

## Changes in the toxicity of procymidone and its metabolite during the photohydrolysis process and the effect of the presence of microplastics

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**Abstract**—Procymidone (PCM), an agricultural fungicide, is attracting attention because it has been detected in all ecosystems, including aquatic environments. This study explored changes in the behavior and toxicity of PCM in water under the influence of photolysis and microplastics (MPs) coexistence. Hydrolysis of PCM was evaluated and UV-A and UV-C lamps were used as light sources for the photodegradation experiments. The Microtox® assay was used to evaluate changes in toxicity during the photodegradation and after sorption on MPs of low-density polyethylene (LDPE) and polyvinyl chloride (PVC) films. The appearance of 3,5-dichloroaniline (DCA), a major metabolite of PCM that is more toxic than its parent compound in water, was confirmed. Both PCM and DCA showed sufficient molar extinction coefficients to be photolyzed under UV-C irradiation ( $\epsilon_{\text{PCM}}=10,300 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{\text{DCA}}=2,400 \text{ M}^{-1} \text{ cm}^{-1}$ ); however, the presence of natural organic matter negatively affected their photodegradation. PVC showed a better sorption potential for PCM and DCA than for LDPE. The higher sorption by PVC significantly reduced the toxic effect of DCA from an average value of 79% to 60% and increased the  $\text{EC}_{50}$  value from 30.4% to 47.6%. These results offer insights into controlling toxic micropollutants, including fungicides, in aquatic environments and water treatment processes.

Keywords: Procymidone, 3,5-Dichloroaniline, Photolysis, Microtox®, Microplastic Adsorption

### INTRODUCTION

Procymidone (PCM), a dicarboximide fungicide, is widely used in modern agriculture to prevent the growth of fungi, which adversely affect fruits, vegetables, and ornamental cultivation [1-3]. Thus, PCM is frequently detected and exists in the agricultural soil for a considerable time and then spreads across the ecosystems through the food chain due to its high stability to temperature, light, and moisture [4,5]. PCM residues in the plant tissues and soil pose a serious threat to public health and ecosystems because they interfere with the endocrine system, resulting in anti-androgen toxicity and developmental/reproductive dysfunction of exposed organisms [3]. The residual PCM in the soil is transported from agricultural fields to surface water through runoff [1,4], which contaminates the aquatic environment and induces metabolic disorders in aquatic organisms (e.g., impacts on the vitellogenin transcriptional levels in the liver of mullet fish) [6]. PCM has been detected at a concentration of 3,904 ng/L, which is the highest among the 82 pesticides, in sampled water from the Jiulong River, Fujian, China [6]. Furthermore, PCM concentration in the river water near the farming area of South Africa was up to 9.06 µg/L after rainfall at the end of the spraying season [7]. Additionally, 3,5-dichloroaniline (DCA), one of the major metabolites formed during the degradation of PCM

in nature, persists in the environment [2,8]. The US EPA has highlighted the risk of cancer from DCA formed during the breakdown of its parent compounds [9], and has identified it as the most potential nephrotoxic compound among the mono- and dichloroanilines [10]. Therefore, a better understanding of the behavior of PCM and DCA in water is required to predict their environmental fate and toxicity.

Photochemical degradation influences the fate of many pesticides in water through direct and indirect mechanisms [11,12]. In general, direct photolysis of pesticides by sunlight is limited because the sunlight reaching the surface of the Earth (mainly UV-A) consists of only very small amounts of short-wavelength UV light. However, UV photolysis is an established method that is regarded as a promising technology in wide use for the treatment of drinking water and wastewater [13,14]. Because high-energy photons produce an excited electronic state, direct photolysis can be used to effectively degrade recalcitrant organic compounds [15]. Absorption of photons by the target compounds during direct photolysis causes bond cleavage or rearrangement to form new products, which, in the case of PCM leads to dechlorination and isomerization [16,17]. In contrast, during indirect photolysis, a photosensitizer absorbs light and affects the degradation of the target compound. Humic and fulvic acids isolated from soil have been reported to act as photosensitizers and enhance the photolysis of PCM; however, more studies are needed for understanding their impact [17].

