D. magna* for other HOCs and trace elements (0.1–1.8 × 10^4 L kg^{-1} d^{-1}) (Dai et al., 2013; Fan et al., 2016; Maes et al., 2014; Thomas et al., 2018).

Several studies observed chemical elimination in *D. magna* via other routes such as maternal transfer to neonates and defecation (Guan and Wang, 2004; Tsui and Wang, 2004). In this study, negligible amount of OP (< 0.1% of the average OP lost during elimination) was detected in neonates and feces (data not shown), suggesting that reproduction and defecation may not affect OP bioaccumulation in *D. magna.* Our results are similar to previous findings where HOCs transfer to neonates was almost zero (Dai et al., 2013).

To evaluate the dietary OP uptake, the IR was estimated based on the changes in dry biomass of food (*C. vulgaris)* between 0 min and 30 min during *D. magna* feeding (Eq. (12)), giving 0.41 d^{-1}. Tsui and

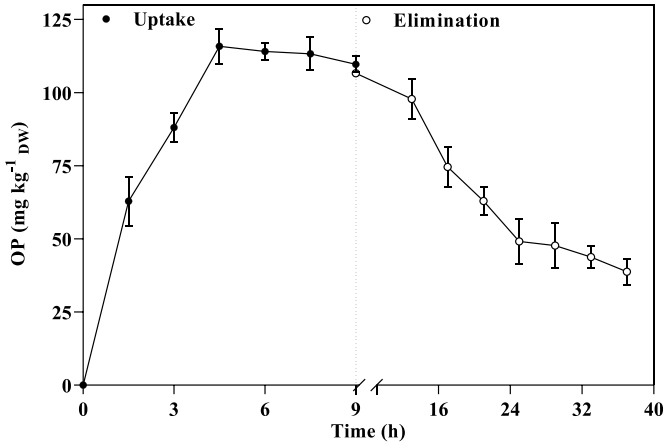

Fig. 3. Uptake and elimination of 4-*tert*-octylphenol (OP) in *Daphnia magna* following 9 h exposure to aqueous OP (0.1 mg L^{-1}). Concentrations are based on dry weight of *D. magna*. Values are presented as mean ± standard deviation (n = 3).

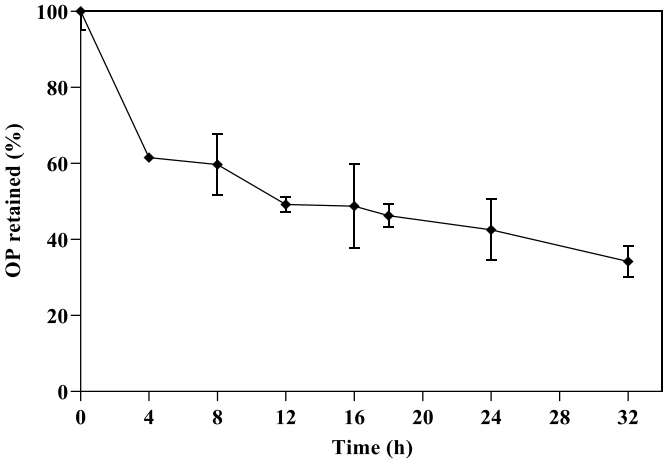

Fig. 4. Assimilation of 4-*tert*-octylphenol (OP) in *Daphnia magna* following 30 min ingestion of OP contaminated *Chlorella vulgaris* (100 ± 13 mg kg^{-1}). Concentrations are based on dry weight of *D. magna*. Values are presented as mean ± standard deviation (n = 3).

Wang (2004) reported similar findings (0.10–0.50 d^{-1}) for *D. magna* exposed to methylmercury in *Chlamydomonas reinhardtii* and *S. obliquus* diets. Additionally, AE of OP through diet was determined based on the OP concentration retained in *D. magna* after ingestion of OP contaminated *C. vulgaris* (Fig. 4). The relatively rapid loss pattern between 0 and 12 h was probably due to the egestion of unassimilated OP and was followed by a gradual loss pattern beyond 12 h, possibly due to complete digestion and assimilation of OP. Preliminary studies indicated negligible elimination of OP via feces and neonates (data not shown).

