Doctoral Dissertation

A study on the environmental fate of organic pollutants adsorbed onto plastics

(プラスチックに吸着した有機汚染物質の環境運命に関する研究)

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Abstract

Plastic debris has become a serious issue because of its ubiquitous distribution and adverse effects on organisms via pollution adsorption and ingestion. In the aquatic environment, floating plastic debris is exposed to sunlight, and the adsorbed pollutants are photodegraded. Although plastic debris may age, plastic texture may affect the photodegradation behaviors of pollutants. Furthermore, if the density of plastic debris exceeds that of seawater, it will settle and become buried in sediment. To consider the risk derived from the adsorbed pollutants, whether the pollutants are photodegraded and whether plastics affect degradation behaviors should be understood. In addition, possible pollutant migration from plastic debris to sediment should be addressed because sediment contamination may cause harmful effects on benthic organisms. This study photodegraded 2,3,4,5-tetrachlorophenol (TeCP) and pentachlorophenols (PCP) on virgin and artificially aged polyethylene (PE), polyvinylchloride (PVC), and polyethylene terephthalate (PET) sheets to investigate effects of plastic textures on chlorophenol photodegradation behavior. On the PE sheet, the photodegradation of TeCP and PCP was 1.50 times higher than that on the glass plate, thereby confirming the acceleration by PE. In contrast, the photodegradation rate was slower on PVC and PET than glass. These results confirmed that plastic textiles affect pollutant photodegradation behaviors. Furthermore, PE accelerated the photodegradation of a polyaromatic hydrocarbon (PAH), naphthacene (NAP), and oxygenated NAP. Naphthacenequinone was detected at an abundant level on the PE sheet with other oxygenated intermediates. Owing to the possibly higher toxicity of oxygenated PAHs than the precursor PAHs, the results confirmed that the existence of pollutants together with degradation intermediates should be considered for the risk assessment. When the artificially aged PE, PVC, and PET plastics were used, photodegradation of the adsorbed 2,4,5-trichlorophenol (TriCP) was suppressed, contributing to changes in the plastic textures such as the surface shapes and transparency. Finally, the migration of the aliphatic and aromatic organochlorines, TriCP, and 1-chlorooctadecane from the PE, PVC, and PET sheets to sediment was confirmed. Dissolution followed by adsorption and direct translation and direct translocation to sediment may be possible as migration mechanisms. These results provide evidence that plastic debris can act as a carrier of pollutants to benthic ecosystems.

Contents

Chapter 1

Introduction

1.1 Plastic pollution

Plastics and their products are widespread throughout the Earth. Chemically, plastics are synthetic organic polymers with enormous social benefits and are used in health, safety, energy-saving, material conservation, and a wide variety of sectors (**Figure 1.1**) [1], [2]. The global demand for plastics has also increased, with an annual growth rate of around 9% [3]. Among the various types of plastics, the demand for polyethylene (PE), polypropylene (PP), polyvinyl chloride (PVC), polyurethane, and polyethylene terephthalate (PET) are the top five single-use plastics (**Figure 1.2**) [2]. In addition, over 1/3 of the manufactured plastics in both the United States and Europe are used to make disposable products, such as packaging materials and trash bags, which are designed to be discarded within three years after their production [4]. Due to their numerous uses and convenient disposal, plastics have gained popularity, and every year a substantial proportion of plastics enter and persist in the marine environment [5], [6]. Among the littered plastics, the most common identified plastics are PE, PP, PVC, and PET [7]–[9]. Unwisely discarded plastic materials pose numerous threats to the marine environment. Due to the mismanagement of plastics, around 4.80 to 12.70 Mt of plastic debris enters the oceans annually [5], [10], [11], [12]. The surging trend of plastics in the environment especially, the aquatic environment, is increasing problems and creating a toxicological milieu for marine organisms.

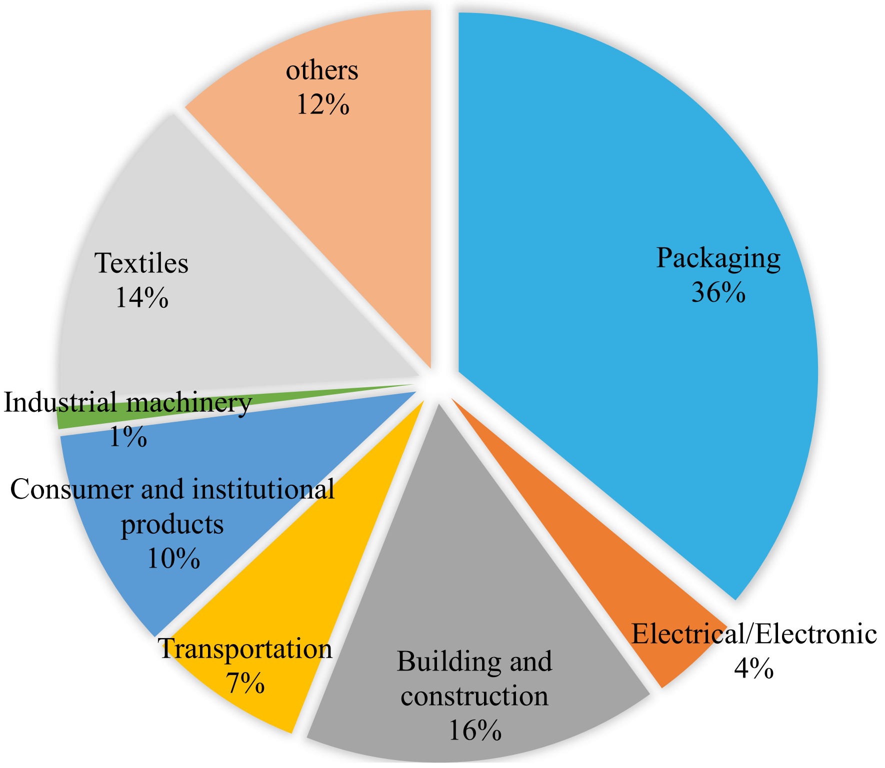

Figure 1.1 Global plastic production by industrial sectors, 2015 [2].

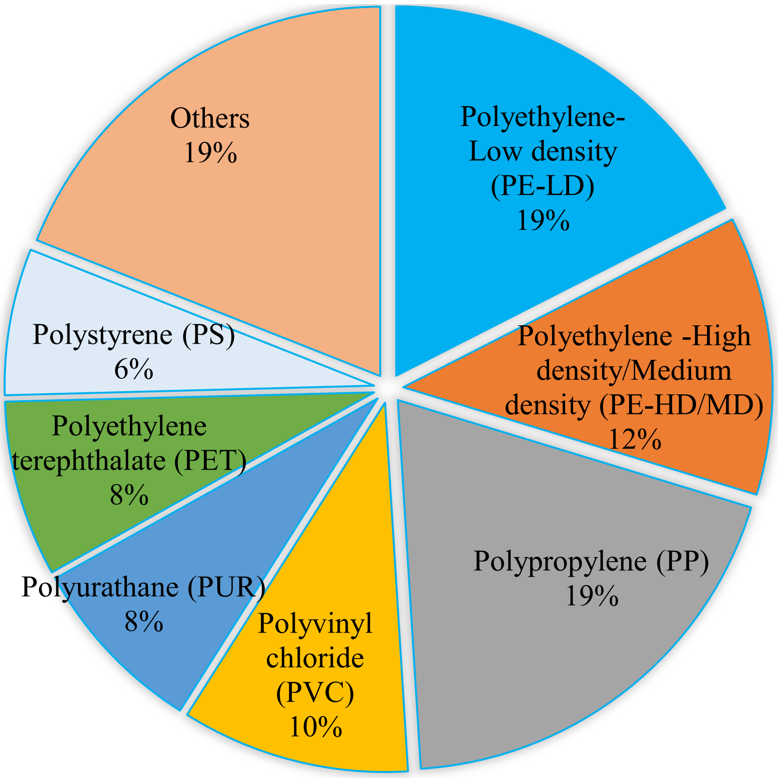

Figure 1.2 Global plastic demand according to types [3].

At present, oceans are unexpectedly the reservoir of plastic debris on a global scale. Approximately 60–80% of the world's litter entering the ocean is in the form of plastics [13], and almost 10% of the world's annually produced plastics end up in the ocean [2]. Prominent routes of plastics into the oceans are beaches and land-based sources like rivers, stormwater runoff, wastewater discharges, or the land litter transport by the wind [5], [10], [11]. The Foresight Future of the Sea report determined that plastic pollution, set to increase threefold between 2015 and 2025 without intervention, has a physical presence in the oceans and can accumulate on the coasts or in particular areas of the sea [14]. Ellen MacArthur Foundation reported that plastic in the oceans will outweigh fish by 2050 [15]. Although the negative effects of plastics on the ecosystems are insufficiently understood, the health damage to sea creatures, restriction on their movement [16], and pollution of beaches with accumulating hydrophobic organic pollutants [17]–[20] have been extensively studied.

1.2 Production and distribution of microplastics

Plastic debris are defined based on their sizes and broken-down pieces (**Figure 1.3**). Andrady et al. [21] defined microplastics as the barely visible particles that pass through a 500-μm sieve and retained by a 67-μm sieve (0.06–0.5 mm in diameter); particles larger than this were called mesoplastics. Betts et al. [22], Eriksen et al. [11], and Fendall and Sewel [22] defined microparticles as being in a size range < 5 mm (recognizing 333 μm as a practical lower limit when neuston nets are used for sampling). However, plastics debris having dimensions ranging from a few μm to 500 μm (5 mm) are commonly found in seawater [4], [21].

Figure 1.3 Size-based definition of plastics. (Image source: (https://www.naturalblaze.com/?s=microplastics), access on October 7, 2021).

Microplastics are also categorized based on manufacturing sources, such as i) primary microplastics and ii) secondary microplastics. Primary microplastics are purposely manufactured for various applications, such as exfoliants (microbeads) in personal care products [24]. Secondary microplastics are fragments of larger plastic debris, including plastic containers, nets, line fibers, films, and tires [5]. The generation of plastic waste is increasing continuously (**Figure 1.4**) [2], [11], with an estimation reported that more than 5.25 trillion pieces of plastics weighing over 268,940 tons are floating on the ocean surfaces [11]. These plastics are continuously degraded on ocean surfaces and at shorelines [25]. The degradation of plastics occurs through chemical changes, resulting in reduced average molecular polymer weight. As the mechanical integrity of plastics invariably depends on their average molecular weight, any significant degradation extent inevitably weakens them [21]. For example, exposure to ultraviolet (UV) radiation catalyzes the photo-oxidation of plastics, making them more brittle. In addition, they undergo degradation by chemical and physical processes in the environment, i.e., by the action of wind and abrasion by waves [16]. Plastics become brittle enough to fall apart into powdery fragments, often invisible to the naked eye. However, at present, nano plastics are also increasingly being manufactured and being used in paints, adhesives, drug delivery vehicles, electronics, and other product types [26]. The size reduction due to uses and environmental degradation may induce unique particle characteristics and influence their potential toxicity.

Microplastics are driven by ocean winds, currents, river outflow, and drifting plastic debris to reach the remote islands and the benthic and pelagic habitats of oceans such as the Pacific, the Arctic, and the deep oceans [4]. For example, the estimated concentrations of microplastics at the surface of seas were 4.38×10^4–1.46×10^6 pieces/km^2 in the Arabian Bay [27], 640–42000 pieces/km^2 in the northwestern Pacific Ocean [28], 1051 pieces/m^3 in South Korea coastal waters (the sampling areas are Busan, Ulsan, Yeongil, Gwangyang, Deungnyang city, and three rural areas) [29], and 0–1.31 and 0–11.5 pieces/m^3 on the Norwegian coast (NIWR, 2017) and subsurface of artic water [30]. In addition, microplastics have been found in sediment samples such as in the Yellow Sea, China at depths of < 20 m, 20–40 m, 40–60 m, and 60–80 m, with microplastic concentrations of 1765, 2135, 2346.7, and 2771.3 pieces/kg (dry weight), respectively [19].

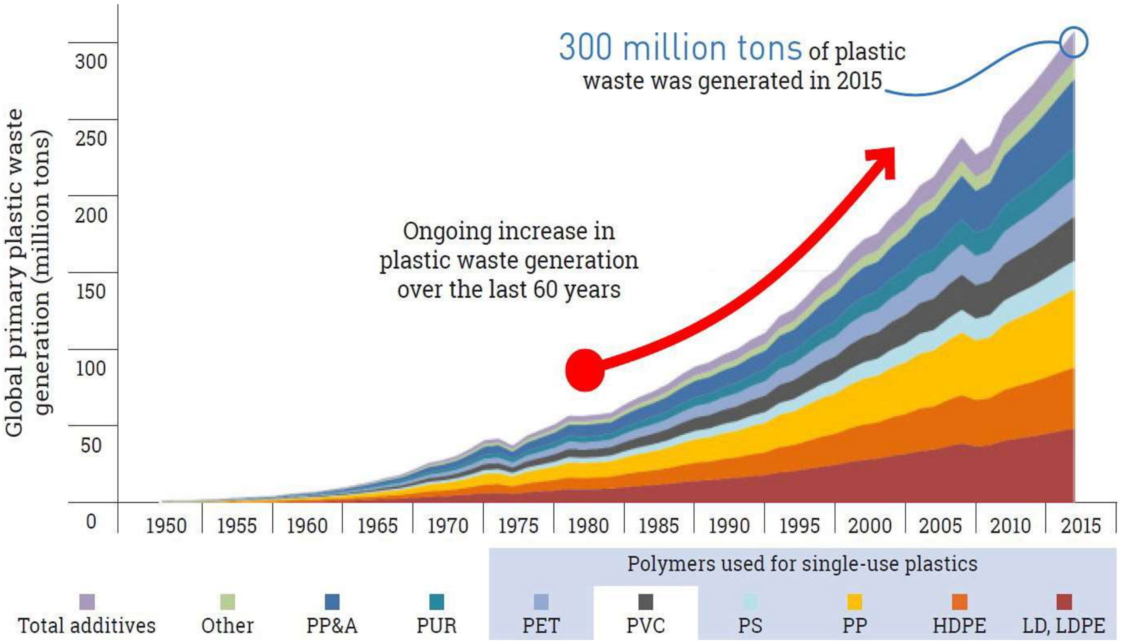

Figure 1.4 Surging trend of plastic waste generation [2].

1.3 Emergence of microplastics in creatures

Ingestion of microplastics by wildlife is a frequently noted problem, with plastic debris found in the guts of seabirds [20], [31], fishes [32], [33], shrimp [34], turtles, and whales [35]. Plastic debris causes the death of marine organisms in different ways, such as entanglement and blockage of the organism's digestive system [31], [36], [37]. Ingestion of microplastics has also been documented in deposit- and suspension-feeding sea cucumbers [5], deposit-feeding lugworms [38], detritivores amphipods [39], and even zooplankton [40] (**Figure 1.5**).

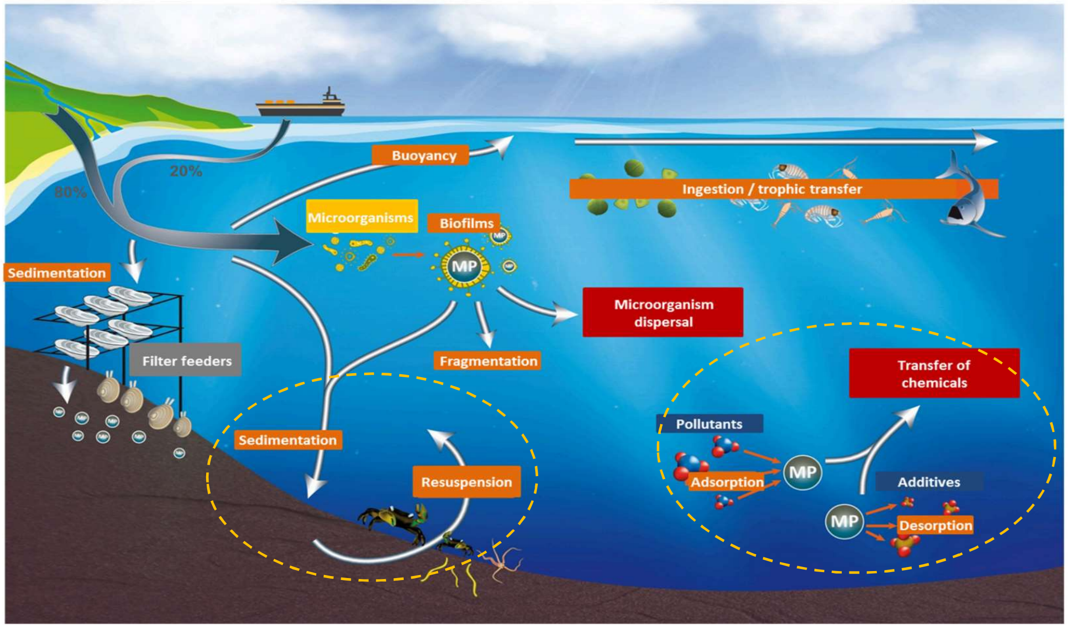

Figure 1.5 Overall focused point where microplastics gained concern [41].

1.4 Potential of microplastics as a carrier of pollutants.

Besides the main polymers, most plastics contain several types of additives to improve plastic features like ductility, hardness, durability, or resistance to weathering. Among these, some plastic additives, including plasticizers, are suspected as endocrine disruptors [42]–[44]. Various kinds of plasticizers are used to modify the properties of plastics, reaching up to 10–70% of the plastic material weight. Plasticizers are mostly phthalates, terephthalates, epoxies, aliphatic, trimellitates, and citrates [7], [45]. These are not chemically bonded with the structure of the main plastics and can, therefore, leach out into the environment [45]. As plastics are accumulated and fragmented in oceans, the leaching of plastic additives also represents another toxicological risk in the marine environment.