The multiple applications of plastic for human needs have eased human life and increased its usage; however, the associated envi-

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ronmental problems, including those related to microplastics (MPs), are a concern. MPs are defined as small plastic particles less than 5.0 mm in size, and many studies have focused on their effects in the marine environment [18,19]. Because of their small particle size, large surface area, and strong hydrophobicity, MPs serve as ideal carriers for hydrophobic substances, such as pesticides, polychlorinated biphenyls, polycyclic aromatic hydrocarbons, heavy metals, and other similar contaminants. This makes it easier for the pollutants to persist and be transmitted in the ecosystems, and thereby lead to serious complex pollution through the action of water flow, movement, and diffusion [20,21]. Thus, MPs in the aquatic environments need to be more comprehensively studied, because they are in vicinity of our living environment and can cause more direct harm to humans than marine MPs. Wang et al. [20] reported that carbendazim, dipterex, diflubenzuron, malathion, and difenoconazole, which are widely used pesticides in farmland, can adsorb to polyethylene-based MPs mainly through hydrophobic interactions. Li et al. [21] confirmed that high pH and low NaCl salinity are conducive to the adsorption of the pesticides (imidacloprid, buprofezin, and difenoconazole) on polyethylene-based MPs in aqueous solution. Fang et al. [22] showed that the adsorption of triazole fungicides onto polystyrene-based MPs is mainly driven by hydrophobic and electrostatic interactions. Although adsorption studies of several pesticides and fungicides have been conducted, to the best of our knowledge, the adsorption of PCM by MPs has never been reported.

Therefore, in this study, we evaluated the behavior of PCM in aqueous solutions, the changes during hydrolysis and photolysis reactions, and the effects of the presence of organic matter on photolysis. In addition, changes in the toxicity of the PCM solution due to photolysis and the adsorption of PCM and its metabolites on MPs were examined. The change in the toxicity before and after adsorption of PCM and DCA on the different microplastic types was also compared.

## MATERIALS AND METHODS

### 1. Chemicals

PCM ( $C_{13}H_{11}Cl_2NO_2$ ,  $\geq 98.0\%$ ), DCA ( $C_6H_5Cl_2N$ ), and humic acid (purity, grade) were purchased from Sigma-Aldrich Co. Ltd. (USA). Sodium phosphate monobasic anhydrous ( $NaH_2PO_4$ ,  $\geq 98\%$ ) and acetonitrile (ACN;  $CH_3CN$ ,  $\geq 99.9\%$ ) for high-performance liquid chromatography (HPLC) were purchased from Samchun Pure Chemical Co., Ltd. (South Korea). Sodium phosphate dibasic anhydrous ( $Na_2HPO_4$ ,  $\geq 99.0\%$ ) was purchased from Daejung Chemicals and Metals (South Korea). Deionized water (resistivity  $18.2\text{ M}\Omega/\text{cm}$ ), used for the preparation of all stock solutions, was obtained from a Direct-Q 3 UV system (Millipore, USA). All the chemicals were used as received.

### 2. Hydrolysis and Photodegradation Tests

The hydrolysis of PCM was conducted in the phosphate buffer solution at  $25^\circ\text{C}$ . In brief,  $5\text{ }\mu\text{mol}$  of PCM powder was added to the 1 L of phosphate buffer solution. After completely dissolving PCM powder for five days, the concentrations of PCM and DCA were determined at predetermined times. Photodegradation experiments were conducted in a black acrylic box photoreactor equipped

