



Photostability and toxicity of pentachlorophenol and phenanthrene

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ABSTRACT

Fate of organic contaminants under UV irradiation as environmental variable was studied. Aqueous solutions of pentachlorophenol and phenanthrene were subjected to simulated solar radiation and monitored during ≤ 93 h. Immobilization tests were conducted using *Daphnia magna* neonates in pre-irradiated water for the assessment of photoproduct-mediated toxicity. We observed a time-dependent decrease in exposure concentrations following irradiation, which correlated positively with reduced immobilization of the animals. A complete disappearance of the lowest and highest concentrations of pentachlorophenol was noted after 25 h and 75 h, respectively. Survivorship of the animals increased until 100% and correlated positively with irradiation time. However, phenanthrene was rather persistent under irradiation, with less than 25% decline in exposure concentrations after 93 h. Neonates were not immobilized at maximum aqueous solubility of phenanthrene. Rate constants (k) for the photodegradation of pentachlorophenol at 0.41, 0.59, 1.1, and 2.1 mg l⁻¹ were in the range of 7.2×10^{-2} and 4.9×10^{-2} h⁻¹, showing a slight decrease with increasing initial pentachlorophenol concentration. Nonetheless, pentachlorophenol degradation in the studied concentration range could still be described by the pseudo-first-order kinetics. K values for phenanthrene at 0.12 and 0.22 mg l⁻¹ were 2.9×10^{-3} h⁻¹ and 4.2×10^{-3} h⁻¹, respectively.

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1. Introduction

Pentachlorophenol (PCP) was once widely used as a broad spectrum biocide in agriculture and wood industry. Despite the restricted use in several countries, PCP remains an important pesticide from the viewpoint of ecotoxicology. In China, PCP was used extensively as molluscicide to control *Oncomelania hupensis*, which is an intermediate host of schistosomes [1]. Apart from its persistence, the widespread use of PCP in the past has caused considerable contamination in the aquatic ecosystems. Bound residues in soil and sediment can desorb and leach, thereby contaminating surface water and ground water. For example, as much as 25.7 mg l⁻¹ has been reported in ground water at a former pesticide manufacturing plant in Taiwan and up to 27 mg l⁻¹ near a dump site in Brazil [2,3]. Stackelberg et al. [4] reported that several contaminants including PCP were present in streams and raw-water supplies in a drinking water treatment plant in the United States. Similarly,

as low as 0.1–1 µg l⁻¹ of waterborne PCP has been reported to cause adverse effects on sensitive organisms [5]. Even higher concentrations were detected in sediment and surface water in Järvelä in southern Finland, which later was linked with several cases of cancer [6,7]. PCP is acutely toxic and known to act as uncoupler of oxidative phosphorylation [8]. Also, polycyclic aromatic hydrocarbons (PAHs) are commonly found in the environment mainly because they are persistent after release from natural and anthropogenic sources. In an inventory, Wild and Jones [9] presented PAH distribution in different environmental matrices including water, sediment, soil, air, vegetation, and sewage sludge. Apart from the freshwater sediment, low molecular weight PAHs were detected in high concentrations in several other matrices. It is particularly interesting to note the relatively high concentration of phenanthrene in several compartments. In spite of the tendency of PAHs to bind strongly to solids, it is logical to expect a relatively higher concentration of phenanthrene in ground water and waste water. Hence, several methods including radiation are applied in the management of contaminated water resources, which is one of the main human sources [10]. Solar radiation of certain contaminants can result to even greater toxicity than the parent compound. Arguably, natural occurrence of this phenomenon may be rare considering that photo-enhanced toxicity depends on the simultaneous presence of oxygen, contaminants, organism, and dissolved

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light absorbing matter in adequate amounts with activating solar radiation [11,12]. Inadequacy of the various components in right amounts may explain the challenge in reproducing a previous study that reported impairments of *Daphnia magna* population in field [13,14].

Pentachlorophenol, an organochlorine pesticide and phenanthrene are common contaminants in the aquatic ecosystems. Although a few studies attempted to address their fate in soil and water [15,16], not much is known about their acute toxicity to *D. magna* after prolonged irradiation. Considering that solar-mediated effect of substances under natural conditions is a matter of scientific debate, irradiation could be harnessed more adequately in waste water treatment technology. Current waste water treatment methods are costly, and the efficacy of singular applications is limited. For this reason, microbial processes are complemented by pre-irradiation, due to the improved cost effectiveness and efficiency of the latter in oxidizing many organic compounds [17]. The resulting photoproducts of prolonged irradiation are less chlorinated [18] and therefore, may undergo faster degradation than the parent compounds [19]. Therefore, preliminary irradiation of waste water prior to microbial treatment may reduce potential effects due to residual parent organic compounds and the photoproducts. Potential toxicity of the contaminants on microbial processes would be minimal and this may improve the success of bioremediation.