Microplastics transport hydrophobic organic chemicals (**Figure 1.5**) (HOCs) [41], [46], [47]. For example, polycyclic aromatic hydrocarbons (PAHs) [48], organochlorine pesticides [49],

[50], polychlorinated biphenyls (PCBs) [51], [52], and chlorophenols (CPs) [49] are adsorbed and concentrated on microplastic surfaces-[53], [54]. In addition, they also accumulate heavy metals such as cadmium, zinc, nickel, and lead [55]. A summary of the adsorption of HOCs on plastics is shown in **Table 1.1**.

Table 1.1: Adsorption of pollutants on MPs.

Pollutants name	**Plastics**	**Experimental Sample/ Medium**	**Adsorption**	**Reference**
Phenanthrene and DDT	PE	Artificial seawater	-	[24]
PAHs	PE, PP, PS	Environmental sample (San Diego Harbor)	0.063–0.208 μg/g	[33]
PCBs	LDPE	Environmental sample (Ocean surface)	3.4-35 ng/g	[33]
PAHs	LDPE HDPE	Aqeuous solutions	-	[48]
2,4,6-trichlorophenol (TriCP) and pentachlorophenol (PCP)	PP PE	River water	126-144 μg/g 53.7-99.5 μg/g	[49]
Phenanthrene and DDT	PE, PVC, uPVC	Seawater	-	[50]
PAHs	PE PVC	Seawater	1.15–15.5 μg/g	[50]
Polychlorinated biphenyls (PCBs) Dichlorodiphenyl trichloroethane (DDT) Nonylphenols	PP	Environmental samples (Collected from Japanese coasts)	4-117 ng/g 0.16-3.1 ng/g 0.13-16 μg/g	[53]

Pollutants name	**Plastics**	**Experimental Sample/ Medium**	**Adsorption**	**Reference**
PCBs PAH DDT PAH	PS, PS-foam	Environmental samples (San Diego beaches, California)	-47 ng/g 30-1900 ng/g 76 ng/g 300-1900 ng/g	[56]
PAH	PS-foam	Seawater	240-1700 ng/g	[56]
Phenanthrene	PE, PP PVC	Seawater	0.6-6.1 µg/L	[57]
PAHs	PE, PVC, PS	Artifical seawater	303.03–714.29 µg/g	[58]
Fuel aromatics	PE PVC PS	Artificial seawater	1-10 µg/g	[59]
17 PCBs	PE,PS	Fresh and seawater	-	[60]
Hexachloro cychlohexanes and chlorinated benzenes	PE, PP, PS	Seawater	-	[61]

Apart from being adsorbed microplastics, HOCs are further ingested by animals, resulting in their transmigration to the food chains (**Figure 1.5**) [41], [62]. A recent research paper reported that the coexistence of polystyrene and nickel exposed toxicity on *Daphnia magna,* losing mobility [18], [63]; moreover, polystyrene altered the bioavailability [18], [64] and phenanthrene transfer into *Daphnia magna* biota cells. In addition, microplastics have been detected in a range of marine biota, including seabirds, crustaceans, and fish [32], [65]. Ma et al. [18] reported that the significant bioaccumulation of phenanthrene occurred by feeding phenanthrene-adsorbed polystyrene to *Daphnia magna*. These results are evidence that microplastics can act HOC carriers to organisms. In addition, the harmful effects of HOCs are also well known. For example, cancer, allergies and hypersensitivity, damage to the central and peripheral nervous systems, reproductive disorders, and disruption of the immune system have been reported [66], though the endpoints are dependent on the species of HOCs. In addition, some HOCs are also considered to be endocrine disrupters, causing health problems including hormonal systems, dysfunctional immune and reproductive systems, greater susceptibility to disease, and the diminished intelligence of exposed individuals and their offspring [67]. Therefore, the behaviors of HOCs adsorbed onto microplastics and the negative impacts on organisms should be understood for environmental management.

1.5 Importance of understanding fates of organic pollutants on plastics

The fate of HOCs and their distribution among different environmental sectors (**Figure 1.5**) are determined via various physical, chemical, and biological processes [68]. HOC degradation occurs by chemical, biological, and/or their combined mechanisms [69], [70]; the former occurs via photochemical, redox, and hydrolysis reactions [69]. Although photodegradation can occur only in the photic zone, this is an essential HOC degradation mechanism during the transport of microplastics.

On the other hand, plastics may potentially alter the photodegradation behaviors of pollutants adsorbed onto microplastics. A previous study showed that the photodegradation of polystyrene films containing brominated flame retardants, such as decabromodiphenyl ether; tetra-bromophenol A produced 14 brominated photodegradation products via the bromination and oxidation of polystyrene [71]. This indicates the necessity of investigating the possible effects of plastics on HOC photodegradation behaviors from the viewpoint of risk assessment. Although many studies have investigated the photodegradation behaviors of HOCs [69], [72];

however, no information is available about the effect of plastic on the photodegradation of the adsorbates.

All plastics age in the environment, changing the plastic's properties and adsorption capacity for HOCs [73], [74]. Aging increases the crystallinity of plastics; however, crystallinity is not a controlling factor of HOC adsorption on plastics [75]. Along with changes in the plastic property, the aging of plastic generates radicals that may also change the fate of pollutants [71]. This implies that aged plastics might show different effects on the photodegradation of HOCs compared to virgin ones. Therefore, the effects of plastic aging on photodegradation behaviors of adsorbed HOCs need to be addressed because of the possible production of more toxic pollutants than the precursors.

Furthermore, once the density of plastic debris reaches that of seawater by the formation of biofilms, these settle in the sediment (**Figure 1.5**) [76]. Once buried, photodegradation does not occur. However, HOCs adsorbed onto microplastics might be distributed to sediment because various types of HOCs have been detected in the marine sediment [52], [77], [78]. Although microplastics are potential HOC carriers to the benthic ecosystem, no study has investigated the migration of HOCs from microplastics.

1.6 Objectives and outlines of this study

For understanding the fates of HOCs adsorbed onto the surface of microplastics in the oceans, the effects of plastics and their aging on the fates of HOCs should take priority to be elucidated for risk assessment. During floatation, microplastics are exposed to sunlight. As plastics can alter the photodegradation pathways of HOCs, the alteration effects of plastics should be understood. In addition, microplastics are expected to be a HOC carrier to the benthic ecosystem. Therefore, this research focused on the photodegradation processes of organochlorines adsorbed onto plastics and migration phenomena from plastics to sediment. The objectives of this research were as follows:

1. To reveal the effects of plastic textures on photodegradation behaviors of HOCs.
2. To investigate how the aging of plastics changes the photodegradation behaviors of adsorbed HOCs.
3. To determine the migration behaviors of adsorbed organic pollutants from plastic surfaces to marine sediment.

This thesis consists of 6 chapters, as follows

In Chapter 1, the background and negative consequences of plastics and the importance of research about the fate of adsorbed organic pollutants onto plastics are described. The description of pollutants adsorption onto microplastics, microplastic numeration, concentration in the environment, and their toxic effect are presented as in summarized form.

In Chapter 2, the photodegradation behaviors of organochlorine TeCP and PCP on the plastics and glass were investigated, and the plastic effects on the photodegradation of organochlorines are discussed.

In Chapter 3, the photodegradation behaviors of NAP as a model PAHs on PE surface and glass were compared to investigate whether PE with hydrogen donation potential accelerates the photodegradation of NAP and or generates new persistence toxic intermediates.

In Chapter 4, the photodegradation behaviors of TriCP on artificially aged plastics were investigated to confirm whether the aging of plastics affects the photodegradation behaviors of adsorbed TriCP and to find causes for the aging effects.

In Chapter 5, migration of organochlorine from plastics to sediment was examined by burying organochlorine-adsorbed plastic sheets into wet sediments, and migration behaviors of organic pollutants from the plastics to sediments were discussed.

In Chapter 6, the general conclusions of all chapters are presented, with recommendations for future study.

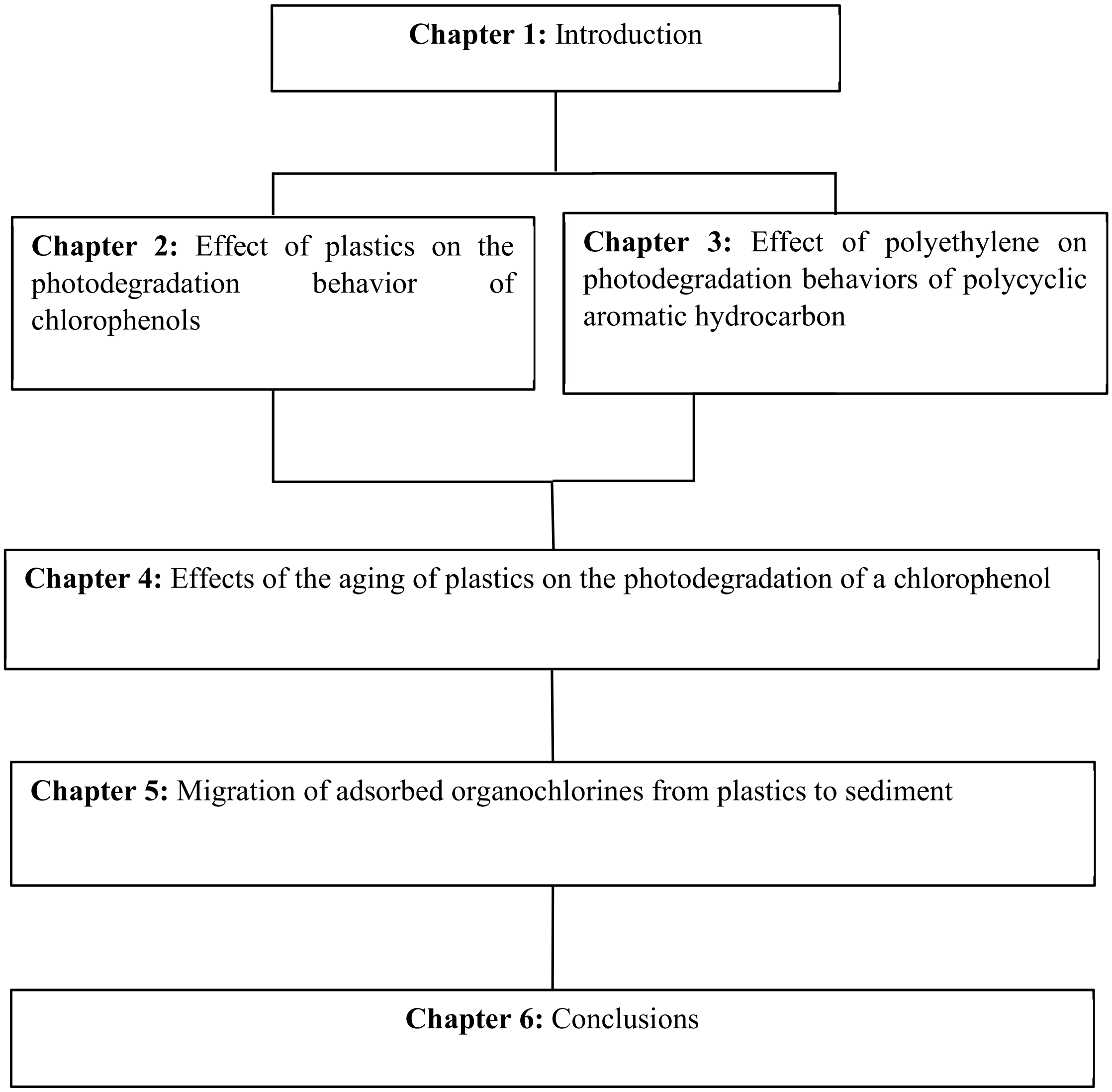

Figure 1.6 The outline of this research

1.7 Literature cited

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Chapter 2

Effect of plastics on the photodegradation behavior of chlorophenols

2.1 Introduction

The marine environment is sensitive to pollution because of its vulnerable ecology. Plastic debris is a new environmental threat to the marine environment because of its adsorption behaviors [1], [2], and littering sizes, including macro-to-micro and nanosized particles [3]. However, these fragmented plastics are enumerated because of their ubiquitous abundance and floatation on ocean surfaces [4]–[6], they have negative effects on the marine environment and biota [7]–[9]. The presence of microplastic and nanoparticles in the environment may have effects on the fate of HOCs, with HOCs adsorbed on their surfaces. The most commonly detected pollutants on plastic litters are PAHs [2], PCBs, hexachlorobenzene (HCB), dichlorodiphenyltrichloroethane (DDT) [10], and CPs [11]. As HOCs, such as CPs and PCBs, are persistent in the environment and act as endocrine disruptors or mutants [12], the fates of hydrophobic pollutants adsorbed on microplastics should be clarified from a risk assessment viewpoint.

The photodegradation of any substance in the natural environment is a combination of reactions of all types of photochemical processes depending on the absorption level, radiation wavelength, quantum yield, radiation exposure duration, and physical state of the transforming compound [13]. For persistent halogenated organic pollutants, photodegradation could be a major cause of transformation on the sea surface. The shortest cutoff wavelength of sunlight hitting the earth's surface (~290 nm) can cause the dechlorination and degradation of PCP and PCBs [14].

Many studies have investigated the photo degradability of organohalogen pollutants in various media, such as water [13] and organic solvents [14]–[16], using UV lamps as the light source.

Interestingly, HCB photodegradation experiments in *n*-hexane, isopropanol, and methanol showed the photodegradation rate in *n*-hexane was the highest [16], while the photosensitized dechlorination of HCB was observed with the coexistence of a polymeric carbazole chromophore [17]. Moreover, Minghui et al. reported chlorination by a photolysis process in CCl_4 by confirming the production of Hexa-, hepta-, and octachlorobenzo-*p*-dioxin (Hx-OCDDs) from 1,2,3,7,8-pentachlorodibenzo-*p*-dioxin (PeCDD) [15]. These results confirmed the matrix effect in the photodegradation process, indicating the need to understand how plastics affect the transformation of organohalogen pollutants.

Most studies on the photodegradation of organohalogen pollutants have revealed the production of dehalogenated intermediates. For example, PCP photodegradation provided mono, di-, tri-, and tetra-CPs as intermediates [13], [16]. Moreover, in the processing of plastics, manufacturers use halogenated compounds as additives. A recent study showed that polystyrene impregnated with brominated flame retardants, such as decabromodiphenyl ether and tetrabromobisphenol, produced 14 new brominated products by oxidation and bromination of polystyrene under UV irradiation [18]. Considering the above-mentioned matrix effect on the photodegradation of organohalogen pollutants, it can be surmised that the characteristics of plastics may also affect the photodegradation behavior of organohalogen pollutants. However, the photodegradation of organohalogen pollutants sorbed on plastics has not been investigated. In this study, the photodegradation behavior of organochlorine pollutants adsorbed on three commonly used plastics, PE, PVC, and PET was compared to investigate the matrix effect of the plastic. Furthermore, the mechanisms of the matrix effect are discussed based on the plastic characteristics and additives.

2.2 Experimental

2.2.1 Materials

Virgin sheets of PE, PVC, and PET with a thickness of 1.0 mm were purchased from Sanplatec Corp. (Tokyo, Japan). Before the photodegradation experiments, each plastic sheet was cut into a circle shape with a 26-mm diameter. As organochlorine pollutants, PCP and TeCP were tested. As the pure PCP reagent was not available, a mixture of 10% PCP and 90% TeCP, TriCP (> 95% purity), and 2,5-dichlorophenol (DCP, > 98% purity) was obtained from Tokyo Chemical Industries (Tokyo, Japan). Sodium dihydrogen phosphate (NaH_2PO_4, 99% purity) and phosphoric acid (H_3PO_4, 85% purity) were purchased from Wako Chemical (Japan). Methanol (99% purity) and *n*-hexane (97% purity) were purchased from Nacalai Tesque Inc. (Japan).

2.2.2 Photodegradation

The circle-shaped plastic sheets were placed at the bottom of quartz glass Petri dishes (diameter 26 mm), and an *n*-hexane solution containing 10 mg/L PCP and 90 mg/L TeCP was poured on them (**Figure 2.1**). After allowing 60 min for the evaporation of *n*-hexane at 25 °C, the Petri dishes were covered with quartz glass lids and then placed in a Navis Schreiner photochemical reactor (DM-05, Daishin Kogyo Co. Ltd., Hiroshima, Japan) equipped with a 10 W low-pressure UV lamp emitting 254 nm wavelength UV light at 32 $\mu W/cm^2$ (**Figure 2.1**). During UV irradiation for 4 h, the photochemical reactor was kept at 25 °C, and three samples were randomly sacrificed to analyze the remaining PCP, TeCP, and the photodegradation products. A control experiment was performed under the shading of UV radiation by wrapping the Petri dishes with aluminum foil.