with a low-pressure mercury lamp (TUV G4T5 4 W, Philips, USA) at 254 nm wavelength. A quartz beaker containing 50 mL of the test solution was placed in the photoreactor, and the distance between the solution surface and UV-C lamp was maintained at 6 cm. The test solutions were prepared by spiking the PCM or DCA stock solutions ( $[\text{PCM}]_0 = 10\text{ }\mu\text{M}$ ,  $[\text{DCA}]_0 = 100\text{ }\mu\text{M}$ ) in deionized water to adjust the initial test concentrations to 2, 5, and  $8\text{ }\mu\text{M}$ . Light intensity was measured using ferrioxalate actinometry [23]. The photon flux was  $1.13 \times 10^9\text{ Einstein}/\text{cm}^2/\text{s}$ , which corresponds to  $0.53\text{ mW}/\text{cm}^2$ . The optical path length of the reactor was 2.76 cm [24]. At a predetermined frequency, 1 mL of the test solution was sampled and analyzed using HPLC. The test solution pH was adjusted to  $7.0 \pm 0.2$  with 10 mM phosphate buffer. To study the effect of humic acid on the degradation of PCM and DCA during UV-C photolysis, humic acid was added to obtain a concentration of 1, 5, and  $10\text{ mg}/\text{L}$  in each test solution containing PCM or DCA. All the experiments were conducted in duplicate, the average value is shown in the figure, and the standard deviation of the mean is represented using an error bar.

### 3. Microplastic Adsorption Experiments

The effect of the presence of microplastics in water on the toxic effects of PCM was studied by running a sorption test followed by a toxicity test. For the sorption experiment, test solutions having PCM  $1.73 \pm 0.12\text{ mg}/\text{L}$  and DCA  $69.1 \pm 4.6\text{ mg}/\text{L}$  were prepared. Microplastics were prepared from low-density polyethylene (LDPE) and polyvinyl chloride (PVC) films by cutting them into pieces ( $<0.5\text{ mm} \times <0.5\text{ mm}$ ). The microplastic pieces (0.5 g) and either the PCM or DCA solution (50 mL) were placed in a 50 mL glass test tube for the sorption test. Tubes without microplastics were used as controls. All the test solutions were prepared in triplicate. The tubes were shaken at 105 rpm for 72 h at ambient temperature. After 72 h, the samples were filtered through a  $0.45\text{ }\mu\text{m}$  membrane filter (MCE04547A, HYUNDAI Micro, Korea), and the residual concentration of PCM or DCA was analyzed using HPLC.

### 4. Microtox® Assay

The changes in the toxicity of the PCM and DCA solutions before and after sorption onto the microplastics were determined using the Microtox® assay. Bioluminescent bacteria, *Allivibrio fischeri*, were exposed to the PCM or DCA samples for 5 min, and then the reduction in the bioluminescence of the serially diluted samples was measured using a Microtox® LX analyzer following the 81.9% basic test method with nine dilutions (Modern Water, USA). Four replicates were used for each assay, and samples containing only water and microplastics without PCM or DCA were used as controls.

### 5. Analytical Methods

The PCM and DCA concentrations were determined using a YL 9100 HPLC system (Youngin Chromass, Korea) with a YL 9120 UV/Vis detector and YL 9150 autosampler, a YL C18-4D column ( $4.6\text{ mm} \times 150\text{ mm}$ ,  $5\text{ }\mu\text{m}$ ), and ACN and deionized water (70 : 30, v/v) as the mobile phase. The mobile phase was isocratically eluted at a flow rate of  $1.0\text{ mL}/\text{min}$ . The column temperature was  $35^\circ\text{C}$ , and PCM and DCA were detected at 220 nm. The detection limit of PCM was  $0.02\text{ }\mu\text{M}$  ( $5.68\text{ }\mu\text{g}/\text{L}$ ). The molar extinction coefficient ( $\varepsilon$ ) of PCM and DCA was obtained by Beer's law ( $A = \varepsilon bc$ ). Here, A is the absorbance of the sample,  $\varepsilon$  is the molar extinction coefficient of the compound, b is the cell path length, and c is the con-

centration of the compound. Therefore, by plotting the molar concentration of compound versus absorbance, the slope of the graph corresponds to the  $\varepsilon$ .