The purpose of this study was to investigate: (a) the stability and photodegradation kinetics of pentachlorophenol, and phenanthrene under continuous simulated solar radiation (b) the effects of the resulting exposure water on *D. magna* fitness and mobility.

2. Materials and methods

2.1. Chemicals

Pentachlorophenol, PCP (purity 99%), and phenanthrene, PHEN (99.5%, Aldrich Chem USA) were used as purchased from the manufacturers. Stock solutions were prepared in double distilled water and test solutions were constituted by diluting the appropriate amount of stock solution with Aachener Daphnien Medium [20]. This is due to the suitability of the medium for culturing zooplanktons including *D. magna*. ADaM is based on synthetic sea salt and analytical grade chemicals added to deionized water [20]. Aqueous concentrations of PCP were in the range of 0.1–2.1 mg l⁻¹ and 0.11–0.22 mg l⁻¹ for PHEN.

2.2. Photo-irradiation chamber

Two different scenarios were chosen for conducting the tests under continuous irradiation. The irradiation chamber comprised two units, each having a set of three lamps (SOL500, Dr. Hoenle, Gräfelfing, Germany) that emit at the range of 200–1100 nm. Lamps were switched on at least 15 min prior to a continuous irradiation of the sample water, in order to ensure a constant output. Glass vials containing the aqueous solutions were capped in order to permit light penetration from the top via a thin glass with a surface diameter of 1.1 cm. Due to the glass lid, about 65% of the overall light intensity reaches the irradiated test water at an average of 27.3 W m⁻².

Constant mixing of irradiated test water was maintained at 400 rpm using a magnetic stirrer. Throughout each test, vials containing test water were maintained at a temperature of 21 ± 1 °C, in a thermostat-controlled recirculating water bath. Irradiation lamps were mounted at a distance of 1.36 m from the sample water bath. Three sample replicate vials were taken at intervals from where analytical samples were drawn. The remaining water sample was used for *D. magna* immobilization test.

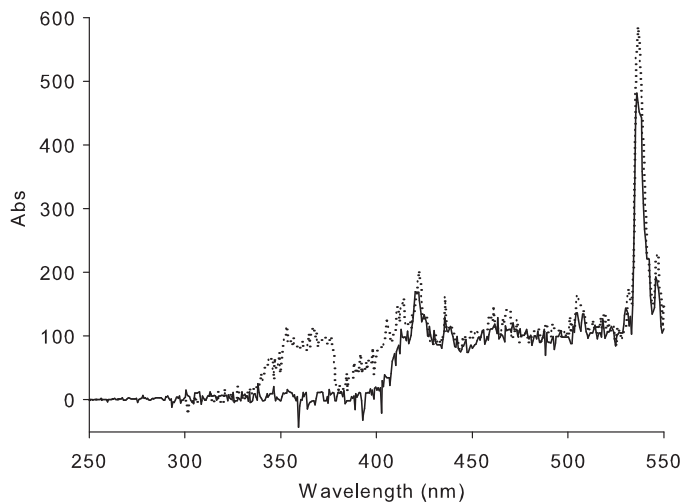


Fig. 1. Spectral measurements in the presence (dotted line) and absence (continuous line) of UV filter during irradiation of aqueous solutions of the test chemicals.

2.3. Chemical analyses and measurements

Absolute intensity of UV light was measured using a quantum photometer (Li-COR Biosciences, Bad Homburg, Germany), linked to an immersion probe (Heinz Walz GmbH, Effeltrich, Germany). The spectral composition of light sources was determined in the presence and absence of UV filter (Fig. 1) using a TRISTAN[®] spectroradiometer (m.u.t GmbH Hamburg, Germany).