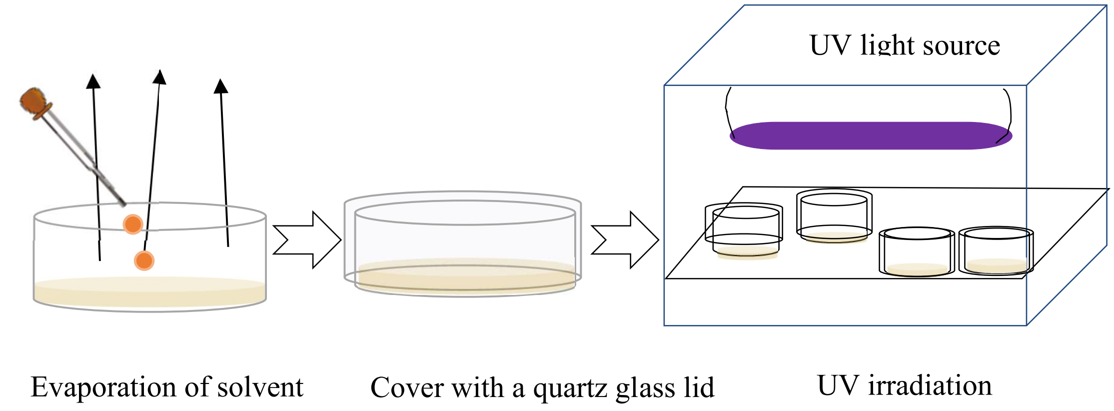

Figure 2.1 Experimental setup for photodegradation of chlorophenols on the plastic surfaces.

2.2.3 Analysis of the CPs and photodegradation products

To measure the remaining concentrations of the CPs and photodegradation products, methanol was poured into the Petri dish for extraction. The methanol extract was mixed with a 20 mM phosphate buffer (pH 2.50) solution at a volume ratio of 4:1. A sample of the mixture (100 µL) was then analyzed by a liquid chromatograph (HPLC) on an octadecyl silica column (Cosmosil 5C18-AR-II, 4.6 mm × 150 mm, Nacalai Tesque Inc., Japan) at a flow rate of 1.0 mL min^{-1}, using a mixture of methanol and phosphate buffer (4:1 volume ratio) as the mobile phase. The CPs were detected by a UV–visible detector at 254 nm (SPD-10A, Shimadzu, Japan).

The photodegradation products were analyzed by liquid chromatography-mass spectrometry (LTQ ORBITRAP XL-20930, Fisher Thermo Scientific, USA) using a high-resolution orbitrap mass spectrometer. The same Cosmosil 5C18-AR-II column was used, while elution was performed with a binary solvent in an isocratic system consisting of methanol and acidified water (0.1% v/v HCOOH) in a 90:10 volume ratio. The flow rate was set at 0.50 mL min^{-1}, and the injection volume was 10 µL. The scan parameters were from m/z = 90 to 800 amu (atomic mass unit) in full-scan negative electrospray ionization mode. For identification, the mass spectrum patterns were compared with those of the authentic TriCP and DCP samples.

2.2.4 Characterization of the plastics

To analyze the functional groups of the plastic surfaces, the UV-irradiated samples were analyzed by a Fourier transform infrared (FTIR) spectrometer (IRPrestige-21, Shimadzu, Japan) equipped with a tungsten-iodide light source. The spectra were recorded from 400 to 4000 cm^{-1} (nominal resolution of 4 cm^{-1}, 32 scan summation).

2.2.5 Statistical analysis

One-way analysis of variance (ANOVA) followed by the Tukey test was performed for the remaining PCP and TeCP concentrations to determine the statistical significance as expressed by a p-value for photodegradation enhancement or suppression on the assumptions of a normal probability distribution and homogeneity of variance.

2.3. Results and Discussion

2.3.1 Photodegradation of the CPs

The change of the PCP concentration on the PE sheet under UV irradiation is shown in **Figure 2.2**. The PCP concentration decreased from 1.75 to 0.04 mg/cm^2 after 240 min of UV irradiation. As the control experiment did not show a change in the PCP concentration, this 98% decrease in the PCP concentration was attributed to photodegradation. Although TeCP could be produced by PCP photodegradation [13], only 4.12% of the initially adsorbed TeCP remained after UV irradiation, whereas 98% of TeCP remained after 240 min in the control experiment (data not shown). This confirmed that PCP and TeCP adsorbed on the PE sheet were photodegraded by UV irradiation. This provided the first evidence for the occurrence of photodegradation of PCP and TeCP on the plastic sheet.

To investigate whether the plastics affected the photodegradation of PCP and TeCP, the photodegradation rate constants were determined based on pseudo-first-order reaction kinetics

(**Figure 2.3**(**a**) and **2.3**(**b**)). Except for PVC, the photodegradation rate constants were estimated at a coefficient of determination (R^2) > 0.85. From 30 to 120 min, the PCP concentration on PE was lower than that on glass ($p < 0.0013$, **Figure 2.3**(***a***)). After 240 min, a significant difference was not observed for this dataset because of the large variance, but the average value on PE was lower than that on the glass. The photodegradation rate constant of PCP on the PE sheet was 1.80×10^{-2} min^{-1}, 1.50 times higher than that on glass (1.22×10^{-2} min^{-1}).

Although the concentration of TeCP might include the fraction produced from photodegradation of PCP by dechlorination [13], the remaining TeCP concentration on PE was lower than that on the glass after 120 ($p = 0.0764$) and 240 min ($p = 0.0409$), and the photodegradation rate constant of TeCP on PE was higher than that on glass (**Figure 2.3**(**b**)). These results confirmed the acceleration of photodegradation of PCP and TeCP by the PE sheet. The degradation products TriCP, DCP, and CPs were detected, as shown in **Figure 2.4**. As these products can be produced by reductive dechlorination [14], [16], PE may act as a hydrogen donor (**Figure 2.6**).

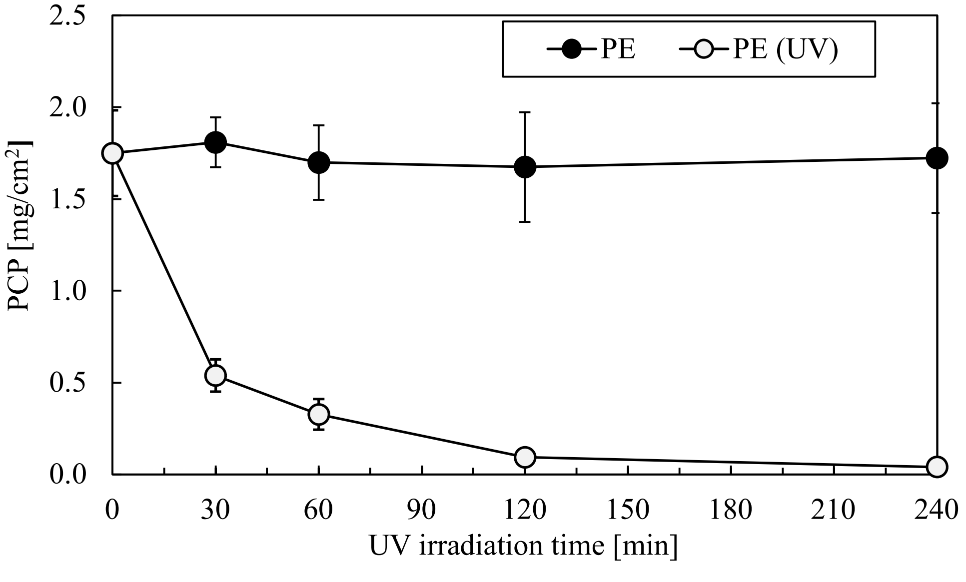

Figure 2.2 Degradation of PCP adsorbed on the PE sheet with and without UV irradiation. The bars indicate the standard deviation ($n = 3$).

The coefficients of determination for PCP and TeCP estimated using second-order reaction kinetics were 0.95 and 0.97, respectively. These were high compared to that of PCP (0.86) and TeCP (0.93), also estimated using first-order reaction kinetics (**Figures 2.3**(**a**), **2.3**(**b**)); however, we used the photodegradation constants of PCP and TeCP estimated using first-order reaction kinetics for a comparison between PET and glass. The PCP and TeCP concentrations on PET were significantly higher than those on glass after 60 min ($p < 0.0221$, **Figure 2.3**(**a**); $p < 0.0138$, **Figure 2.3**(**b**)), except for TeCP after 120 min ($p = 0.133$). The photodegradation rate constants on the PET sheet were 8.10×10^{-3} min^{-1} for PCP and 7.00×10^{-3} min^{-1} for TeCP, lower than those on glass (1.22×10^{-2} min^{-1} for PCP and 1.09×10^{-2} min^{-1} for TeCP). This showed a photodegradation suppression by the PET sheet. A possible reason for this is a decrease of UV radiation reaching PCP and TeCP owing to sorption by the PET sheet and/or additives, as discussed in Section **2.2.3**.

Surprisingly, PCP on the PVC sheet showed a different response under UV irradiation, where the photodegradation rate slowed and then stopped after 60 min (**Figure 2.3**(**a**)). A possible reason for the PCP behavior on PVC is the rechlorination of the intermediates by chlorine radicals produced from PVC. If rechlorination occurs, TeCP might transform into PCP and TriCP. A previous study confirmed the production of Hx-OCDDs from PeCDD by photolysis in CCl_4 [15], indicating the occurrence of chlorination. Additionally, the production of chlorine radicals during the deterioration of PVC under UV irradiation has been reported [19].

As for TeCP, the concentration on PVC was lower than on the other plastics and glass during the first 120 min ($p < 0.0285$, **Figure 2.3**(**b**)), and this did not contradict the possible occurrence of rechlorination. However, the degradation behavior did follow second-order reaction kinetics (R^2=0.97) better rather than first-order reaction kinetics (**Figure 2.3**(**b**)). The possible reasons for this difference in suitable reaction order kinetics might be different photodegradation mechanisms.

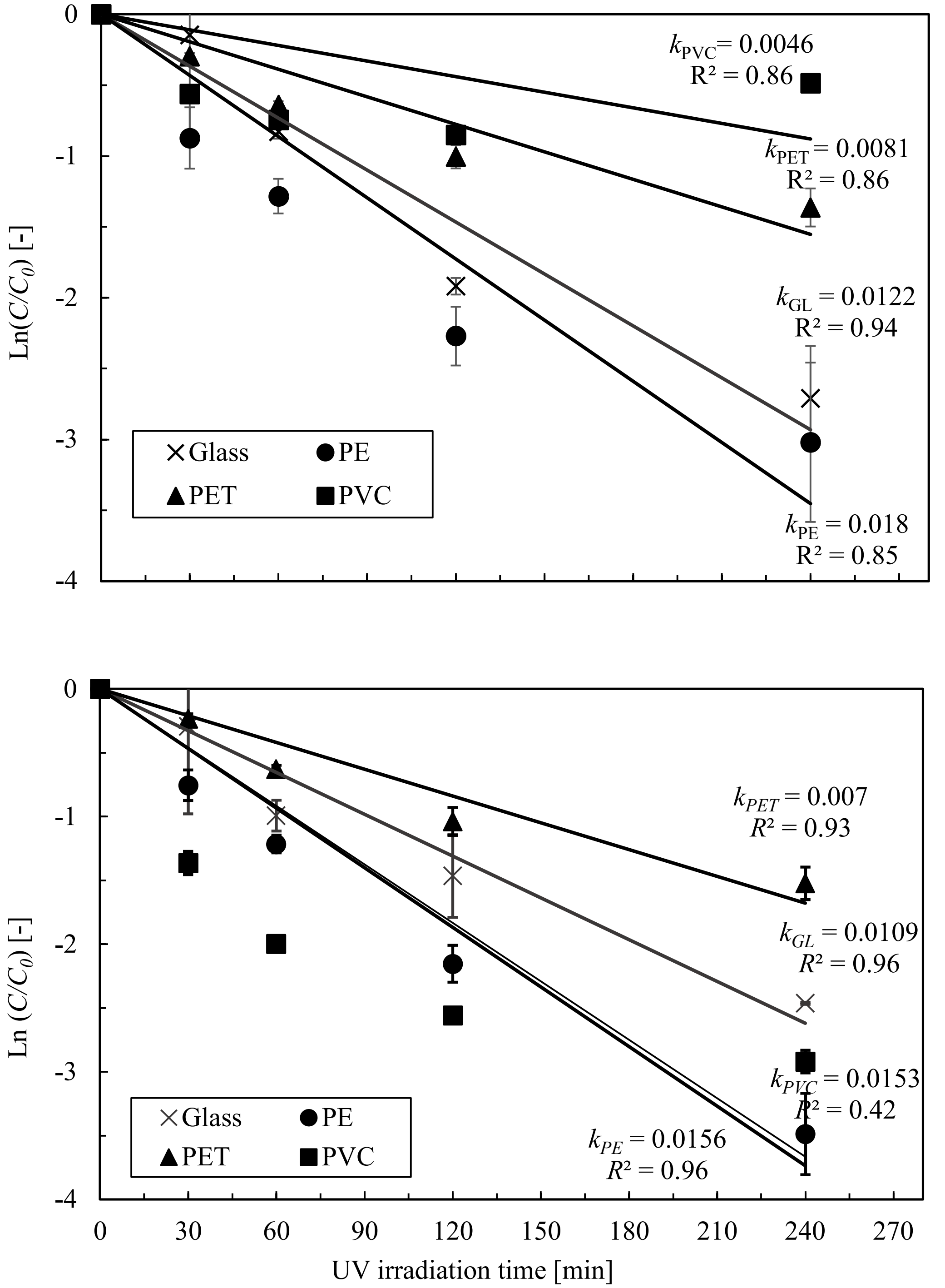

Figure 2.3 Photodegradation of (*a*) PCP and (*b*) TeCP on PE, PET, and PVC. Bars indicate the standard deviation (*n* = 3).

For example, photodegradation and rechlorination might consume TeCP on PVC if rechlorination occurs.

These findings confirmed that the photodegradation behavior of organochlorine pollutants is affected by plastics, although the effect might depend on the plastic characteristics and additives. To investigate the different effects of plastics, the changes in the plastic molecular structures by UV irradiation were analyzed.

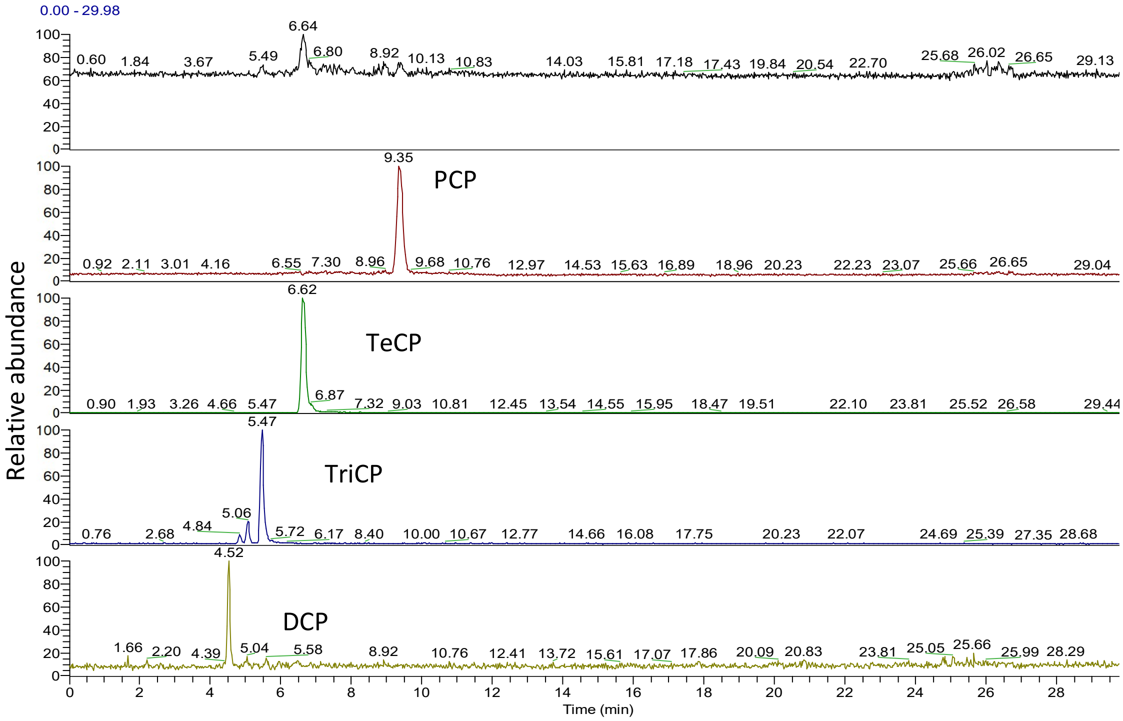

Figure 2.4 Total ion chromatograms of the CPs formed by UV irradiation of PCP and TeCP on the PE sheet.

2.3.2 Factors that affect photodegradation

Photolysis and photo-oxidation are mechanisms of polymer photodegradation. Polymer radicals are formed by UV irradiation and readily react with oxygen molecules to form peroxy radicals [20]. Peroxy radicals abstract hydrogen from polymers to form hydroperoxide groups

(R′–O–O–H), dissociated by UV irradiation or heat [21]. Finally, carbonyl groups are formed and give different dissociative intermediates and products according to the Norrish I and II mechanisms [22]. The Norrish I mechanism involves radical scission of the bond adjacent to the excited carbonyl group with the formation of two radicals leading to terminal alcohol and carboxyl acid groups. The Norrish II mechanism involves intramolecular hydrogen abstraction from the γ-carbon atom with chain scission without producing radicals to give an unsaturated polymer chain end and a polymer chain with an end carbonyl group [22], [23].

The roughness of the plastic surface was expected to change the photodegradation rate of CPs at some degrees. As discussed here, the deterioration of the PP, PET, and PVC surfaces was observed in FT-IR analyses, suggesting the change of surface roughness during the photodegradation. As the surface roughness of plastic samples was not measured, this paper addressed the effects of the chemical characteristics of the plastics on the photodegradation of CPs.

2.3.2.1 PE

Photodegradation of PCP and TeCP was accelerated on the PE sheet (**Figure 2.3**(**a**) and **2.3**(**b**)). Owing to photodegradation by reductive dechlorination, the possible acceleration mechanism might be hydrogen donation from the PE sheet (**Figure 2.6**).