## RESULTS AND DISCUSSION

### 1. Photodegradation of PCM in Water

#### 1-1. Identification of PCM Hydrolysis Metabolite

The change in the concentration of PCM and its major metabolite DCA, [2], during the hydrolysis of PCM at room temperature, is shown in Fig. 1. During the 28 d of hydrolysis, the PCM concentration decreased from 5.00 to  $3.00 \pm 0.17 \mu\text{M}$ , while the DCA concentration increased to  $0.49 \pm 0.03 \mu\text{M}$ . PCM hydrolysis in aqueous media may occur via the attack of hydroxide ions [25]. The results indicate that PCM can be degraded by hydrolysis and DCA can be produced in the natural aquatic environment.

#### 1-2. Effect of Initial PCM Concentrations on Photodegradation

In addition to the natural hydrolysis reaction, PCM can be degraded by photolysis. To assess the effect of UV irradiation on the degradation of PCM and DCA, each sample was irradiated with UV-A or UV-C. PCM was not affected when irradiated with UV-A (<0.1% degradation at 30 min); however, it decreased signifi-

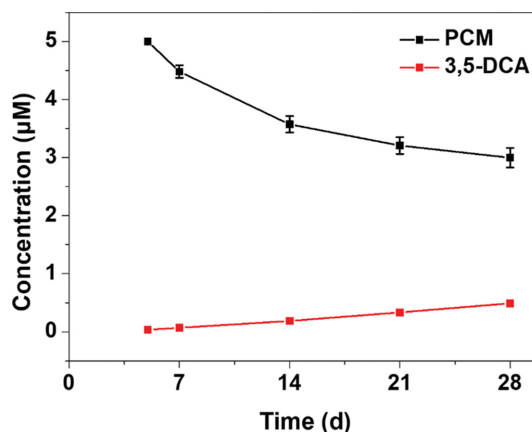


Fig. 1. Change in the concentration of procymidone (PCM) and dichloroaniline (DCA) during procymidone hydrolysis.

cantly with UV-C irradiation. The rate of photodegradation of PCM decreased slightly with increase in initial concentration from 2 to  $8 \mu\text{M}$ , but the difference was insignificant (Fig. 2(a)). The slight decrease of photodegradation with initial concentration increase might be attributed to the enhanced internal quenching effect [26].

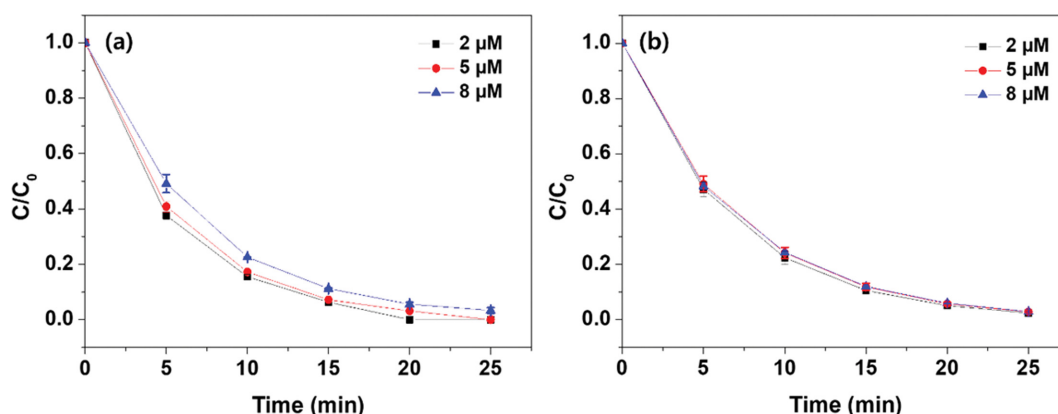


Fig. 2. Photolysis of procymidone (PCM) (a) and dichloroaniline (DCA) (b) under UV-C irradiation ( $0.53 \text{ mW}/\text{cm}^2$ ) at different initial concentrations (2, 5, and  $8 \mu\text{M}$ ). All the experiments were performed in duplicate. The error bars represent the standard deviations from the mean of duplicate measurements.