On the basis of the required sensitivity, separate chromatographic methods were used to analyze the water samples. Concentrations of pentachlorophenol were analyzed by high performance liquid chromatography (HPLC Series 1100, Agilent Technology, USA), equipped with a diode array detector (DAD, Agilent Technology, USA). The mobile phase was a mixture of 70% acetonitrile and 30% water (adjusted to pH 4 with H₃PO₄). The injection volume was 100 µl. Analyses were performed using an Adsorbosphere XL C18 column (250 mm × 4.6 mm, 5 µm, Alltech, Germany). Pentachlorophenol was quantified at a detection wavelength of 210 nm based on external calibration. A reversed phase HPLC equipped with fluorescent and UV (λ = 250 nm, L-7400) detector from Merck-Hitachi (Darmstadt, Germany) was used for the analysis of phenanthrene. Eluents were degassed prior to the injection of samples on a Lichrospher 60 rp-C18 column (5 µm). A mixture of acetonitrile/water (65:35) at a flow rate of 0.5 ml/min at 25 °C was used to analyze phenanthrene.

2.4. Kinetics of photodegradation

Rate constants (*k*) at different concentrations of the test substances were determined by fitting photodegradation data to the first-order equation [21]:

$$\ln \frac{C_0}{C_t} = kt \quad (1)$$

where *C*₀ and *C*_{*t*} are the concentrations of the test substances at times zero and *t*, respectively. The rate constant *k* was determined from Eq. (1) upon analysis (MicroMath Scientific, Salt Lake City, UT, USA). We calculated the half-lives from Eq. (2) by substituting *C*_{*t*} with *C*₀/2:

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.6931}{k} \quad (2)$$

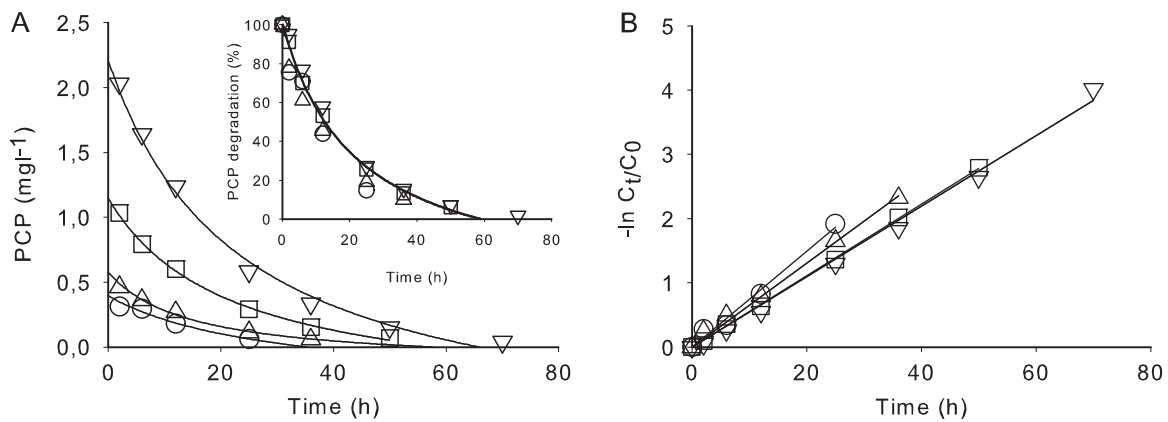


Fig. 2. Photodegradation of pentachlorophenol (PCP) in aqueous solutions at t_0 concentrations of 0.41 mg l⁻¹ [○], 0.59 mg l⁻¹ [△], 1.13 mg l⁻¹ [□], and 2.14 mg l⁻¹ [▽] under direct UV radiation (A). Inset represents percentage degradation of pentachlorophenol in time. Degradation kinetics are shown (B) for C_0 concentrations (mg l⁻¹) of 0.41 [○], 0.59 [△], 1.13 [□], 2.14 [▽].

2.5. Exposure conditions

D. magna was maintained in ADaM in the laboratory. Neonates (<7 day old) were used throughout the study, and all bioassays were performed without UV irradiation in pyrex glassware. Prior to irradiation, test water was sampled for *D. magna* bioassay. Similarly, control tests were conducted in ADaM without the test substances, and organisms were monitored for immobilization during ≤72 h duration of exposure. Throughout the period under UV radiation, aqueous solution of each substance was sampled at intervals and used for *D. magna* immobilization tests. Five neonates were exposed in each tube containing 10 ml of irradiated water that was maintained at 21 ± 1 °C and pH of 7.5 ± 0.2 in four replicates while exposures lasted for ≤48 h [22]. At the lapse of each exposure time, glass tubes were observed for movement of neonates. Immobilization of *D. magna* neonates was determined as endpoint for monitoring the efficacy of photo-radiation on the survivorship of test animals. Not more than 10% of neonates were immobilised, showed any other signs of stress or abnormal behaviour in the control test. Animals are considered to be immobilised when they are not able to swim within 15 s after a gentle agitation of test vessel, even if they can still move their antennae [22,23]. The median effective concentration (EC₅₀) values were calculated for both exposure time points using the REGTOX-EV7.0.3 software (Vindimian, 2005). This model determines the dose–response relationship with the non-linear Hill equation, and calculates effective concentration values with corresponding 95% limits by optimizing the curve fit with successive iterations.