Hydrogen and alkyl radicals and carbonyl groups are formed on PE by UV irradiation owing to structural defects or chromophore impurities. These radicals are formed by C–C bond scission, hydrogen abstraction, double bond formation, and crosslinking of polymer radicals [20]. In terms of the Norrish I mechanism, the photolysis of the carbonyl group in PE involves the scission of α and β C–C bonds after electronic excitation of the C=O group to form hydrogen and alkyl radicals and ketones. In terms of the Norrish II mechanism, the crosslinking of macroradicals removes hydrogen atoms from the PE sheet following γ-/β-hydrogen abstraction [24].

The FT-IR spectra of the virgin PE sheet and the PE sheet irradiated by UV light for 240 min are shown in **Figure 2.5**. After UV irradiation, there were increases in the bands representing (i) C=C disubstituted (*cis*) unsaturated bonds at 730 cm^{-1} [25], (ii) CH_2 asymmetric stretching at 1440 cm^{-1}, and (iii) CH_2 symmetric band stretching or CH_2 end groups at 1360–1300 cm^{-1} [23], [26]. Moreover, the bands for oxygen-containing groups at 3200–3600 cm^{-1} and carbonyl groups at 1728 cm^{-1} revealed that oxidation occurred, and the broad weak band at 2685 cm^{-1} for olefinic CH_2 stretching supported hydrogen abstraction from the carbon backbone or crosslinking of macromolecules [24].

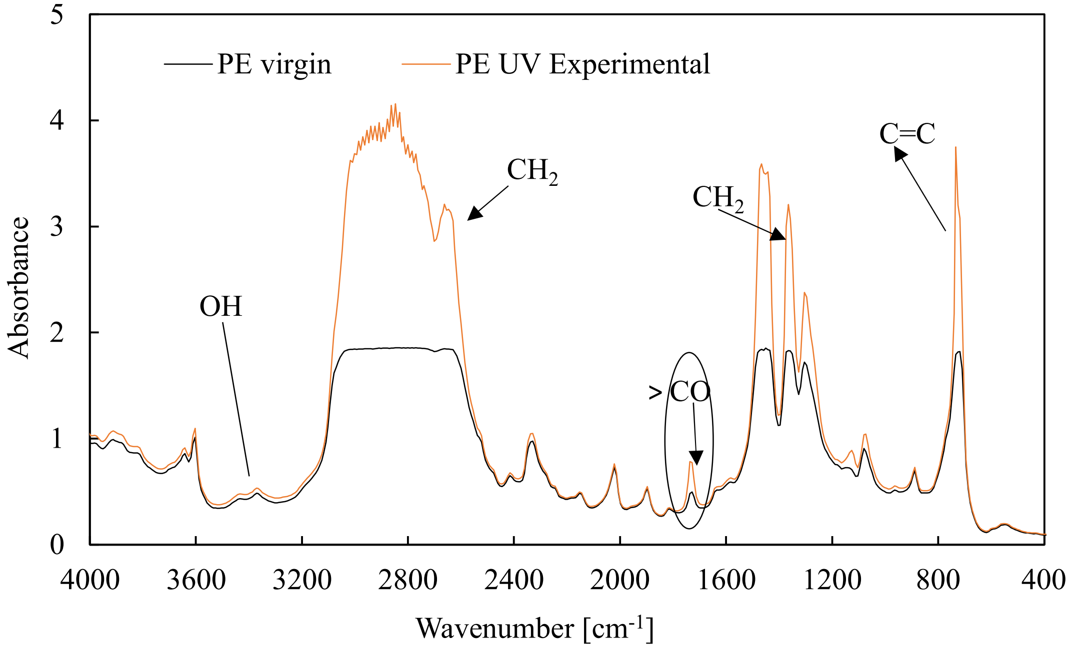

Figure 2.5 FT-IR spectra of the virgin PE sheet and the PE sheet irradiated by UV light for 240 min.

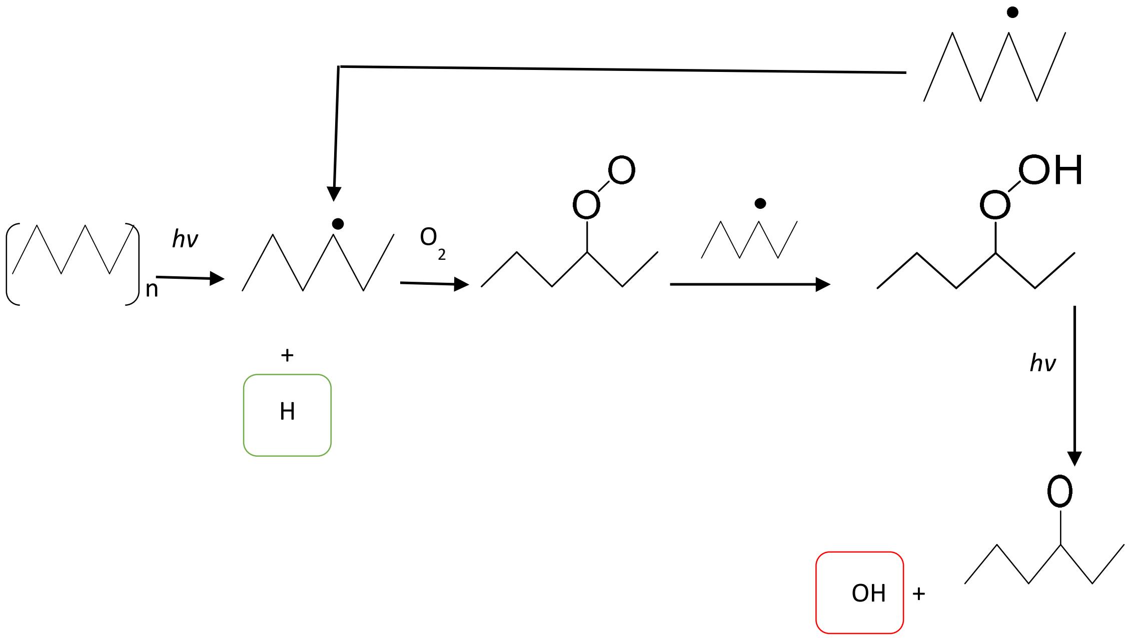

Figure 2.6 Photodegradation mechanism of PE [27]**.**

2.3.3 Possible effect of additives

Generally, chemical additives, such as plasticizers, antioxidants, and softeners, are added to plastic products to extend their lifetime, prevent oxidation, and improve their stability [27]. For example, UV absorbers, such as hindered amine light stabilizers, are often used to obtain resistance to weathering. Antioxidants inhibit the propagation phase of photo-oxidation [28] and impede the reaction. Based on these properties, the photodegradation process of CPs can be affected by plastic characteristics and additives. On PVC, the lowest TeCP concentration was observed among the four media during the first 60 min; however, PVC might include additives at the highest level (**Figure 2.7**). A plausible explanation for these results might be the inclusion of additives inert to photodegradation in addition to rechlorination; however, the additives have not yet been identified. Future studies should investigate the effect of additives on the photodegradation of organic pollutants and rehalogenation to clarify the fate and risk assessment of organic pollutants in microplastics.

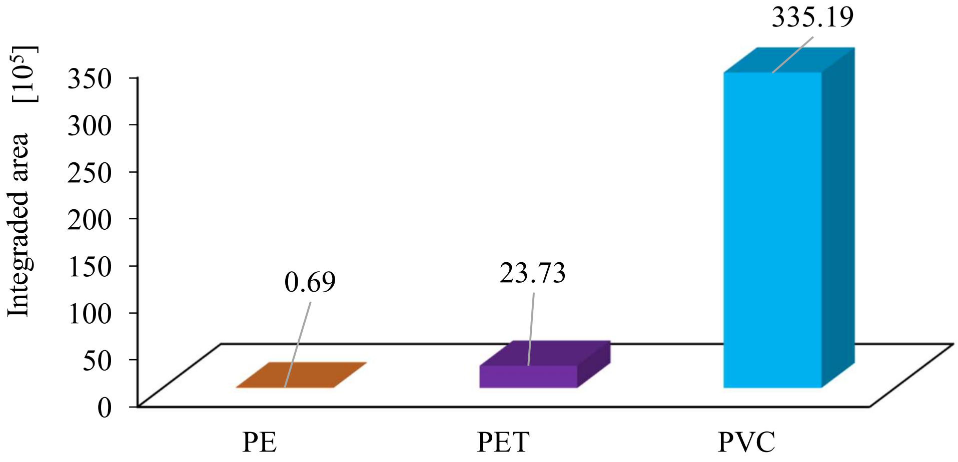

Figure 2.7 Total areas of the unknown peaks surmised as additives for the virgin plastics detected by HPLC for the plastic matrices.

2.4 Conclusions

The photodegradation of PCP and TeCP by dehalogenation of sorbed CPs on PE, PET, and PVC sheets was confirmed. Photodegradation of the CPs was accelerated by PE because of possible hydrogen donation, whereas PET suppressed photodegradation. A possible reason is UV absorption by the surrounding PET additives. For PVC, the photodegradation reaction was suppressed owing to possible rechlorination because chlorine atom migration was observed in the PVC sheet. This study suggests that plastic characteristics should be considered to assess the fate of organic pollutants sorbed on plastics through photo transformation.

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Chapter 3

Effect of polyethylene on photodegradation behaviors of a polycyclic aromatic hydrocarbon

3.1 Introduction

More than five trillion pieces of plastics weighing equal to 25000 Mt are floating on the ocean surface [1]. During floatation, plastics are broken down into smaller pieces, microplastics (< 5 mm) and nanoplastics (< 0.1 mm) by light, waves, and currents [2], [3]. Microplastics are widely spread into different environmental sections such as freshwater [4], open ocean [2], [5], coastal ecosystems [6], sediment [7], and arctic beaches [8], adsorbing HOCs because of a strong affinity due to hydrophobic interactions [9]–[11].

PAHs are a type of HOCs widely distributed in the atmosphere, water, soil, and sediment [12]–[15]. PAHs are easily absorbed at higher amounts on plastics due to π-π interactions [16], [17]. In addition, planar PAHs molecules can demonstrate higher sorption efficiencies than nonplanar HOCs with the same hydrophobicity [18]. Several studies have reported the adsorption of PAHs on plastics in laboratory-scale experiments [9], [19]. In addition, PAHs have been detected in the plastic debris samples collected from the aquatic environment [19]–[21].

In a previous study, the photodegradation of PAHs such as anthracene and benzo(a) pyrene in soil under sunlight was examined [22]; although these were photodegradable, more harmful intermediates such as 1(2H)-acenaphthylenone and 9,10-phenanthrenedione were produced [22]. In addition, another study reported the production of 1-hydroxy-anthraquinone by photodegradation of anthracene [23]. Chapter 2 reported the accelerated photodegradation of PCP and TeCP on the PE sheet and suppressed photodegradation on the suppressed one on the PET and PVC sheets. As the possible cause for this acceleration by PE, hydrogen donation was expected. Owing to the previously reported oxidative photodegradation pathways of PAHs [22], [23], it was reasonable to expect that PE might affect the photodegradation of PAHs.

Although PAHs were detected in the microplastics [19]–[21], the effects of plastics on the photodegradation of PAHs have not been addressed. Therefore, in this chapter, the photodegradation of a PAH on PE was examined to investigate whether photodegradation behaviors of the PAH were affected by PE.

3.2 Experimental

3.2.1 Materials

As a model PAH, NAP (> 97.0% purity) (**Figure 3.1**) and oxy-PAH, naphthacenequinone (NAPQ) (> 98% purity), were purchased from Tokyo Chemical Industry, Tokyo, Japan. PE 1.0 mm in thickness was chosen as a model plastic (Sanplatec, Osaka, Japan). Before use, PE sheets were washed three times with distilled water and then dried at 50 °C. A mixed solvent of 90% (v/v) toluene (> 99.5% purity, Sigma-Aldrich, Mo, US) and 10% (v/v) cyclohexane (> 99.5% purity, TCI) was used to extract NAP and photodegradation intermediates.

3.2.2 Photodegradation test of NAP and NAPQ

The PE sheet was cut to 2.2 mm × 7.0 mm and then put on the bottom of the quartz glass Petri-dishes (diameter 26 mm). Then, 2.0 mL of NAP solution (40.0 mg/L) was added dropwise on the plastic sheets and allowed to stand in a dark place under laminar airflow for 2 hours to vaporize the mixed solvent (**Figure 3.1**). As mentioned in **3.3.2**, NAPQ was produced by photodegradation of NAP, photo degradability of NAPQ was investigated using the NAPQ-adsorbed PE prepared in the same manner of NAP photodegradation method. The NAP-absorbed and NAPQ-adsorbed PE sheets were respectively transferred into the quartz cuvettes and capped with a rubber stopper and then irradiated under UV rays of 32 μW cm^{-2} for 2 hours (λ=254 nm, DM-5, Daishinkogyo, Osaka, Japan). The cuvettes were kept at 15 °C by a cooling plate (CP-120; Scinics Cool Plate, Tokyo, Japan) during UV irradiation time. Three cuvettes were randomly taken for analysis of NAP and NAPQ at each sampling time. For extraction, 2.0 mL of the mixed solvent was added dropwise to the cuvettes. The resulting solution was analyzed by GC-quadrupole mass spectrometry (GC/MS) (GC-8860 and MS-5977B, Agilent Technologies, California, US) under the conditions described in **Table 3.1**. The mass spectrum patterns generated by GC/MS were compared with NIST library data (NIST MS Search) to search for photodegradation products. In the control experiment, a glass plate was used. Experiments without UV irradiation were also carried out.

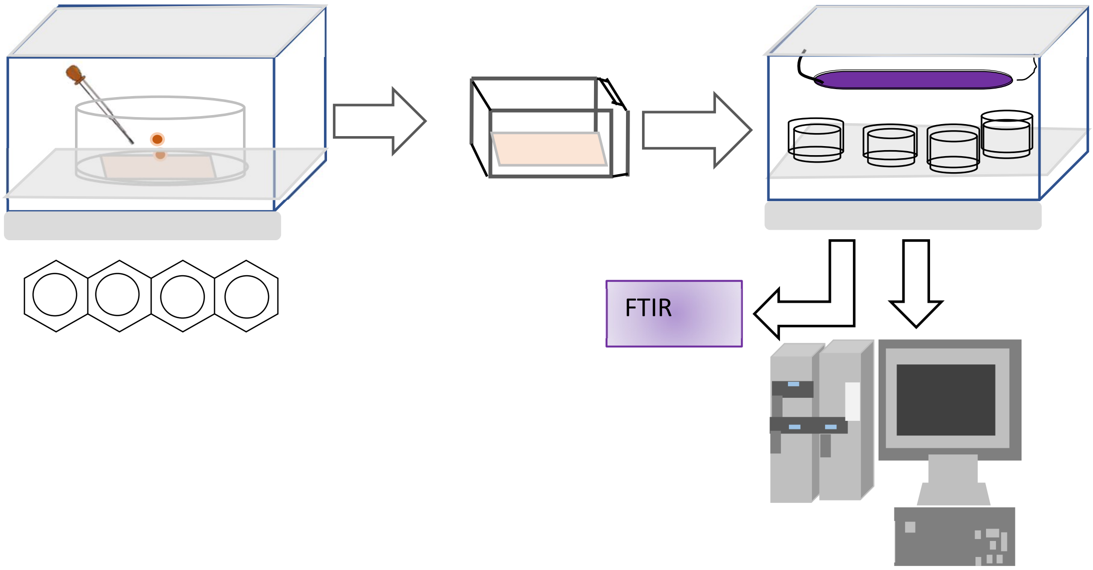


Figure 3.1 Photodegradation of NAP on the PE sheet and measuring technique.

Table 3.1 Analytical condition of GC/MS

Gass chromatograph	GC 8860 (Agilent Technologies, California, US)
Mass spectrometry detector	MSD 5977B (Agilent Technologies, California, US)
Column	HP-5ms (30 m×0.32 mm, 0.25 µm, (Agilent Technology, US)
Inject volume	1 µl (Split ratio15:1）
Inlet temp.	270°C
Pressure	97.3 kPa
Temperature profile	100°C（hold 3min）
	15°C/min to 270°C (hold 4 min)
	20°C/min to 300°C (hold 5min）
Carrier	He, 1.3 ml/min
Ionization	Electron Impact (70 eV)
Scan range	15.0 to 500.0 m/z
Hold time	5.0 min

3.2.3 Analyses

To verify the consecutive degradation pathway of NAP via NAPQ production on PE, the concentration of NAPQ during UV irradiation time was calculated from the degradation of NAP assuming a sequential reaction of NAP to NAPQ.

$$C_{NAP} \xrightarrow{k_1} C_{NAPQ} \xrightarrow{k_2} \text{Further photodegradation intermediates} \qquad (1)$$

where k_1 and k_2 are the photodegradation rate constants for NAP and NAPQ [min^{-1}], respectively, and C_{NAP} and C_{NAPQ} are the NAP and NAPQ concentrations [mg/L], respectively. As the ratio of k_2 to k_1 (0.0111/0.0144) does not equal 1, equation (4) can be derived from the equations (2) and (3):

$$dC_{NAP}/dt = -\, k_1 C_{NAP} \qquad (2)$$

$$dC_{NAPQ}/dt = k_1 C_{NAP} - k_2 C_{NAPQ} \qquad (3)$$

$$\frac{C_{NAPQ}}{C_{NAP*}} = \frac{1}{1-k}\left(e^{-k_2 t} - e^{-k_1 t}\right) + \frac{C_{NAPQ*}}{C_{NAP*}} e^{-k_2 t} \qquad (4)$$

where C_{NAP*} and C_{NAPQ*} are the initial NAP and NAPQ concentrations [mg/L], respectively.