Based on the long time (> 4 h) required to completely digest and assimilate OP in the daphnids and negligible elimination via other routes such as feces (Wang and Fisher, 1999), the AE was estimated during physiological loss (12–32 h) according using Eq. (17), giving 58% (Fig. S7). This result indicated that 58% of the OP in *C. vulgaris* was successfully incorporated into *D. magna* for metabolism (Reinfelder et al., 1998; Wang and Fisher, 1999). The reported AE of methylmercury (55%) in *D. magna* for algae diet is comparable to our result (Tsui and Wang, 2004). Differences in AEs can be attributed to difference in food digestibility and concentration, gut retention time, and feeding behavior of *D. magna* (Ashiwaza, 1996; Tsui and Wang, 2004). Meanwhile, physiological turnover rate constant (k) indicates OP elimination due to physiological and metabolic processes in *D. magna* (Tsui and Wang, 2004). The estimated k value (0.01 d^{-1}) was much lower than the k_{el} value (0.95 d^{-1}), suggesting insignificant OP loss by metabolism.

The bioaccumulation factor (BAF_{dm}) of OP in *D. magna* was determined to be 2.7 × 10^4 L kg^{-1} according to Eq. (11). Generally, chemicals with BAF values greater than 5000 L kg^{-1} are considered to be bioaccumulative in aquatic organisms (Kelly and Gobas, 2001; Xie et al., 2020). The contribution of aqueous uptake to OP bioaccumulation in *D. magna* (C_{fr}) was determined to be 0.63 according to Eq. (14), implying that dietary uptake only contributed to 37% of OP accumulation in *D. magna*. The predominance of the aqueous uptake route can be explained by the higher volume of water passing through their ventilations compared to the quantity of food ingested (Dai et al., 2013; Gomes et al., 2004; Opperhuizen, 1991) and the high k_{up} (1.6 × 10^4 L kg^{-1} d^{-1}) obtained in this study (Ashiwaza, 1996; Lam and Wang, 2006).

The TTF can be used to describe a possible biomagnification of a contaminant across trophic levels (Mathews and Fisher, 2008). In this study, TTF of less than unity (0.25) was estimated using Eq. (19), indicating that the biomagnification of OP in *D. magna* via *C. vulgaris* was unlikely. Ding et al. (2015) and Kim et al. (2014) also reported lack of biomagnification of other HOCs in *D. magna* via algae diet. However, a more precise estimation of chemical biomagnification across trophic level can be determined through lipid normalization (Guo et al., 2017). Therefore, in future studies, it would be interesting to investigate and validate biomagnification of OP in *D. magna* via *C. vulgaris* diet by normalizing OP concentrations by lipid contents in the planktons.

4. Conclusion

The biococentration of OP in *C. vulgaris* was greatly influenced by algal growth dilution and algal exudate sorption. The sorption of OP on algal exudates significantly reduced OP bioavailability to *C. vulgaris* by 1–11%. The loss of OP by algal growth (0.80 d^{-1}) was greater than the one by elimination (0.60 d^{-1}). Additionally, the bioaccumulation of OP in *D. magna* was more attributable to aqueous uptake (63%) than dietary uptake (37%). These findings suggest a strong potential for OP accumulation in both *C. vulgaris* (BCF = 4.0 × 10^4 L kg^{-1}) and *D. magna* (BAF = 2.7 × 10^4 L kg^{-1}). However, the TTF (0.25) of OP suggested that biomagnification of OP in *D. magna* via *C. vulgaris* diet was not likely. In this study, biotransformation of OP in the aquatic organisms was not considered. Given the possible biodegradation of OP by these organisms, future studies are recommended to include this process in the modeling. Additionally, the role of lipid contents in the accumulation of OP should be further evaluated.

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CRediT authorship contribution statement

Jerry Collince Achar: Conceptualization, Data curation, Methodology, Formal analysis, Investigation, Writing - original draft. **Du Yung Kim:** Methodology. **Jung-Hwan Kwon:** Conceptualization, Writing - review & editing. **Jinho Jung:** Conceptualization, Funding acquisition, Supervision, Writing - review & editing.

Declaration of competing interest

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.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ecoenv.2020.110379.

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