3. Results and discussion

3.1. Kinetics of photodegradation

Pentachlorophenol decreased by 5–25% of the initial [t_0] concentrations after 2 h (Fig. 2A). Under continuous irradiation, only 71–77%, 44–58%, and 15–27% of the initial [t_0] concentrations were measurable after 6 h, 12 h and 25 h, respectively (Fig. 2A). However, residual PCP concentrations in the samples with initial [t_0] aqueous concentrations of 0.41, 0.59, 1.1, and 2.1 mg l⁻¹ were not measurable beyond 25 h, 36 h, 50 h and 70 h of continuous radiation, respectively (Fig. 2A). The detection limit for PCP was 50 µg l⁻¹. The disappearance of PCP from solution suggests that under extensive direct irradiation, contaminating pentachlorophenol can be reduced considerably from waste water.

Rate constants (k) for the degradation of PCP at concentrations of 0.41, 0.59, 1.1, and 2.1 mg l⁻¹ were 7.1 × 10⁻² h⁻¹, 7.2 × 10⁻² h⁻¹,

Table 1

Kinetic parameters for the photodegradation of different t_0 concentrations of aqueous pentachlorophenol [PCP] and phenanthrene [PHEN] under simulated solar radiation (27.3 W m⁻²).

	k (1 × 10 ⁻² h ⁻¹)	$t_{1/2}$ (h)	R^2
PCP (mg l ⁻¹)			
0.41	7.12	9.74	0.9965
0.59	7.15	9.69	0.9996
1.13	5.46	12.7	0.9972
2.14	4.92	14.1	0.9843
PHEN (mg l ⁻¹)			
0.12	0.42	166	0.9712
0.22	0.29	241	0.9661

5.5 × 10⁻² h⁻¹, and 4.9 × 10⁻² h⁻¹, respectively (Table 1), showing a slight decrease with increasing initial PCP concentrations. This can be due to the fact that at higher PCP concentration, complete absorption of the incident photon flux can occur over a shorter path length. However, this trend is not much pronounced, which conforms to the reasonable fitting of the data by pseudo-first-order kinetics even for the solutions with the highest applied initial PCP concentrations (Fig. 2B). The k values for aqueous solutions of phenanthrene at 0.12 and 0.22 mg l⁻¹ were 0.42 × 10⁻² h⁻¹, and 0.29 × 10⁻² h⁻¹, respectively (Table 1); and kinetics of degradation are shown in Fig. 3. These constants suggest that the rate of photodegradation again varied slightly with substance concentrations, but was considerably higher for PCP than PHEN (Table 1).

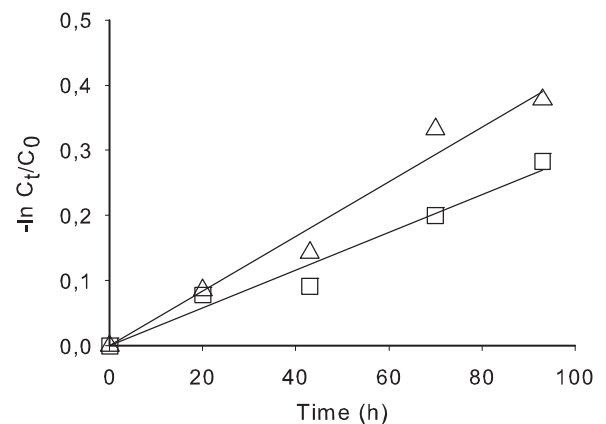


Fig. 3. Photodegradation kinetics of phenanthrene under direct UV irradiation at t_0 concentrations of 0.12 mg l⁻¹ [△] and 0.22 mg l⁻¹ [□].