3.3 Results and Discussion

3.3.1 Photodegradation of NAP

The NAP concentration changes on the glass and PE sheets under UV irradiation are shown in **Figure 3.2 (a)** and **(b),** where NAP on the glass and PE sheets decreased along with the irradiation time. However, without UV irradiation, the NAP concentration on the glass and PE sheet did not significantly decrease. These results confirmed that NAP was photodegradable on the glass and PE sheet. Although NAP was degraded on glass, the photodegradation rate on PE was higher than that of glass. The photodegradation of NAP on the glass and PE sheet followed pseudo-first-order reaction kinetics (**Figure 3.2 (c)**), similar to the photodegradation of anthracene in soil [22]. The photodegradation rate constants on glass (k_{glass}) and PE (k_{PE}) were 0.0101 and 0.0144 min^{-1}, respectively (**Figure 3.2 (c)**); these values showed an acceleration of NAP photodegradation by PE.

Accelerated photodegradation of PCP and TeCP was observed for PE, as described in Chapter 2. PE produces polymer alkyl radicals by removing hydrogen atoms by UV irradiation [24], [25]. Possible mechanisms on the accelerated photodegradation of NAP on the PE sheet might be (i) hydrogen donation by PE and/or (ii) production of alkyl radicals and hydroxyl radicals produced by the reaction of the alkyl radical and oxygen (**Figure 2.6**).

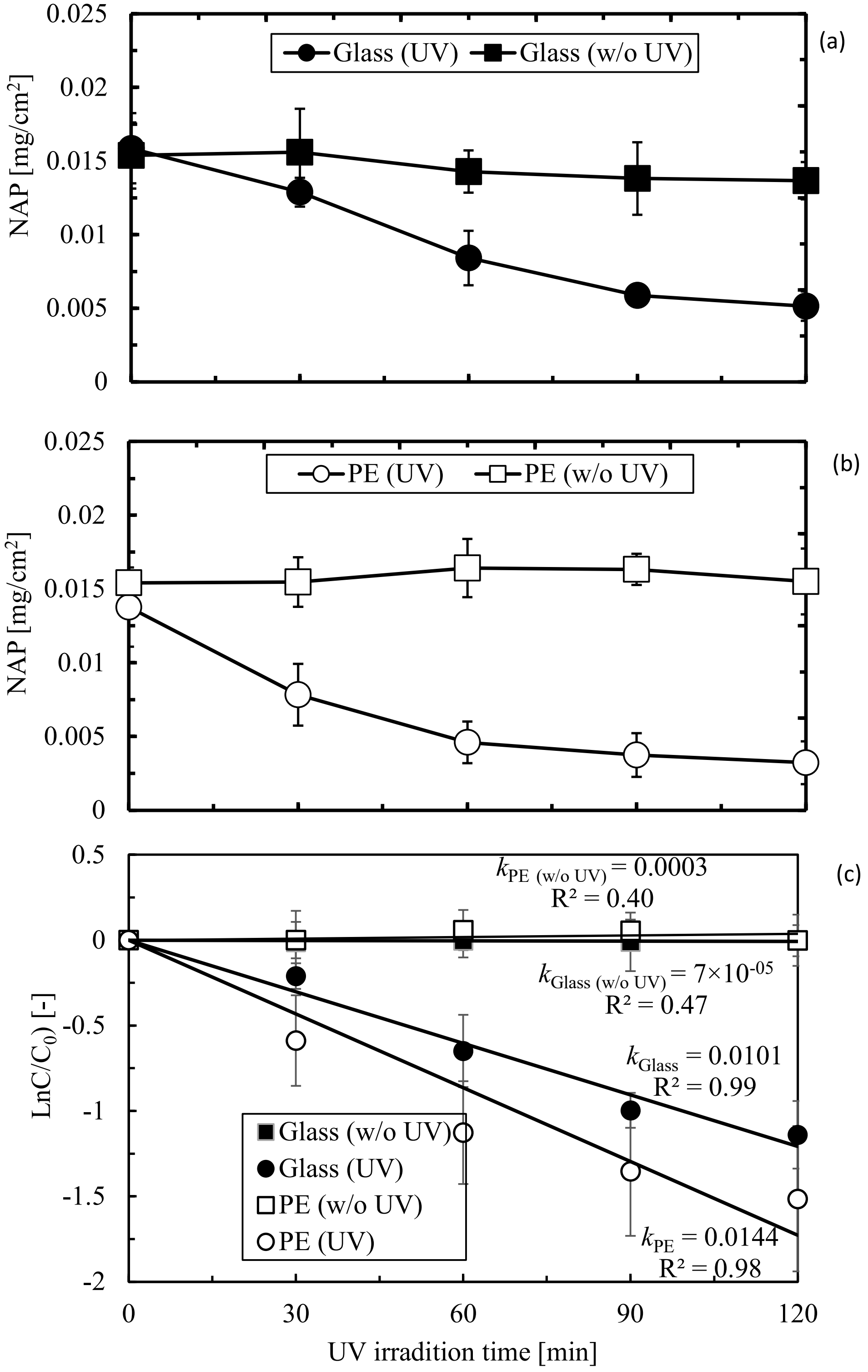


Figure 3.2 Change of remaining NAP concentration on (a) the glass and (b) PE sheet and (c) the result of photodegradation behavior analysis by the first-order reaction kinetics. Bars indicate standard deviation (n=3).

3.3.2 Photodegradation intermediates produced from NAP

To investigate the photodegradation pathways of NAP, its photodegradation intermediates were analyzed. **Figure 3.3** shows the total ion chromatogram of NAP and its photodegradation intermediates obtained from the PE sheet after 120 min of irradiation. There were the two major peaks at A and C. Based on the mass spectra of peak A, this was expected to be NAPQ (**Figure 3.4**). As its authentic sample showed the same retention time and mass spectra, peak A was identified as NAPQ. In addition, the mass spectra of peaks B and D were respectively identical for 1-phenyldibenzofuran and 2,5-diphenyl-1,4-benzoquinone. These results showed that NAP was degraded via the production of the oxygenated NAP, with NAPQ as an intermediate. This result agreed with the previous studies reporting the production of oxygenated PAHs containing quinone structure by photodegradation of the precursor PAHs [26].

Although NAPQ was detected on the glass plate, its abundance was negligible (**Figure 3.3**). This may be because NAPQ can easily evaporate from the glass plate, as described in **3.3.3**. In addition, it has been reported that oxygenated PAHss are more carcinogenic than the precursor PAHs [27], [28]. The carcinogenicity of NAPQ is unknown; however, these results provided evidence that plastics may hold photodegradation intermediates of PAHs, although some of them are highly toxic. As for the possible reason for the retainment of photodegradation intermediates, this might be their strong interaction with PE via π - π interaction, hydrophobic interaction, and hydrogen bonding [11], [30]. The nascent hydrogen radical generated from plastics might react with peroxy radical or alkyl peroxide radical, altering NAP degradation pathways producing oxygenated intermediates.

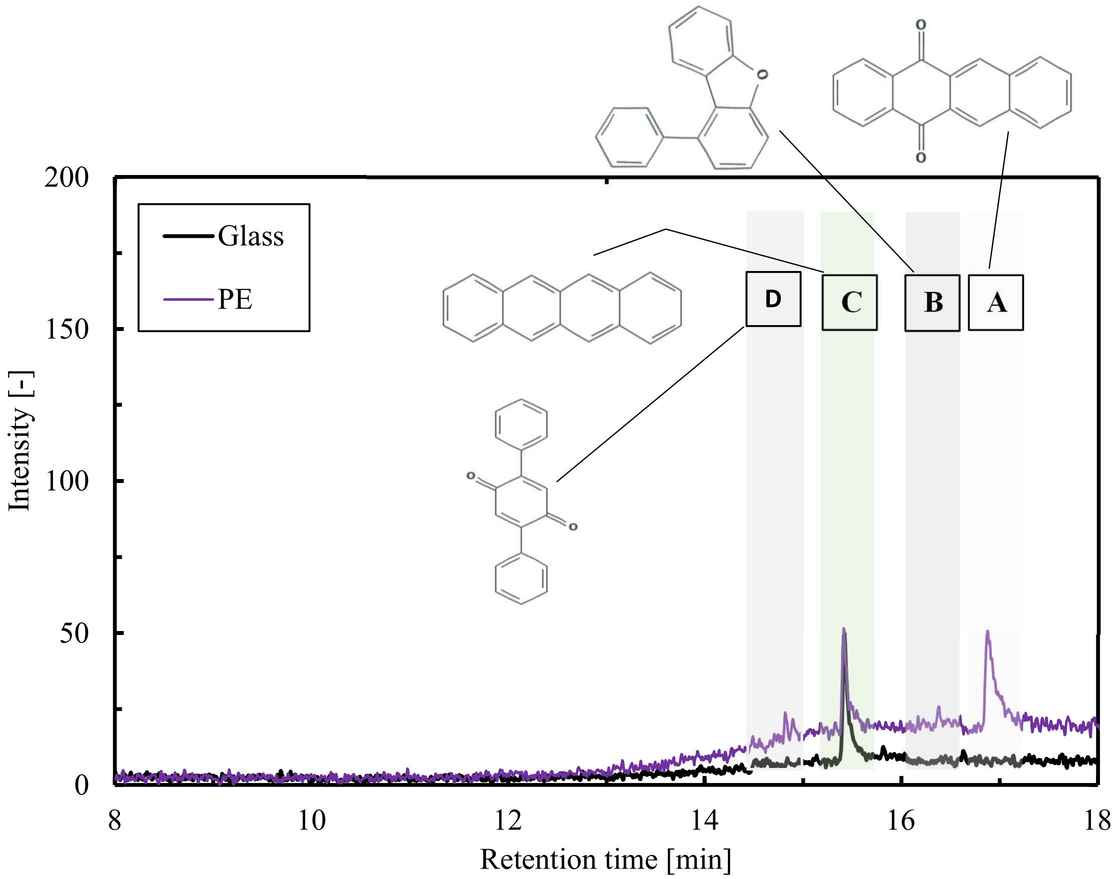
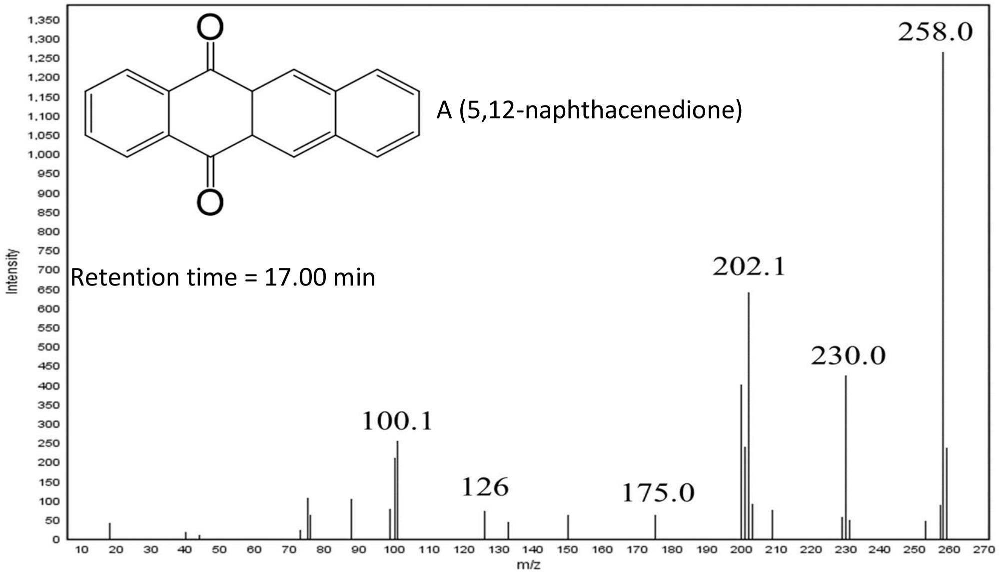


Figure 3.3 Total ion chromatogram of the NAP and its photodegradation intermediates on PE after 120 min of UV irradiation.



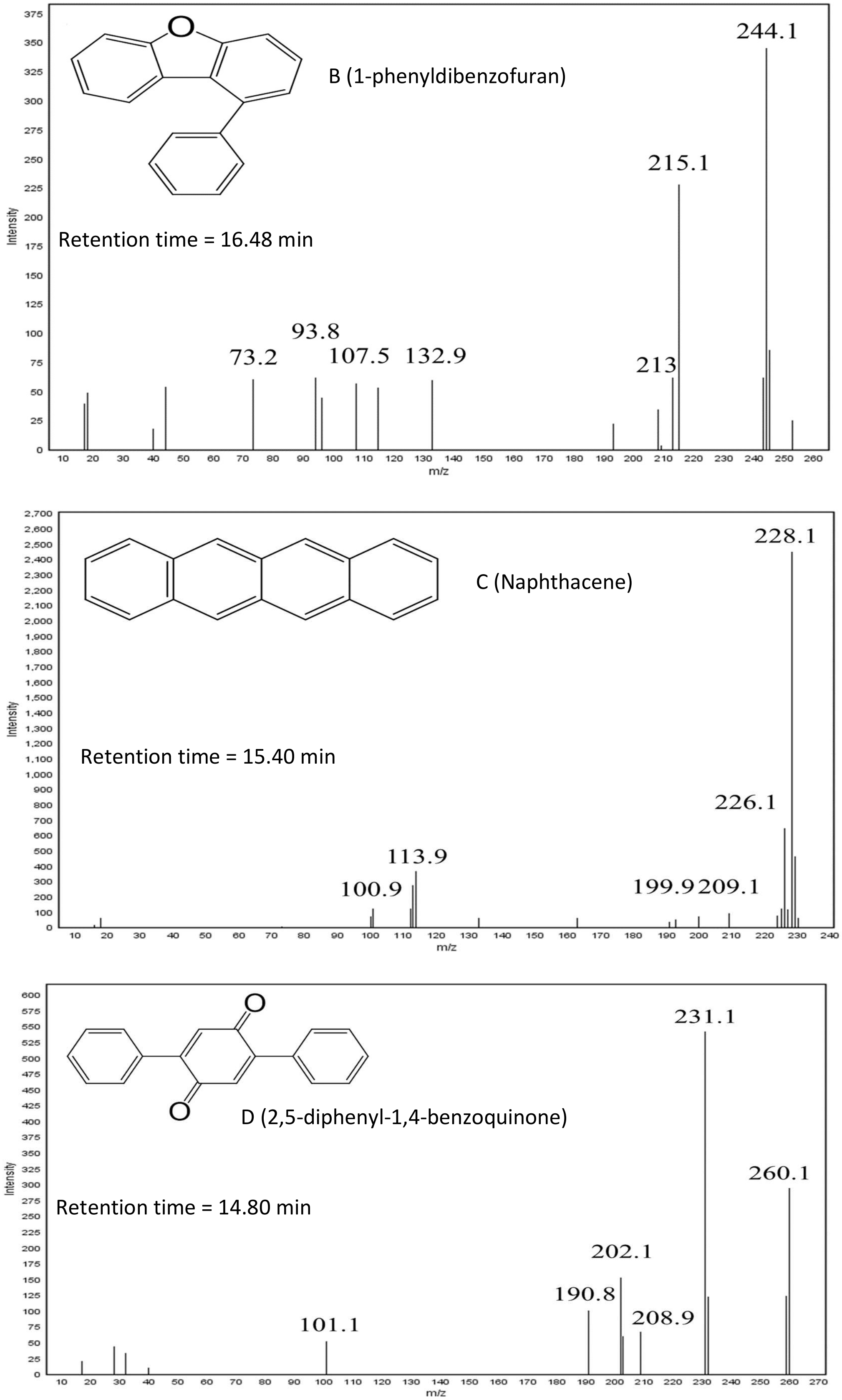


Figure 3.4 Mass spectra of naphthacene and the 3 photodegradation intermediates.

3.3.3 Photodegradation pathways of NAP

As NAPQ was detected on the glass plate and PE sheet, it was surmised that photodegradation NAP produces NAPQ; then, NAPQ is further degraded (Reaction 1).

NAP → NAPQ → Further photodegradation intermediates such as

2,5-dipheny-l-1,4-benzoquinone (Reaction 1)

In this study, a difference in the photodegradation pathways of NAP was not observed between the glass and PE sheet; however, it was expected that the photodegradation of NAPQ might also be accelerated by the PE sheet. Therefore, photodegradation of NAPQ was examined on the glass plate and PE sheet.

Owing to the vaporization of NAPQ from the glass, the photodegradation rate constant (k_{Glass}) may include NAPQ loss, and therefore, a comparison of photodegradation rate constants was not possible (**Figure 3.5**). However, considering the vaporization rate constants ($k_{\mathrm{Glass\ w/o\ UV}}$), the photodegradation rate constants of NAPQ on the glass plate and PE sheet seem to be the same.

In the photodegradation experiment of NAPQ on the PE sheet, the intermediate compounds 1-phenyldibenzofuran, and 2,5-dipheny-l-1,4-benzoquinone were detected on the photodegradation of NAP were not observed. However, the concentration of NAPQ was decreased compared to samples without UV irradiation.