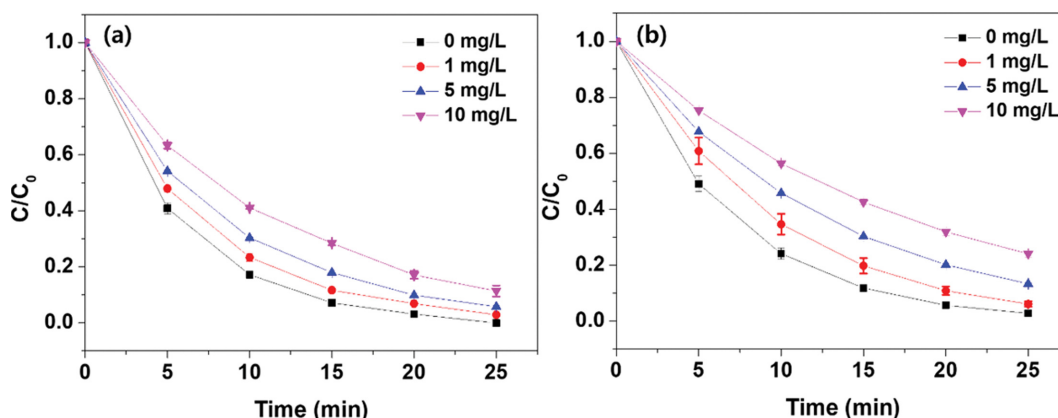


Fig. 3. Degradation of procymidone (PCM) and dichloroaniline (DCA) in the presence of humic acid (0, 1, 5, and  $10 \text{ mg}/\text{L}$ ).

With UV-C irradiation, the removal percentage of PCM at initial concentrations of 2, 5, and 8  $\mu\text{M}$  at 25 min was  $100.00 \pm 0.00\%$ ,  $100.00 \pm 0.00\%$ , and  $96.68 \pm 1.00\%$ , respectively. Similar trends were observed for DCA photolysis (Fig. 2(b)). The removal percentage of DCA at 25 min was  $97.65 \pm 0.75\%$ ,  $97.22 \pm 0.27\%$ ,  $97.15 \pm 4.13\%$  for initial concentrations of 2, 5, and 8  $\mu\text{M}$ , respectively. The efficient degradation of PCM and DCA by direct photolysis can be explained by their light absorptions capacity [24]. The estimated molar extinction coefficients of PCM and DCA were  $\epsilon_{\text{PCM}} = 10,300 \text{ M}^{-1} \text{ cm}^{-1}$  and  $\epsilon_{\text{DCA}} = 2,400 \text{ M}^{-1} \text{ cm}^{-1}$ , respectively, which indicates that both compounds have sufficient absorbance at 254 nm [27].

### 1-3. Effect of Organic Matter on PCM Photodegradation

The photolysis of contaminants such as PCM and its metabolites in the aquatic ecosystems can be affected by the presence of

natural organic matter. The degradation of both PCM and DCA was inhibited in the presence of humic acid (Fig. 3). With increasing humic acid concentration, the degradation of PCM and DCA decreased. Specifically, the presence of 10 mg/L humic acid decreased the degradation of PCM and DCA by  $11.38 \pm 1.98\%$  and  $21.25 \pm 0.85\%$ , respectively. The inhibition of PCM and DCA photolysis in the presence of humic acid can be explained by the light-screening effect of humic acid [28]. As seen in Fig. S1,  $\text{UV}_{254}$  absorbance increased with increase in the humic acid concentration ( $\epsilon_{\text{humic acid}} = 0.0184 \text{ mg/L/cm}$ ), so the photons absorbed by the PCM and DCA proportionately decreased, thereby inhibiting their photolysis.