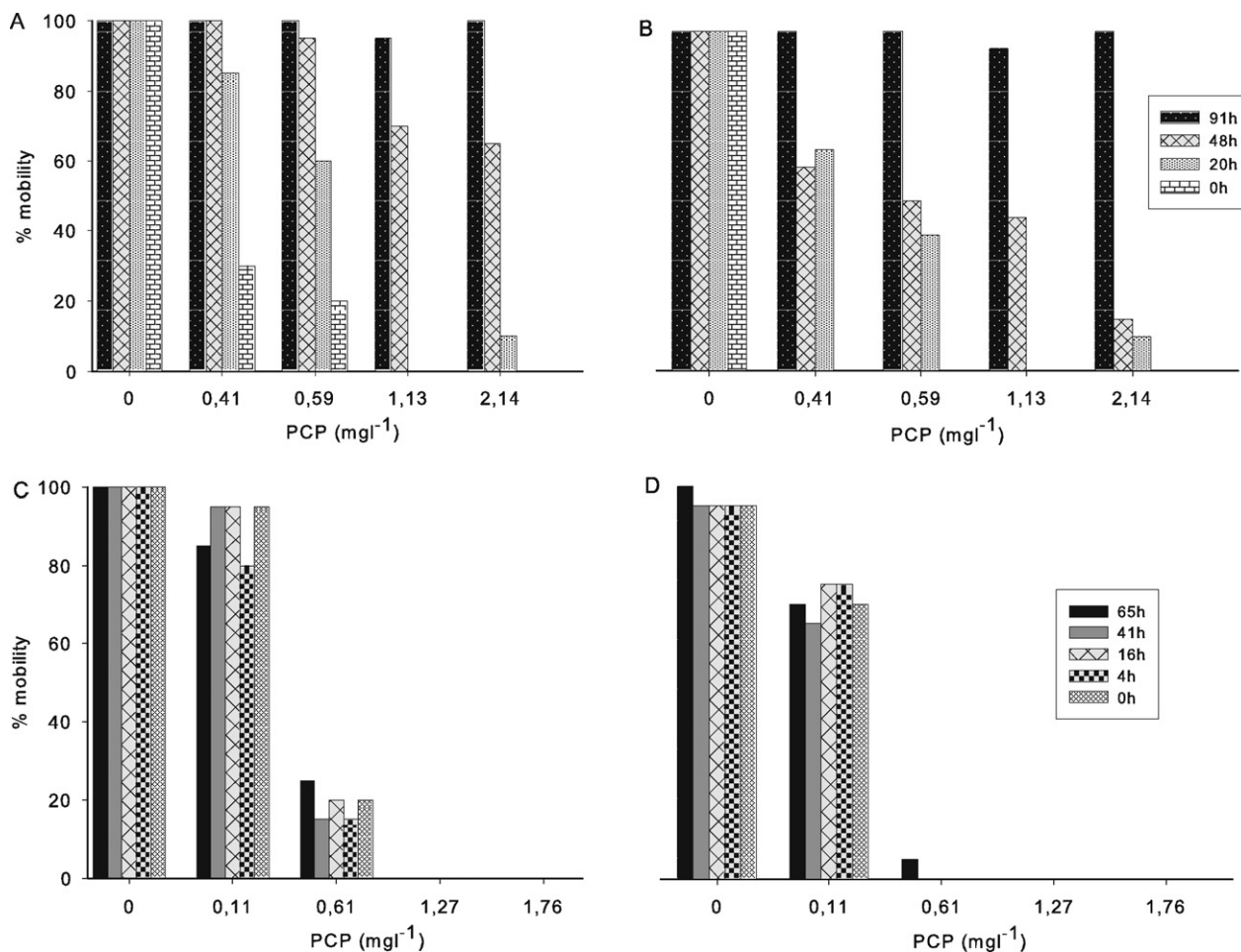


Fig. 4. Mobility of *D. magna* neonates after 24 h (A) and 48 h (B) exposures in aqueous solutions of pentachlorophenol that were pre-irradiated at 0, 20, 48 and 91 h. Mobility of the animals in test solutions that were pre-irradiated in the presence of UV filter for 0, 4, 16, 41 and 65 h are shown after 24 h (C) and 48 h (D) exposures.