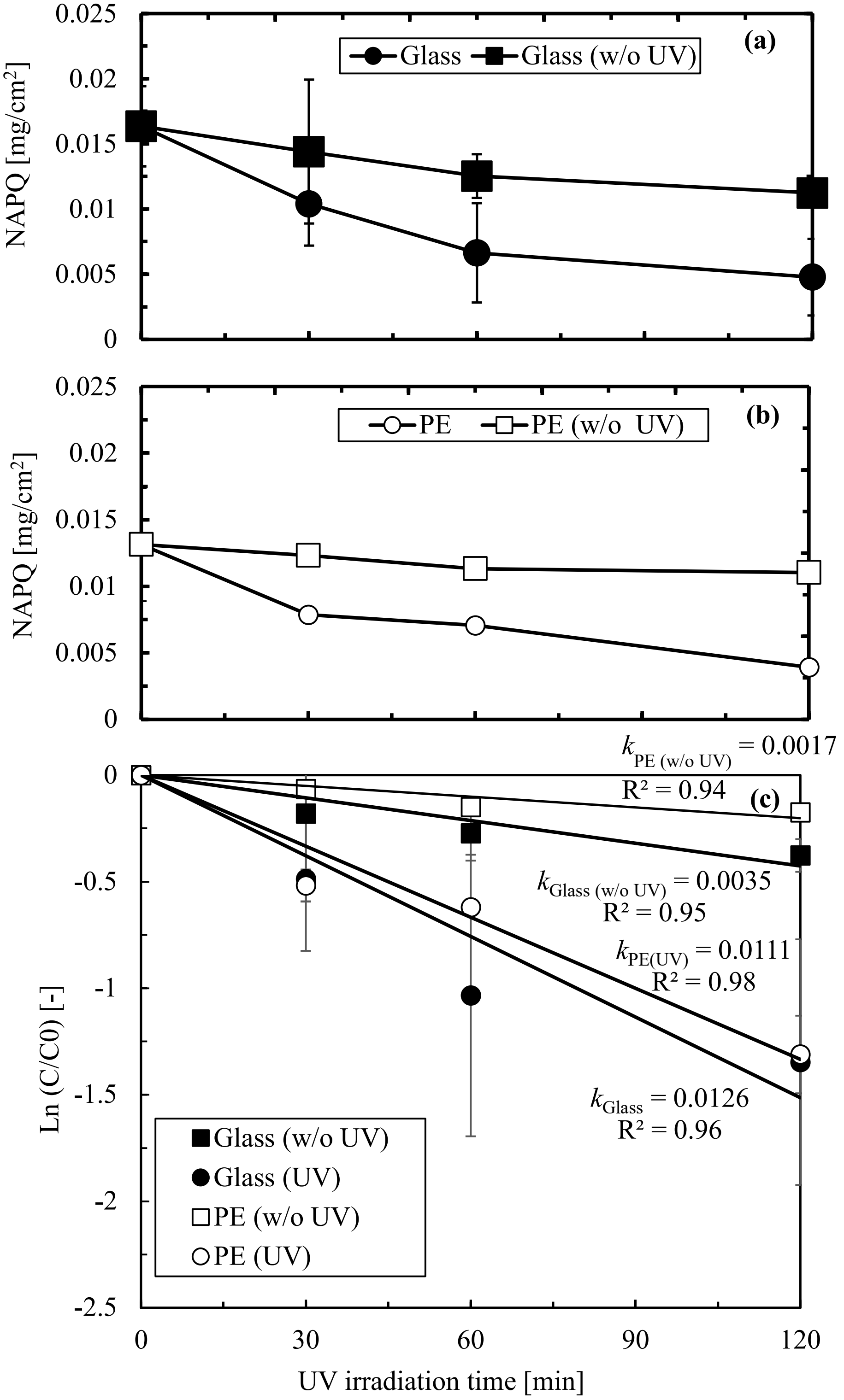


Figure 3.5 Change of remaining NAPQ concentration on (a) the glass and (b) PE sheet and (c) the result of photodegradation behavior analysis by the first-order reaction kinetics. Bars indicate standard deviation (n=3).

Next, to verify the hypothesized photodegradation pathway of NAP (Reaction 1), a sequential reaction analysis was carried out to estimate a NAPQ concentration using the photodegradation rate constants for NAP and NAPQ. Because the detection level of NAPQ was negligible on the glass plate, here the degradation behaviors on the PE sheet were analyzed. As shown in **Figure 3.6,** the estimated NAPQ concentration was higher than that of the actual NAPQ concentration, thereby suggesting the existence of other photodegradation pathways of NAP. As described in **Figure 2.6**, PE can provide alkyl, hydrogen, and hydroxyl radicals, and this might result in other degradation pathways from NAP, though evidential degradation intermediates are still in the quest.

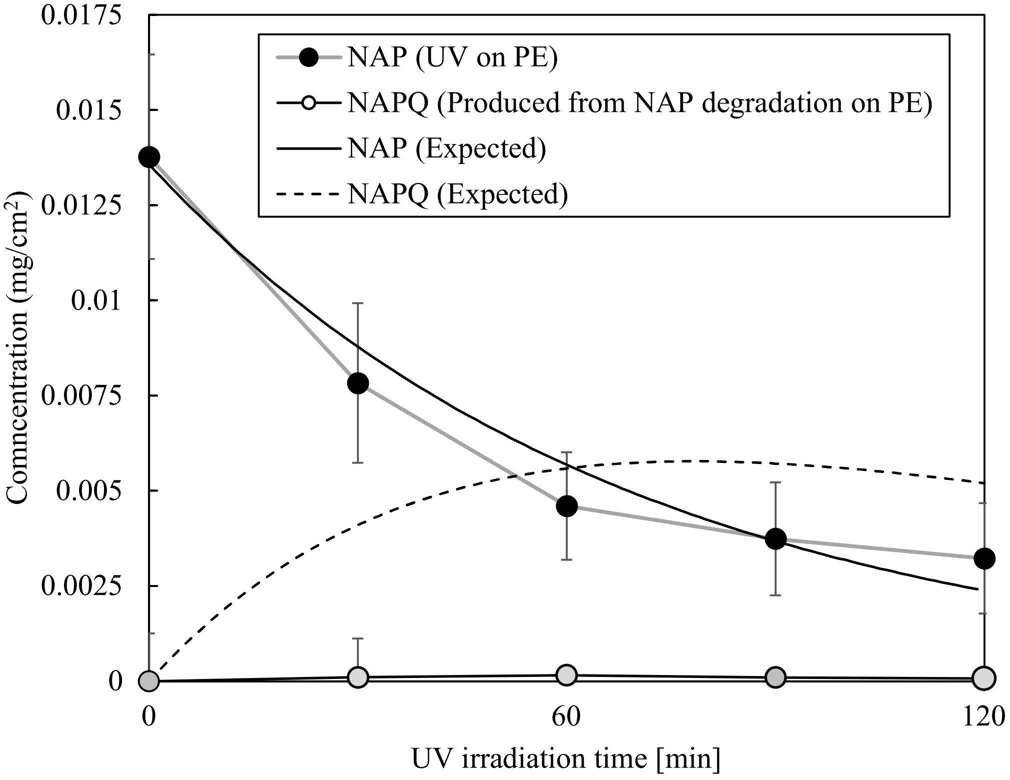


Figure 3.6 Simulation of NAP photodegradation pathway and production NAPQ on PE following first-order reaction. Bars indicate standard deviation (n=3).

3.4 Conclusions

The photodegradation of NAP on the glass plate and PE sheet was confirmed. The photodegradation rate constant of NAP on the PE sheet was higher than that on glass, likely due to the radicals produced by the photolytic degradation of the PE structure. The photodegradation of NAP produced the oxygenated NAP and NAPQ. Surprisingly NAPQ was remarkably abundant on the PE sheet but not the glass plate. As oxygenated PAHs may be more toxic than the precursor PAHs, these results confirm that attention should be paid to retaining organic pollutants and their photodegradation intermediates on plastics for risk management. Photodegradation pathways of NAP via production of NAPQ were checked by the sequential reaction analysis; however, unknown degradation pathways adding to the production of NAPQ might exist.

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Chapter 4

Effects of the aging of plastics on the photodegradation of a chlorophenol

4.1 Introduction

The global estimated mass of the floating plastic particles indicates that the amount of plastic waste entering the ocean from land ranged from 4.8 to 12.7 Mt in 2010 [1]. Floating plastics are continuously fragmented into smaller plastic pellets, such as microplastics, through aging processes such as physical abrasion [2], [3], ocean turbulence [4], UV photo-oxidation [3], and biodegradation [5]. Thus, the proportion of such fragments in total marine debris is growing [3], [6]. Fragmented plastics adsorb hydrophobic organic pollutants such as PAH [7], PCBs [8], and DDT [9] in seawater with a 10^5–10^6 concentration factor [10]. Microplastics can enter the food chain through ingestion by aquatic organisms such as deposit and suspension feeders [11], acting as organic pollutant carriers. Therefore, the interaction of organic pollutants and microplastics must be studied.

Microplastics floating in seawater are exposed to sunlight, and the photodegradation of adsorbed pollutants may occur. In addition, microbial degradation may occur; however, hydrophobic organic pollutants, such as PAH and PCBs, are generally recalcitrant to microbial degradation. Furthermore, chemical degradation caused by natural oxidants, such as hydroxyl radicals, may occur; however, photodegradation is generally dominant in the environment [12]. Therefore, this research focused on photodegradation. In chapter 2, plastics effect on the photodegradation of tetra- and PCP adsorbed on plastic sheets showed that the degradation was affected by the texture of the plastic sheets. The photodegradation of CPs was accelerated on PE sheets but suppressed on PVC and PET sheets. Hydrogen donation is a possible cause of the acceleration of the photodegradation on the PE sheet. Another study investigated the photodegradation of polystyrene films containing brominated flame retardants, such as decabromodiphenyl ether and tetrabromobisphenol A, observing 14 brominated products, including tetrabromoacetophenone and bromobenzoic acid, via bromination and oxidation of polystyrene [13].

Aging processes can change the chemical and physical characteristics of plastics [14], causing plastic fragmentation in marine environments. Aging increases the specific surface area and oxygen content of plastics [15], changing the color and transparency of the plastic. A previous study indicated that UV radiation increased the number of carbonyl groups in PP and strengthened its yellowness index [15], [16]. In addition, plastic additives such as di-isobutyl phthalate, dimethyl phthalate, and diethyl phthalate can leach into aquatic environments [18]. These changes suggest that aging affects the photodegradation of organic pollutants adsorbed on plastics. Ultimately, all plastics are aged in marine environments. Despite the importance of understanding the effects of the aging of plastics on the photodegradation of organic pollutants adsorbed on plastics, previous studies [13],[14] have not addressed this issue.

In this study, the photodegradation of an organochlorine adsorbed on virgin and aged plastic sheets was investigated to determine the effects of plastic aging on organochlorine photodegradation. Chemical and physical properties of plastics, such as functional groups, surface roughness, and transparency caused by aging, were investigated to establish the aging effects of plastics. Owing to the possible elution of the plastic additives in the marine environment, the effects of plastic additives were also investigated using methanol-extracted plastics.

4.2 Experimental

4.2.1 Materials

For the materials, 1.0-mm-thick Virgin PE, PVC, and PET sheets were purchased from the Sanplatec Corp., Japan. This thickness was chosen as the thickness of microplastics is generally lower than 5 mm. Each sheet was washed thrice with distilled water before use and dried at 50°C. TRiCP (Tokyo Chemical Industries, Tokyo, Japan) was used as the model organochlorine pollutant.

4.2.2 Plastic sample preparation and additive extraction

Plastics drift in oceans and are distributed at shorelines and beaches by tides [18]–[22]. Aging treatments need to reproduce both dry and wet conditions; however, our aging test chamber could not reproduce wet conditions. Therefore, artificially aged plastics were prepared under dry conditions in this study. Aged plastic samples were prepared by irradiating PE, PVC, and PET sheets at an intensity of 75 mW cm^{-2} in a Q-SUN Xenon test chamber (Q-SUN1000, Q-panel, China) at 40°C and 50% humidity for 24 h. The effects of additives in the PE, PVC, and PET sheets were examined using additives extracted from the plastic samples. Briefly, each plastic sheet (approximately 5 g) was immersed in 50 mL of methanol at 25 °C for 72 h. Next, 2-mL samples of the methanol extracts containing plastic additives equivalent to 0.20 g per plastic sheet were decanted onto the 0.50 g virgin plastic sheets. Additive-spiked plastic samples were obtained by evaporating the methanol at 25 °C for 60 min in a laminar airflow chamber. Additionally, the plastic samples from which additives had been removed by methanol extraction were tested after methanol evaporation.

4.2.3 Photodegradation

All plastic sheet samples were cut into circles (diameter, 26 mm). The circular plastic sheets were placed at the bottom of quartz glass Petri dishes (diameter, 26 mm), and TriCP was then adsorbed onto the plastic sheets by decanting 2-mL samples of an *n*-hexane solution containing 100 mg L^{-1} TriCP onto the plastic sheets. After *n*-hexane evaporation in a laminar airflow chamber at 25°C, the Petri dishes were covered with quartz glass lids and placed in a Navis Schreiner photochemical reactor (Model DM-05, Daishin Kogyo Co., Ltd., Japan) (**Figure 4.1**) equipped with a 10 W low-pressure UV lamp (Model: NEC GL-10; UV-C) emitting 254 nm UV light at 32 $\mu W/cm^2$. Although the tested TriCP concentration and the light intensity utilized may be higher than that in the actual environment, we carried out photodegradation experiments under this condition because our objective was to determine the effects of plastic aging on the organochlorine photodegradation rate rather than to precisely measure the photodegradation rate.

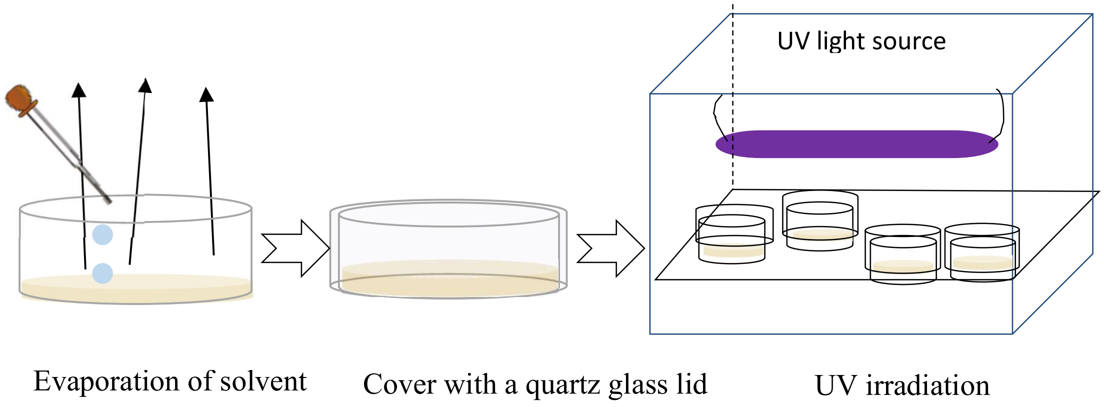

Figure 4.1 Experimental setup for photodegradation of TriCP.

4.2.4 Characterization of plastic sheets

Surface texture changes of the plastic sheets were investigated. The plastic sheet samples were placed in a carbon coater in a vacuum and coated with a carbon layer (thickness, approximately 2 nm) (Meiwa Forsis CADE, MeiwaForsis Co., Ltd., Tokyo, Japan). The samples were examined using field-emission scanning electron microscopy after carbon coating (FE-SEM; High-Tech S-5200, Hitachi, Tokyo, Japan). Images were acquired at 3.0 kV to avoid charging effects during image acquisition. FE-SEM images of each sample were used to estimate the changes in each plastic surface. The images were analyzed by the local surface roughness method [23] using the ImageJ 1.53a SurfCharJ plugin (http://imagej.nih.gov/ij). The arithmetic mean deviation (R_a) and skewness (R_sk) were estimated using the following equations [24]:

$$R_\mathrm{a} = \frac{1}{N_x N_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} \left| Z_{ij} \right| \qquad (1)$$

$$R_\mathrm{sk} = \frac{1}{Rq^3} \frac{1}{N_x N_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} Z_{ij}^3 \qquad (2)$$

$$R_\mathrm{q} = \left(\frac{1}{N_x N_y} \sum_{i=1}^{N_x} \sum_{j=1}^{N_y} Z_{ij}^2 \right)^{1/2} \qquad (3)$$

where N_x is the arithmetic mean deviation for the x-axis, N_y is the arithmetic mean deviation for the y-axis, Z_{ij} represents the assessed surface, and R_q represents the kurtosis.

Although the TriCP distribution in the plastic sheets was not studied, it is plausible that a proportion of the added TriCP could enter the sheets by penetrating the TriCP-containing *n*-hexane. The transparency of the plastic sheet was therefore examined by measuring the intensity of the transmitted light with a UV meter (CUSTOM, UV-340c, Taiwan). The UV meter was placed 10 cm below a UV light source. The plastic sheet samples were placed on the UV sensor, and UV attenuation was determined. An FT-IR spectrometer (IRPrestige-21, Shimadzu, Japan) equipped with a tungsten iodide light source was used to investigate the changes in functional groups on the surfaces of the plastic sheet samples. The FT-IR spectra were recorded from 400 to 4000 cm^{-1} at a nominal resolution of 4 cm^{-1} for a total of 32 scans.

4.2.5 Analyses

Changes in the TriCP concentration caused by UV irradiation were determined as follows. Extraction was performed by pouring methanol into a Petri dish containing a plastic sample. The methanol extract was mixed with 0.1% formic acid (pH 2.70) solution at a volume ratio of 4:1. Next, 100 μL of the sample mixture was subjected to chromatography on an octadecyl silica column (Cosmosil 5C18-AR-II, 4.6 × 150 mm, Nacalai Tesque Inc., Japan) at a flow rate of 1.0 mL min^{-1}, with a mixture of methanol and formic acid (4:1 volume ratio) as the mobile phase. A UV-visible detector with a wavelength of 254 nm (SPD-10A, Shimadzu, Japan) was used for detection.