## 2. Toxic Effects of PCM and its Metabolite in Water

### 2-1. Effect of PCM Photolysis on Its Toxicity

Fig. 4 shows the changes in the toxic effects of the PCM during the 25 min photolysis. The toxic effects of PCM on *A. fischeri* increased after photolysis (Fig. 4(a)-(b)). Before photolysis (0 min), toxic effects of the PCM solution were negligible ( $2 \pm 9\%$ ); however, after 5 and 25 min of photolysis, the toxic effects increased to  $26 \pm 6\%$  and  $20 \pm 8\%$ , respectively (Fig. 4). The maximum toxic effects

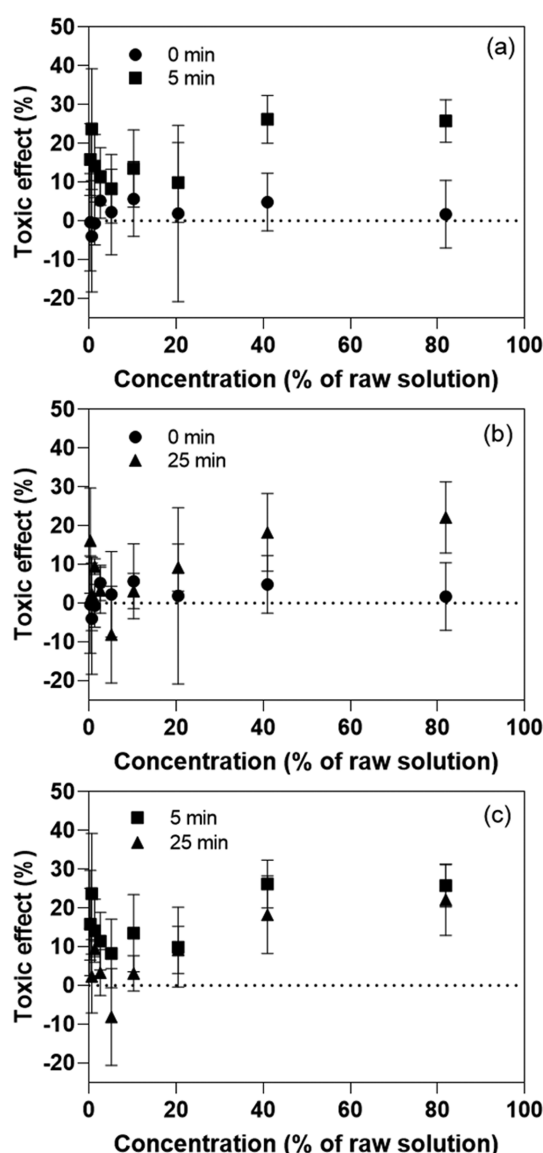


Fig. 4. Toxic effect of the procymidone solution on *Allivibrio fischeri* during the 25 min photolysis test: (a) comparison between the toxic effects at 0 and 5 min reaction time, (b) comparison between the toxic effects at 0 and 25 min reaction time, and (c) comparison between the toxic effects at 5 and 25 min reaction.