3.2. Photostability of PCP and effect on *D. magna* mobility

Even though the intensity of simulated solar radiation exceeds a realistic environmental level, it could be harnessed adequately in waste water treatments for the degradation of contaminating organic substances. In view of its geographical relevance, the extent of contaminant removal from surface water and solid matrices would be sizeable on a long term under natural conditions. We did not observe any measurable decrease in PCP concentrations, following direct irradiation in the presence of UV filter. These observations suggest that seasonal changes, sunshine duration and vegetation shields may affect the stability of water borne PCP in nature. Considering that the photoproducts may constitute new threats, we assessed the potential toxicity of irradiated water to *D. magna* neonates. For the various concentrations that were tested, the mobility of *D. magna* neonates in irradiated aqueous solutions of PCP increased with irradiation time until 91 h. Mobility of the neonates was used as an indicator for fitness, and showed that the animals moved more noticeably within 24 h (Fig. 4A) than after 48 h (Fig. 4B) in irradiated aqueous solutions of PCP. Irradiation of exposure water influenced the test concentrations and this correlates positively with neonate mobility, but differs considerably between tests in the presence and absence of the UV filter. Less than 16% of neonates were mobile after 48 h exposure in the pre-irradiated water at the highest initial PCP concentration. Due to increased duration of irradiation until 91 h, neonate survivorship mostly reached 100% after 48 h exposure (Fig. 4A and B). Evidently, the influence of direct UV radiation on the stability of PCP and

Table 2

D. magna toxicity index [EC_{50} s] after exposures to pre-irradiated solutions of pentachlorophenol ($mg\ l^{-1}$) in direct UV light compared to corresponding values under UV filter.

Time (h)	EC_{50} (24 h)	EC_{50} (48 h)
Direct UV irradiation		
0	0.321 (0.297–0.344)	0.159 (0.159–0.159)
20	0.635 (0.597–0.713)	0.515 (0.468–0.567)
48	2.844 (2.104–3.768)	0.641 (0.503–0.841)
91	nd	nd
Irradiation under UV filter		
0	0.538 (0.532–0.543)	0.146 (0.146–0.146)
4	0.234 (0.223–0.243)	0.155 (0.154–0.155)
16	0.537 (0.532–0.543)	0.155 (0.154–0.155)
41	0.519 (0.510–0.528)	0.136 (0.136–0.136)
65	0.520 (0.234–0.525)	0.163 (0.162–0.164)

nd: not determined.

survivorship was apparent in all test concentrations and *D. magna* neonate exposure time. On the other hand, hardly any movement of neonates was noticed in test water that was irradiated in the presence of UV filter, for the two highest concentrations of PCP (Fig. 4C and D). We noted that the predicted effect concentration (EC_{50}) values varied with the duration of *Daphnia* exposures in pre-irradiated solution of aqueous PCP (Table 2). Similarly, EC_{50} s varied with the duration of pre-irradiation, and increased until its determination was no longer possible after 91 h. While this observation further confirms the disappearance of parent PCP due to extensive irradiation, it also supports our views that the resulting photo-

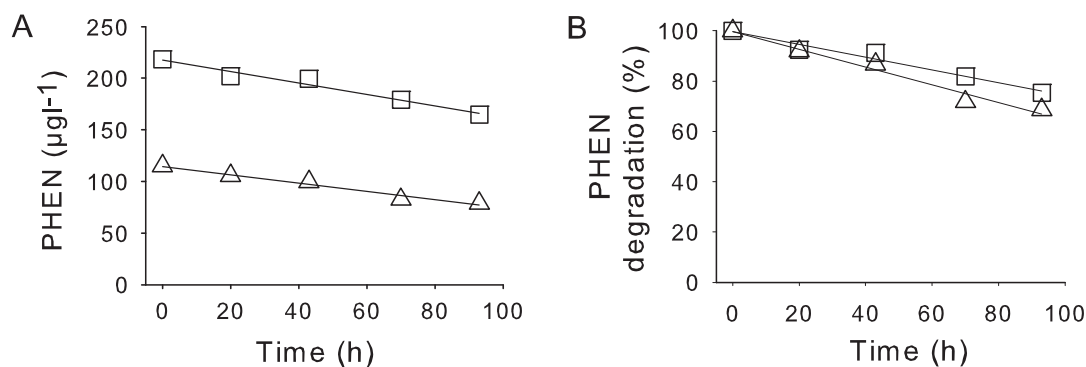


Fig. 5. Photodegradation of phenanthrene (PHEN) in aqueous solutions at t_0 concentrations of 0.12 mg l^{-1} [△], and 0.22 mg l^{-1} [□] under direct UV irradiation (A) and percentage degradation in time (B).