4.2.6 Statistical analysis

ANOVA and subsequent Tukey tests were performed to determine the statistical significance of the photodegradation rate constant. Normal probability distribution and homogeneity of variance were assumed.

4.3 Results and Discussion

4.3.1 Comparison of photodegradation rates of TriCP on virgin and aged plastics

The TriCP photodegradation on virgin and aged plastic sheets followed pseudo-first-order reaction kinetics is shown in **Figures 4.2(a)** and **(b)**. The rate constant for TriCP photodegradation on glass was 1.6×10^{-2} min^{-1}. The recorded rates of degradation on virgin plastic sheets were 2.8×10^{-2} min^{-1}, 8.9×10^{-3} min^{-1}, and 1.2×10^{-2} min^{-1} on the PE, PET, and PVC sheets, respectively (**Table 4.1**). The photodegradation constants indicate that photodegradation was accelerated on the virgin PE sheet but suppressed on the PET and PVC sheets. This is consistent with the results of a previous study on the photodegradation of tetra and PCP on PE, PET, and PVC sheets; the acceleration on PE might be attributed to hydrogen

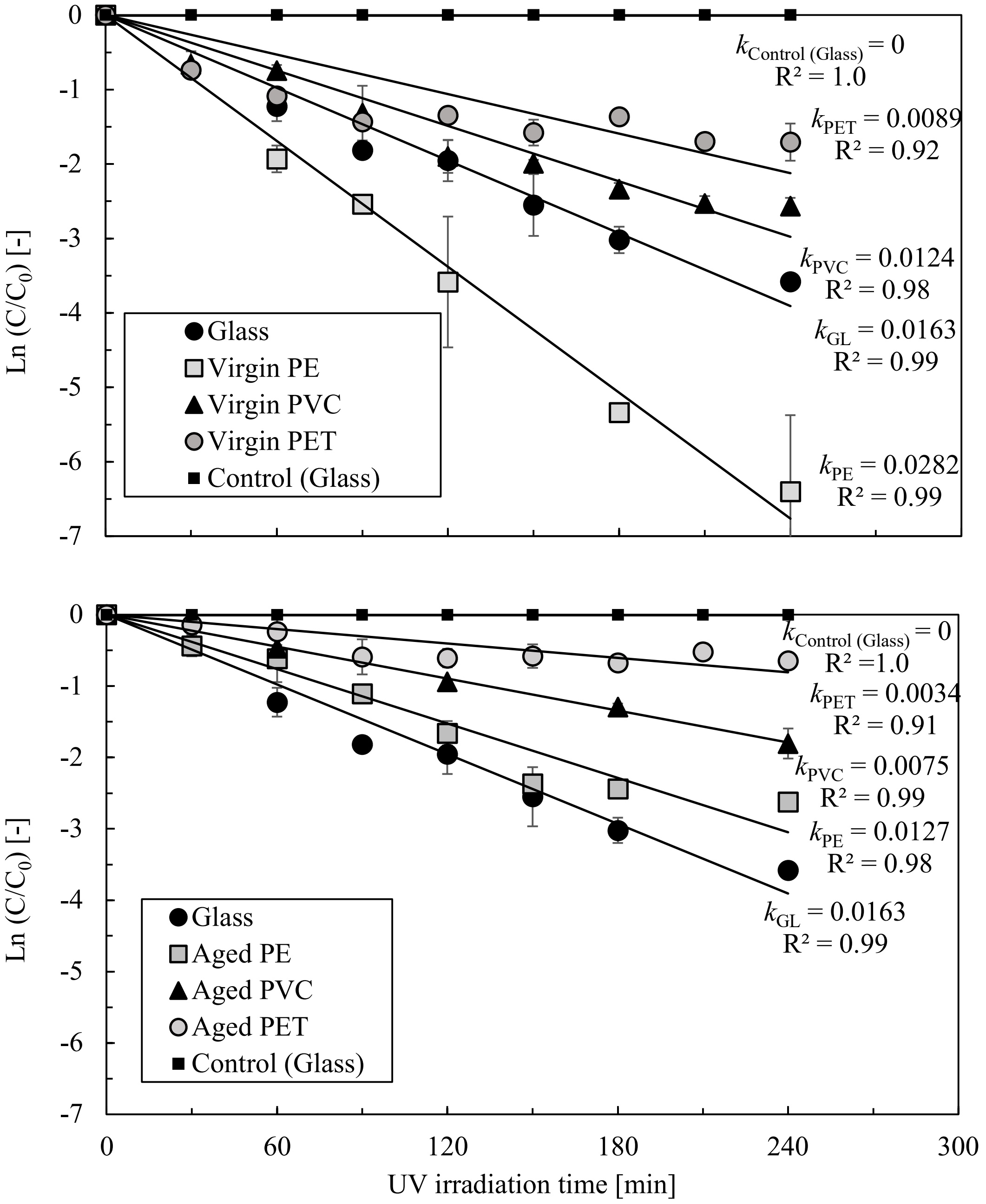

Figure 4.2 Photodegradation of TriCP on PE, PET, and PVC sheets: (a) virgin and (b) aged plastics. Bars indicate standard deviations (n = 3) except the aged PVC and PET (n=2). Bars for the aged PVC and PET indicate the differences between the averaged and measured values.

donation (**Figure 2.6**). The reason for the large error bar for the virgin PE after 120 min is unknown; however, it can be attributed to independent samples. The photodegradation rate constants on aged PE, PET, and PVC sheets were 1.2×10^{-2} min^{-1}, 3.4×10^{-3} min^{-1}, and 7.5×10^{-3} min^{-1}, respectively; these rates are lower than those of the corresponding virgin plastic samples. Although photodegradation of TriCP was accelerated on virgin PE ($p = 1.9 \times 10^{-6}$), aging significantly suppressed photodegradation on PE ($p = 1.9 \times 10^{-6}$). These results confirm that organochlorine photodegradation is suppressed on aged plastics.

Such degradation suppression can be attributed to the surface textural changes, causing UV shading and interception due to changes in the functional groups in the plastic sheets. Therefore, the changes in surface roughness, skewness, transparency, and functional groups in the aging plastics were investigated.

Table 4.1 TriCP Photodegradation rate constants [min^{-1}] on plastic surfaces

Plastic name	Virgin	Aged	Methanol-treated	Extracted additive-spiked
PE	2.8×10^{-2}	1.2×10^{-2}	2.2×10^{-2}	2.3×10^{-2}
PVC	1.2×10^{-2}	7.5×10^{-3}	7.2×10^{-3}	2.6×10^{-3}
PET	8.9×10^{-3}	3.4×10^{-3}	8.7×10^{-3}	5.2×10^{-3}

4.3.2 Changes in surface textures

Figure 4.3 indicates that aging changed the surface textures of all the plastic samples. Aging treatment resulted in valley formation (R_{sk}). Valleys can shade light; therefore, surface changes could contribute to the decreased photodegradation rates on the aged plastics (**Figure 4.2**). Aging increases the plastic's surface roughness (R_{a}) by causing cracks, crevices, and morphological changes [25]. Analysis of the changes in surface roughness showed that the R_{a} values decreased ($p < 3.3 \times 10^{-5}$) (**Figure 4.4(a)).** This might be because of differences between our artificial and natural aging processes. In aquatic environments, plastic additives can leach during aging [17]. The plastic samples did not come into contact with water in artificial aging with a Q-SUN Xenon test chamber, indicating that the treatment might simulate aging on lands under fine weather rather than that in aquatic environments. However, the aging treatment led to increases in the R_{sk} values at the surfaces of all the plastic sheets ($p < 0.047$) (**Figure 4.4**(**b**)), evidential for the observed valleys (**Figure 4.3)**.

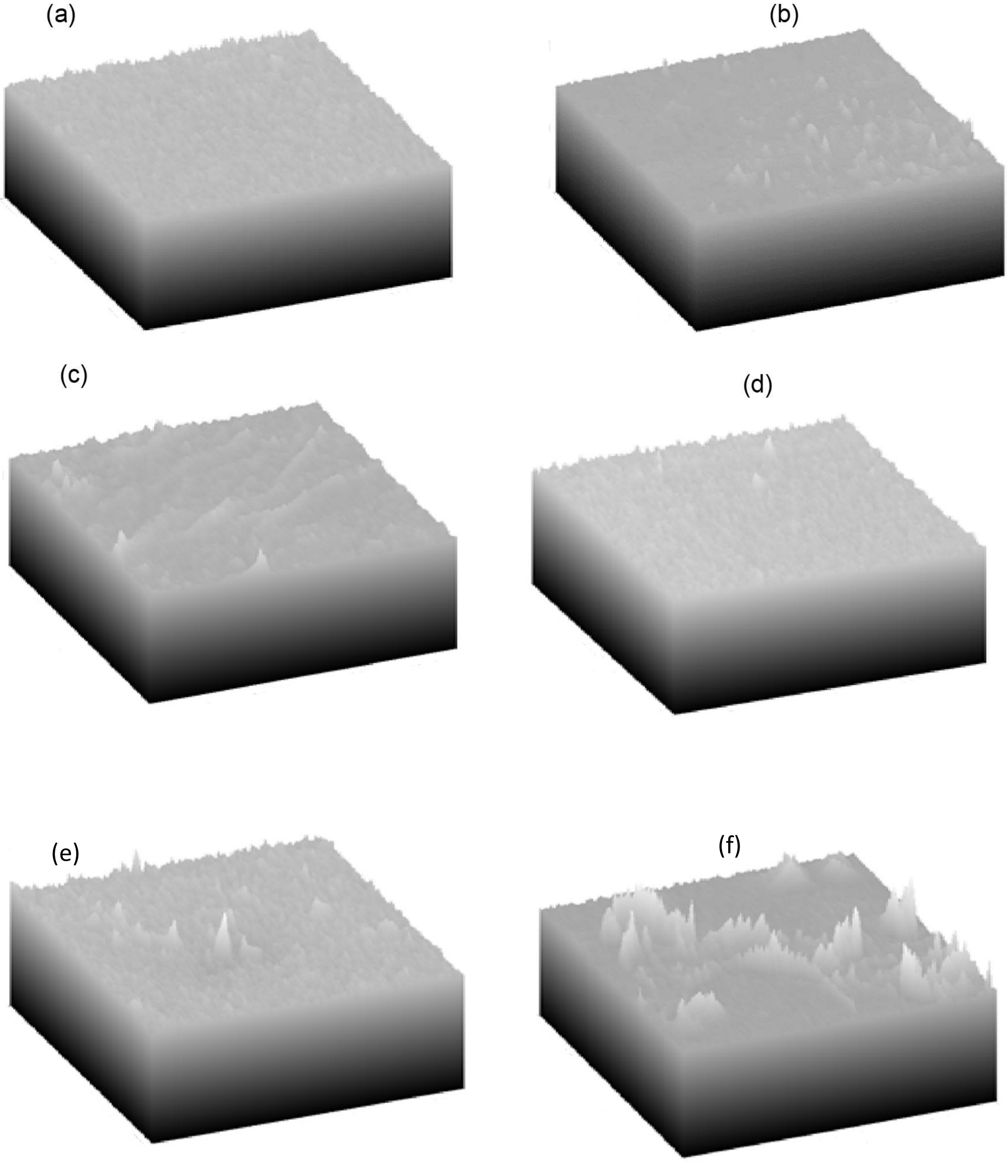

Figure 4.3 Three-dimensional SEM images of (a) virgin PE, (b) aged PE, (c) virgin PVC, (d) aged PVC, (e) virgin PET, and (f) aged PET sheet surfaces.

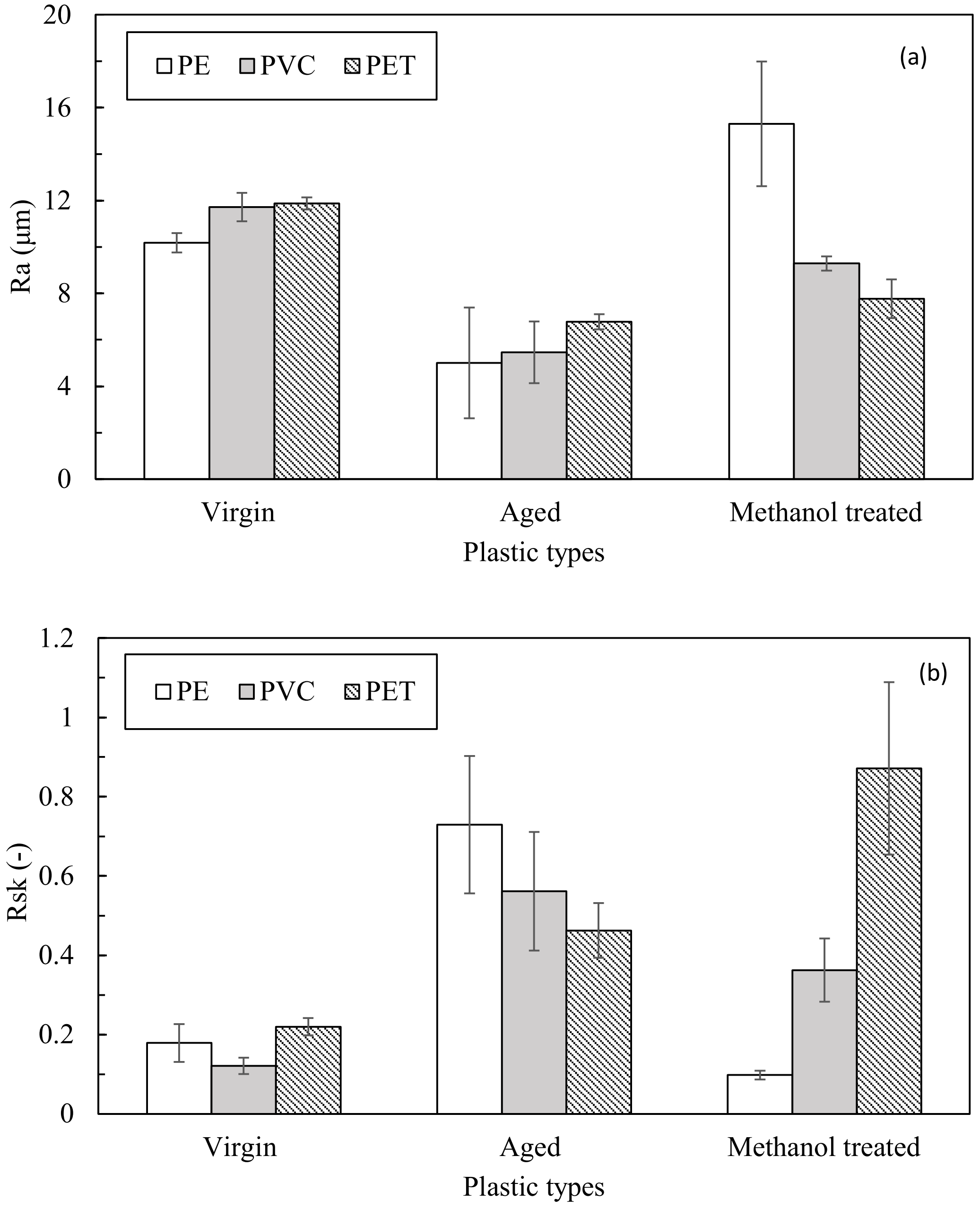

Figure 4.4 Changes in the plastics (a) surface roughness (R_a) and (b) skewness (R_{sk}) caused by aging and methanol extraction. Bars indicate standard deviation ($n = 3$).

The methanol extraction process did not alter the R_{sk} value of PE but increased that of PET and PVC ($p < 0.049$). The extraction treatment increased the R_a value of PE ($p = 3.0 \times 10^{-5}$) but not that of PET and PVC. A comparison of the TriCP photodegradation rate constants on the virgin and methanol-extracted plastic samples indicated that the latter samples produced lower photodegradation rate constants (**Table 4.1**). We do not have any evidence as to whether R_a or R_{sk} significantly reduce photodegradation rates. However, the photodegradation rate constants decreased when the R_a or R_{sk} values increased due to aging or methanol extraction (**Figure 4.4**(**a**) and (**b**)).

A comparison of the TriCP photodegradation rate constants on the methanol-extracted plastic samples and aged plastic samples indicates that the rate constants of the methanol-extracted plastic samples were higher than those of the aged plastic samples (**Table 4.1**). However, the methanol extraction process significantly increased the R_a value for PE ($p = 3.0 \times 10^{-5}$) and R_{sk} values for PET and PVC ($p < 0.049$) (**Figure 4.4**(**a**) and (**b**)). This inconsistency can be attributed to the fact that certain plastic additives that suppress the TriCP photodegradation can be removed by methanol.

4.3.3 Suppression of photodegradation by the methanol extract

The TriCP photodegradation was suppressed by spiking the plastic samples with the methanol extract (**Table 4.1**). In the manufacturing of plastics, anti-UV agents, free-radical scavengers, and hydroperoxide decomposers, such as hydroxybenzophenones, hydroxyphenylbenzotriazoles, and derivatives of phenyl salicylates are added as radical scavengers to hinder plastic photodegradation [14], [26]. These scavengers penetrate the material, and energy is rapidly dissipated because of the fall in UV intensity; therefore, degradation is concentrated near the surface. Although we did not analyze the methanol extracts of each plastic sample, it is reasonable to expect that commercially obtained virgin plastic sheets contain such agents.