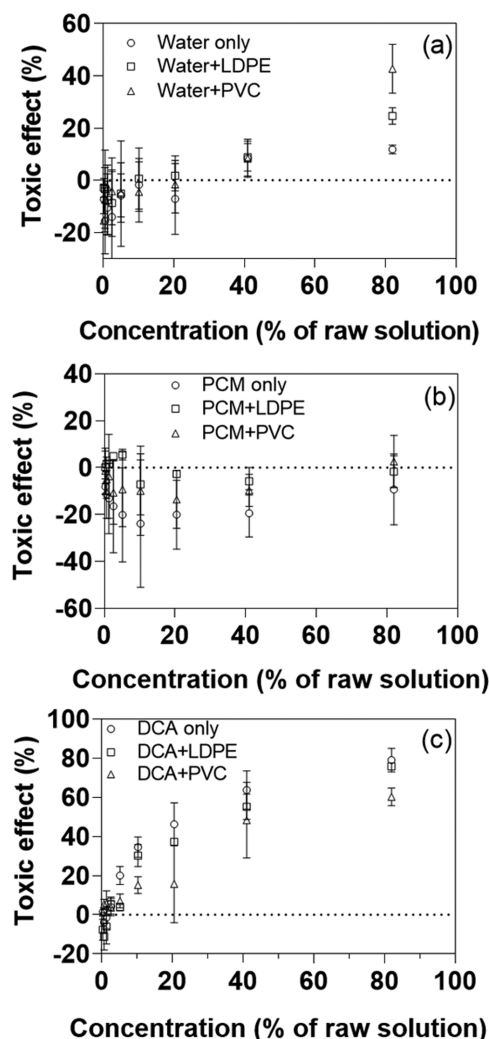


Fig. 5. Toxic effects of (a) water, (b) procymidone (PCM), and (c) 3,5-dichloroaniline (DCA) in the presence of microplastics (PE: polyethylene, PVC: polyvinyl chloride).

at 0 min were statistically different from those after 5 min and 25 min of photolysis ( $p < 0.05$ ), while the maximum toxic effects after 5 min and 25 min of photolysis were statistically similar ( $p > 0.05$ ) (Fig. 4(a)). The increase in toxic effects after photolysis can be attributed to the formation of more toxic photoreaction products such as DCA [29]. Previous study reported that the toxic effect of DCA ( $LC_{50}$  of 1.64 mg/L at 96 h), a metabolite of PCM, on zebra fish was greater than that of PCM ( $LC_{50}$  of 2.00 mg/L at 96 h) [30]. Thus, there is a need to appropriately manage both PCM and DCA when they are present in the natural aquatic environments.

## 2-2. Effect of Microplastics on Toxicity of PCM and its Metabolite

Fig. 5 shows toxic effects of PCM and DCA in the presence and absence of microplastics (LDPE and PVC). The toxic effects of the control (water samples) were negligible, except for the samples with the highest concentration (samples at 81.9% of the initial solution) (Fig. 5(a)). At 81.9% concentration, the toxic effects in the presence of LDPE and PVC were  $25 \pm 3\%$  and  $43 \pm 9\%$ , respectively (Fig. 5(a)). The increased toxic effects in the presence of LDPE and PVC can be explained by the release of chemicals from the microplastics [31,32]. This is supported by the increase in the total organic carbon (TOC) concentration of the water+LDPE and water+PVC samples by 2.1 and 1.5 times, respectively, compared to the TOC of the water control sample. However, the estimated half-maximal effective concentrations ( $EC_{50}$ ) were  $>100\%$ , suggesting no toxic effects (Table 1).

In the presence of LDPE and PVC, the PCM removal rate was  $19.5 \pm 9.1\%$  and  $76.8 \pm 3.7\%$ , respectively, after the 72 h sorption period. Because the toxic effects of the PCM solution were negligible at all the test concentrations (Fig. 4), it is expected that the toxic effects of the PCM solution after sorption on the microplastics are negligible. The toxicity of PCM solution before and after sorption was negligible, regardless of the reduction in PCM concentration (Fig. 5(b)). The estimated  $EC_{50}$  values were  $>100\%$  for all the PCM samples (Table 1). Overall, the results showed that the reduction in PCM concentration after sorption on LDPE and PVC did not affect the toxicity.