products did not cause any apparent effects on *Daphnia* mobility. Predicted EC_{50} s from this study after 24 h *Daphnia* exposure to non-irradiated water, are in agreement with literature values [24]. Even though the corresponding EC_{50} s after 48 h *Daphnia* exposures were expectedly lower than after 24 h exposure, these values also increased with increasing pre-irradiation time (Table 2). However, EC_{50} values were consistent for exposures under UV filter, and this suggests that UV was responsible for the disappearance of parent PCP. Consistency in EC_{50} values for measurements under UV shield correlates with the measured concentrations, and further confirms the presence of PCP in animal exposure water until 65 h.

3.3. Photostability of PHEN and effects on *D. magna* mobility

As much as 69% and 75% of phenanthrene were measurable after 93 h direct irradiation of the initial aqueous concentrations of 0.12 mg l^{-1} and 0.22 mg l^{-1} , respectively (Fig. 5A and B). In spite of the extensive direct irradiation, we did not observe any substantial decrease in phenanthrene concentration. Identification of the photoproducts was beyond the scope of this study; however, the maximum concentration of aqueous phenanthrene was not sufficient to immobilize *D. magna* neonates. Similarly, we did not observe any toxicity due to exposure of neonates to irradiated aqueous solution of phenanthrene at 0.22 mg l^{-1} . Smith et al. [25] reported in a recent study that PHEN was able to immobilize *D. magna* neonates at EC_{50} value of 0.48 mg l^{-1} . While the maximum tested concentration in this study might have been too low to immobilize the animals, we speculate that animal mobility may not have improved with increasing irradiation time given the stability of PHEN. However, carrier solvents or buffered polymer materials in passive dosing [25] could be applied in future studies in order to maintain stable concentrations while determining the influence of irradiated aqueous solutions of PHEN on *Daphnia* mobility.

3.4. Environmental implications

Geographical location and seasonal changes may influence the degradation of contaminants under natural sunlight. Considering the ease whereby certain substances could be degraded in relation to the stability of others under extensive solar radiation, it is a useful property that could be harnessed in making decisions for the remediation of organic contaminants. Although the intensity of simulated solar radiation exceeds a realistic environmental level [26], it could be harnessed adequately in waste water treatment for the degradation of contaminating organic substances. Additionally, UV light penetrates to significant depths in aquatic ecosystems [26]. It is possible to subject thin layers of dredged organics and sediment matter to natural sunlight to potentially break down

contaminating organic chemicals to non-toxic forms. Apart from its cost effectiveness, it is possible to harness the vast amount of annual tropical solar radiation for in situ remediation of contaminated water. However, photodegradation of sorbed contaminants in soil and sediment matrices may be slower than for waterborne contaminants. This might be due to the filter effects from soil and sediment organic matter.

4. Conclusions

This study highlights the relevance of natural remediation of waterborne organic contaminants by simulated solar radiation. Within the tested levels, photodegradation rates of substances were concentration dependent, showing a slight decrease with increasing initial contaminant concentration. Results suggest that UV irradiation was responsible for the degradation, considering the stability of PCP in direct exposures under UV filter. As an indication of greater persistence in ambient conditions, phenanthrene was more photostable under direct simulated solar radiation. The photodegradation rate constants (k) for PCP at aqueous concentrations of $0.41\text{--}2.1 \text{ mg l}^{-1}$ were in the range of $7.1 \times 10^{-2}\text{--}4.9 \times 10^{-2} \text{ h}^{-1}$. The k values for aqueous solutions of phenanthrene at 0.12 and 0.22 mg l^{-1} were $0.42 \times 10^{-2} \text{ h}^{-1}$ and $0.29 \times 10^{-2} \text{ h}^{-1}$, respectively. The results demonstrate the utility of simulated sunlight for the degradation of waterborne PCP, but also offer a possibility for toxicity monitoring using *D. magna* neonates. The duration of the photo irradiation treatment and its consequence on the disappearance of PCP from solution, correlates positively with the fitness and mobility of *D. magna* neonates. However, photoproduct-mediated toxicity on the mobility of the test animals was indiscernible. Only a slight decrease in aqueous concentrations of phenanthrene was observed following UV irradiation. We did not observe any visible adverse effect of phenanthrene on mobility of the animals.

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