In the presence of LDPE and PVC, the DCA removal rate was  $8.4 \pm 1.1\%$  and  $71.2 \pm 1.2\%$ , respectively, after 72 h of sorption. Similar to PCM, PVC showed a greater sorption potential for DCA than for LDPE. Because the DCA concentration used in this study demonstrated toxic effects, the decrease in DCA concentration

after sorption resulted in a reduction in its toxicity (Fig. 5(c)). As the reduction by LDPE was only 8.4%, the toxic effects of DCA after sorption on LDPE were statistically similar to those of DCA before sorption ( $p > 0.05$ ) (Fig. 5(c)). However, the higher sorption by PVC resulted in a notable change in the toxic effect ( $p < 0.05$ ). The toxic effect of the highest concentration of DCA tested was reduced from 79% to 60% on an average after sorption (Fig. 5(c)). This is also reflected in an increase in the  $EC_{50}$  values from 30.4% to 47.6% (Table 1). These results suggest that the toxic effect of DCA in water is affected by the presence of microplastics. Similarly, a previous study showed that the toxic effect of the ozonation byproduct of triclosan was higher than that of the parent compound, and the toxic effect was reduced in the presence of microplastics [33]. This suggests that the presence of microplastics in the natural environment might have a positive effect on the removal of trace organic compounds, as well as on the toxic effect of the more toxic byproducts formed during natural degradation processes such as photolysis. However, the toxic effect associated with ingestion of microplastics for larger organisms needs to be further studied in subsequent studies.

## CONCLUSIONS

This study demonstrates the change in the toxicity of water with respect to the photolytic degradation of PCM and its metabolite DCA, and the reduction of toxicity in the presence of microplastics. DCA was formed during the hydrolysis of PCM, and both PCM and DCA were found to have sufficient molar extinction coefficients to be photolyzed under UV-C irradiation. The presence of natural organic matter in water adversely affects the photodegradation of PCM and its metabolites by absorbing the photons. The toxicity of the aqueous solution during the photolysis of PCM increased initially during the reaction because the toxicity of the photolysis metabolites, including DCA, was greater than that of the parent compound. The removal of PCM from aquatic solution by PVC was better than that by LDPE, but the change in the toxicity of the solution before and after PCM adsorption on microplastics was negligible in both the cases. The sorption of DCA by microplastics showed a similar pattern to that of PCM, but the toxicity of the solution was reduced after the adsorption of DCA by PVC. These results suggest that the change in the toxicity during the photodegradation of micropollutants in water, and the presence of microplastics in the aquatic environment may have a positive role in reducing the toxicity of the metabolites.

## ACKNOWLEDGEMENTS

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## SUPPORTING INFORMATION

Additional information as noted in the text. This information is

**Table 1. Effect of the presence of microplastics on the  $EC_{50}$  values determined for water, DCA, and PCM**

Sample	$EC_{50}$ -5 min (%)
Water only	$>100$
DCA only	30.4
PCM only	Cannot determine
Water+polyethylene (PE)	$>100$
Water+polyvinyl chloride (PVC)	$>100$
DCA+PE	34.7
DCA+PVC	47.6
PCM+PE	$>100$
PCM+PVC	$>100$

available via the Internet at <http://www.springer.com/chemistry/journal/11814>.

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## Supporting Information

### Changes in the toxicity of procymidone and its metabolite during the photohydrolysis process and the effect of the presence of microplastics

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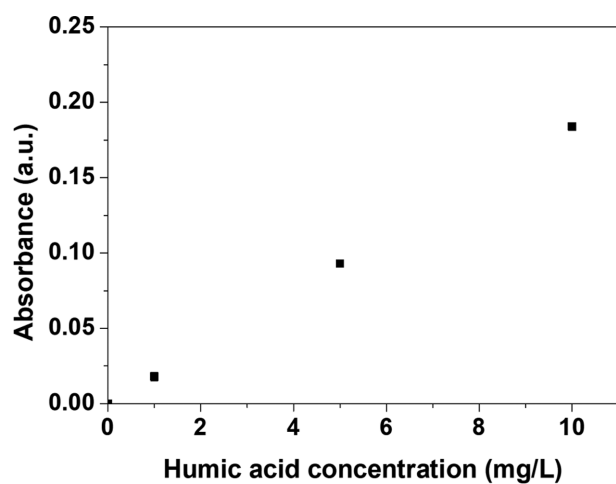


Fig. S1. UV 254 absorbance at different humic acid concentrations.