4.3.4 Changes in transparency

Aging changes color [14] and opacity of plastic surfaces [16]. All plastic sheets possessed yellowish discoloration in this study. As the transparency of the PVC sheet to UV could not be measured using our method, only the virgin and aged PE and PET sheets were tested. We established that the aging treatment reduced the transparency of the PE and PET sheets by approximately 4 μW m^{-2}; however, methanol extraction did not affect the transparency (**Figure 4.5**). These results indicate that a decrease in transparency can suppress the TriCP photodegradation rate in aged plastics. The photodegradation rate constants on the PE and PET sheets were reduced by 46% and 56%, respectively (**Table 4.1**) by the aging treatment. Although the reduced transparencies of the PE and PET sheets remained the same at approximately 4 μW m^{-2}, the reduction percentages were different (70% for PE and 0% for PET) (**Figure 4.5**). This suggests that the transparency reduction did not primarily suppress photodegradation.

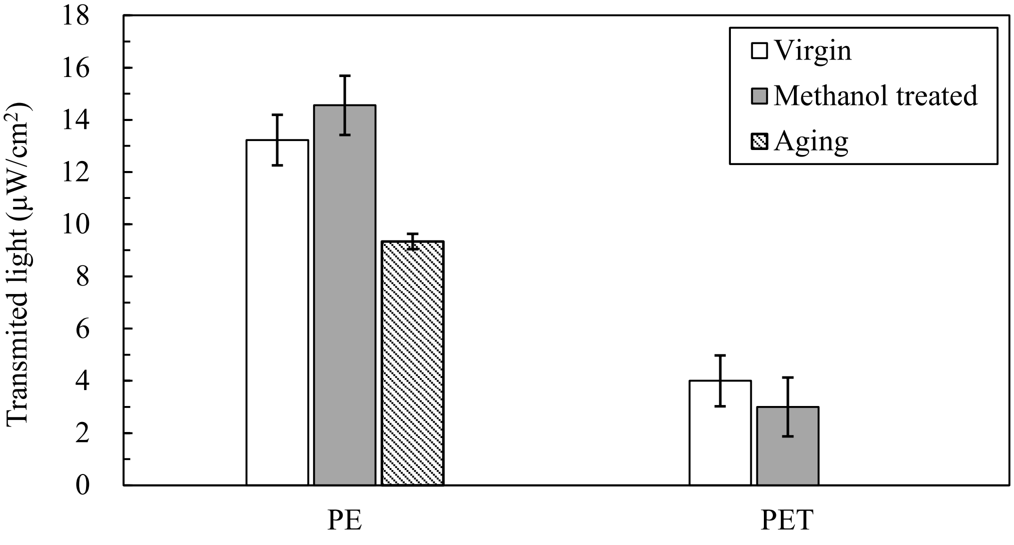

Figure 4.5 Changes in UV transparency of PE and PET sheets caused by aging. Bars indicate standard deviation (n = 3).

4.3.5 FT-IR analysis of aged plastic sheets

Polymer degradation is initiated by C–H bond breakage. During propagation, carbonyl groups are formed during the aging of plastics through Norrish Type I and II reactions [14]. This leads to plastic fragmentation [3] via termination [14], [27]. UV irradiation increases the plastic fragmentation rate because of the production of intramolecular polymers, hydroperoxy, and hydroxyl radicals [14], [26], slowing hydrogen abstraction [28]. The FT-IR spectra of the model plastic samples indicated that molecular changes were caused by plastic aging (**Figure 4.6**(**a**)–(**c**)).

In the spectrum of the aged PE sheet, peaks corresponding to alkene stretching vibrations appeared at 990 cm^{-1} and 890 cm^{-1} (**Figure 4.6**(**a**)). These peaks provide evidence of hydrogen abstraction caused by aging. As dechlorination occurs during the photodegradation of CPs on PE [29], the suppression of TriCP photodegradation on an aged PE surface could be caused by decreased hydrogen donation. In addition, a new peak was observed at 1120 cm^{-1}, corresponding to –C=O aldehyde stretching or carboxylic acid ester bending. Magnification peaked at 2660 cm^{-1}, corresponding to –C–H aldehyde stretching or carboxylic acid ester bending. These peaks normally appear in the spectra of aged plastics [30], possibly increasing and decreasing the surface skewness and transparency, respectively.

The PVC aging weakened the C–H bending peaks at 638 cm^{-1} and 705 cm^{-1} in the PVC spectrum (**Figure 4.6(b)).** In addition, the signals at 1400 cm^{-1} from C–H bending, 1580 cm^{-1} from cyclic alkenes, and 1716 cm^{-1} from C–O bending were weakened. This suggests that aging causes unsaturation of PVC. Dehydrochlorination and C=C formation in PVC have been previously reported [31]; our desaturated data agree with these findings. However, the C=C peak did not appear in the aged PVC spectrum. This might be attributed to crosslinking [31] rather than alkene formation. The FT-IR spectra provide evidence of molecular changes caused

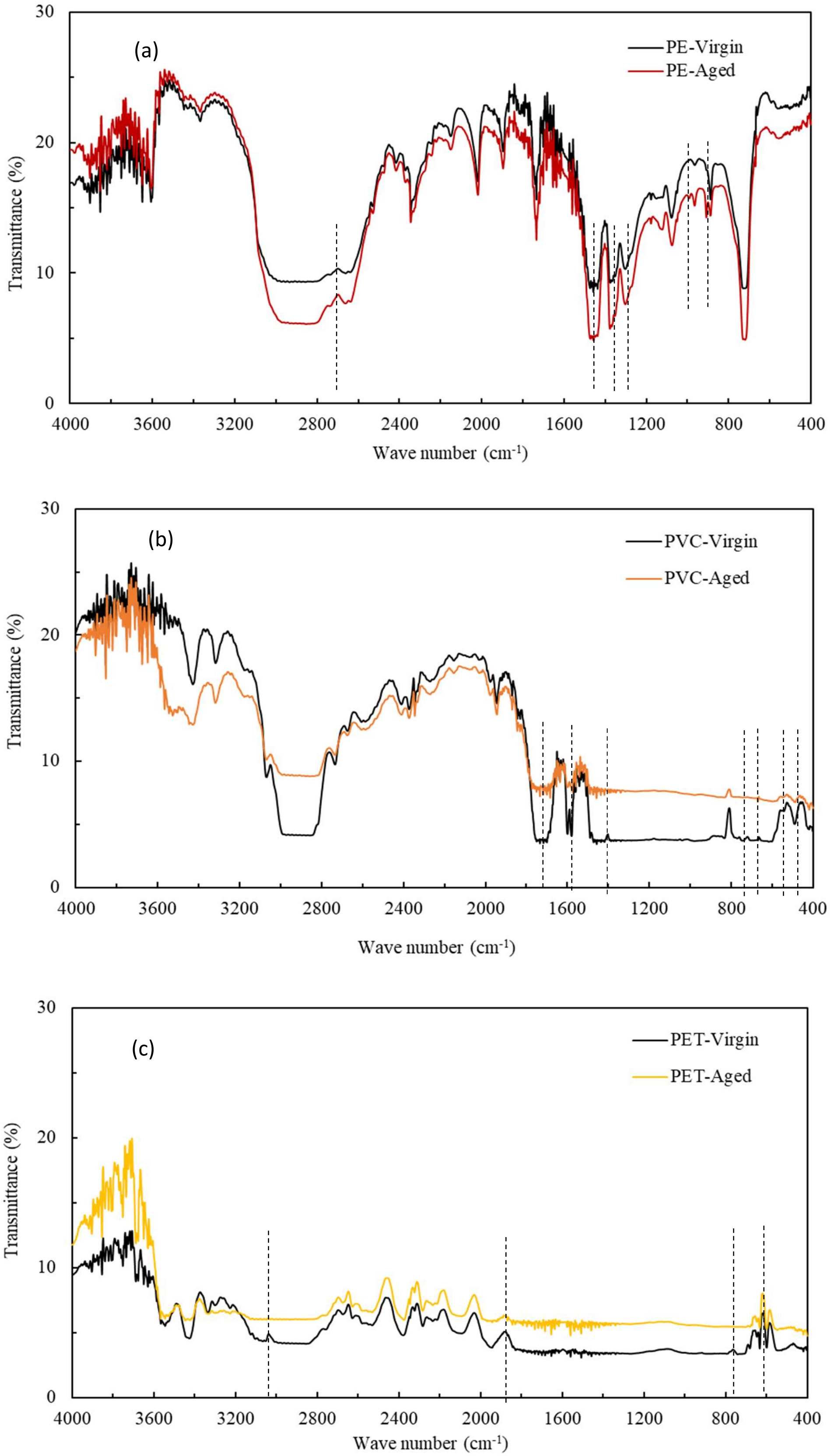

Figure 4.6 FT-IR spectra of the virgin and aged (a) PE, (b) PVC, and (c) PET sheets.

by PVC aging. These changes might contribute to surface textural changes, such as increased skewness.

PET photodegradation is caused by chain scission, leading to a decrease in the molecular weight of the polymer and generating carboxyl end groups [32]. We found that the aging of PET weakened the alkene bending peaks at 3030 cm^{-1} and 1942 cm^{-1}, and the C–H bending peak at 745 cm^{-1} (**Figure 4.6**(**c**)). These changes indicate that the aging of virgin PET changed the surface structure of PET, altering PET skewness and transparency.

The plastic samples did not come into contact with water in the aging treatment; however, it is plausible that aging processes might be affected by water in aquatic environments. Future research needs to analyze plastic samples aged in contact with water, to understand the changes in the chemical structures of plastics due to aging in the aquatic environment.

4.4 Conclusions

TriCP photodegradation on plastic surfaces was suppressed by plastic aging. This could be caused by changes in the plastic surface due to aging, such as valley formation in the surface texture. In addition, the decrease in plastic transparency caused by plastic aging can also suppress photodegradation. Furthermore, the TriCP photodegradation was suppressed by the addition of methanol extracts of the plastics. These results indicate that the aging of plastics can affect the photodegradation of contaminants through changes in the surface texture and behavior of plastic additives.

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Chapter 5

Migration of adsorbed organochlorines from plastics to sediment

5.1 Introduction

Microplastics are now omnipresent in the environment and have been detected in significant amounts in different environments such as freshwater [1], soil [2], beaches, and sediment [1], [5]–[7]. It was reported that microplastics adsorb HOCs at a concentration factor of $10^{5\text{-}6}$ [1] greater than the surrounding ocean surface. Thus, it is apparent that microplastics can act as a carrier of HOCs for translocation, magnification, and accumulation into different environmental sections, including living biota [2]–[4].

The density of buoyant microplastic debris may increase during their residence in the ocean environment by biofouling. Microplastics start sinking upon reaching seawater density [5]. Microplastics have been detected in the different sediment zones of the seas, including deep-sea shorelines [6], [7]. As such, sediment is the final destination of microplastics in the marine environment [4], [8]. Microplastics cause negative impacts on the survival, growth of benthic invertebrates [9]. As microplastics are apparent on the benthic zone sediment [4], [7] and a potential carrier of HOCs [1], [10], [11], the migration behaviors of HOCs-adsorbed onto plastics to sediment needs to be evolved, but no study has been focused on this issue.

In this study, the migration of TriCP and 1-chlorooctadecane (ClOD) from PE, PVC, and PET to sediment was examined in sediment under control conditions.

5.2 Experimental

5.2.1 Materials

Virgin sheets of PE, PVC, and PET with a thickness of 1.0 mm were purchased from Sanplatec Corp. (Tokyo, Japan). Before use, each pristine sheet was washed with distilled water three times and then dried in the oven at 50 °C to remove potential pollutant interference. TriCP and ClOD were obtained from Tokyo Chemical Industries (Tokyo, Japan). Methanol (99% purity), phosphoric acid (H_3PO_4), potassium hydroxide (KOH) (99% purity), acetone (98% purity), and hexane (98% purity) were purchased from Nacalai Tesque Inc. (Japan).

5.2.2 Sediment preparation

Sediment was collected at the mouth of Enkougawa River, Hiroshima, Japan, in October 2019, at a habitat of many sediment-dwelling invertebrates. Sediment samples were wet sieved through a 60-mesh stainless steel sieve to remove larger particles and debris, and then the sieved sediment was weighed and storaged in glass jars. To obtain microplastic-free sediment, the sediment was washed with milli-Q water with passing air for floating light debris adhered to the sediment [12]. After removing the excess water by decantation, the sediment sample was obtained. The characteristics of the sediment samples are summarized in **Table 5.1**. To avoid microbial interference and biological degradation, the sediment sample was autoclaved at 120°C for 30 min before its use.

Table 5.1 Characteristics of the sediment sample.

Water content	31%
Ignition loss (IC)	5.2%
pH	7.9
Dissolve organic carbon (DOC) of interstitial water	50.54 mg/L
Salinity of interstitial water	0.60 psu

5.2.3 Migration of adsorbed organochlorine from plastic to sediment

Approximately 5.0 g of wet sediment was kept in a round cap glass bottle and autoclaved. Before use, the glass bottles were washed with methanol and distilled water, respectively. For preparing the organochlorine-adsorbed plastic samples, 2.0 ml of 100 mg/L containing TriCP and 2 mL of 100 mg/L containing ClOD were respectively put dropwise on 5.30 cm^2 of PE, PET, and PVC sheets, and the solvent was removed by evaporation for two hours. Then, about 0.5 g of each plastic sheet onto which TriCP and ClOD were respectively adsorbed at amounts 7.53 and 1.88 mg/cm^2 were buried in the sterile sediment sample separately at around 2–3 mm depth. The glass bottles were sealed with a rubber cap and incubated in a dark room at 25 °C for 72 hours. To measure the migrated amount of TriCP and ClOD to the sediment, the plastic samples were picked up from the sediment every 24 hours, and TriCP and ClOD were recovered from plastics by methanol extraction. Migration of TriCP and ClOD into the artificial interstitial water was estimated using equation (1).

5.2.4 Mechanism of the migration process

HOC migration may occur (i) via dissolution followed by adsorption onto sediment and (ii) direct translocation by contact with sediment particles. To verify these hypotheses, HOC dissolution into the interstitial water was checked. Briefly, formic (HCOOH) acid was added to Milli-Q water to attain the same DOC (50 mg/L) as that of the interstitial water and adjusted to pH 8.0 using H_3PO_4 and 0.1 M KOH solutions according to the ratio as determined by the Henderson-Hasselbalch equation. Then the organochlorine adsorbed plastic sheets were put into this artificial interstitial water and maintained at 25 °C in the darkroom. To estimate the dissolved amount of TriCP and ClOD, the remaining TriCP and ClOD were extracted from the plastics using methanol and acetone respectively. The migration of TriCP and ClOD into the artificial interstitial water was estimated using equation (1).

5.2.5 Analysis of TriCP and ClOD

The methanol extracted TriCP was analyzed using an HPLC-UV detector; a 20-mM phosphate buffer (pH 2.50) solution was mixed at a volume ratio of 4:1 and used as mobile phase. A mixture sample (100 μL) was then analyzed by chromatography on an octadecyl silica column (Cosmosil 5C18-AR-II, 4.6 mm × 150 mm, Nacalai Tesque Inc., Japan) at a flow rate of 1.0 mL min^{-1}. The TriCP was detected by a UV–visible detector at 254 nm (SPD-10A, Shimadzu, Japan).

The acetone solution was analyzed for ClOD by GC/MS (GC-8860 and MS-5977B, Agilent Technologies, CA, US) under the conditions described in **Table 5.2**.

Table 5.2 Operating condition of GC/MS for analysis of ClOD.

Gass chromatograph	GC 8860 (Agilent Technologies, California)
Mass spectrometry detector	MSD 5977B (Agilent Technologies, California)
Column	HP-5ms (30 m×0.25 mm, 0.25 μm)
Inject volume	1 μl (Split ratio 15:1）
Inlet temp.	270°C
Pressure	97.3 kPa
Temperature profile	100°C（hold 3 min）
	15°C/min to 270°C (hold 4 min)
	20°C/min to 300°C (hold 5min）
Carrier	He, 1.3 ml/min
Ionization	Electron Impact (70 eV)
Scan range	15.0 m/z to 500.0 m/z
Hold time	5.0 min

5.2.6 Data analysis

A migration ratio of the organochlorines from the plastic sheets to the sediment and artificial interstitial water was estimated as the basis of the initial and remaining concentration of organochlorines on the plastics using the following equation:

$$\text{Migration (\%)} = \frac{\text{Remaining concentration of organochlorine on plastics}}{\text{Initial concentration of organochlorine on plastics}} \times 100 \ \ldots\ldots\ldots\ldots\ldots\ldots \ (1)$$

5.3 Result and Discussion

5.3.1 Migration of organochlorine

As shown in **Figure 5.1**(**a**), more than 90% of the adsorbed TriCP migrated from PE to sediment after 24 hours of incubation; however, the PET sheet showed the highest migration ratio of ClOD (**Figure 5.1**(**b**)). These results confirmed that the organochlorine adsorbed onto the plastic sheets can migrate into the sediment; however, the migration behaviors were dependent on the properties of organochlorine and plastics. An aliphatic organochlorine, ClOD, showed the highest migration ratio for PET; however, its migration from PVC and PE seems to be the same. On the other hand, an aromatic organochlorine, TriCP, showed the lowest migration ratio for PET. These might be due to their different adsorption mechanisms.

HOCs are adsorbed on plastics via hydrophobic interaction, π-π interaction, electrostatic interaction, and hydrogen bonding [13]–[15]. In contrast, HOC desorption from plastics to animals in gut conditions such as pH and temperature is enhanced; however, migration into sediment is not elucidated [16]. The migration probability of HOCs was higher in sediment from plastic surfaces because of the leaching of additives and interaction with interstitial waters. The migration of TriCP from plastics to sediment was in the order of PE > PVC > PET **(Figure 5.1** (**a**)**)** and PET > PE > PVC **(Figure 5.1** (**b**)**)** for C1OD. These results provide evidence that that migration of organochlorine from plastic to sediment occurred, and that migration behaviors depend on plastics and HOCs interaction.

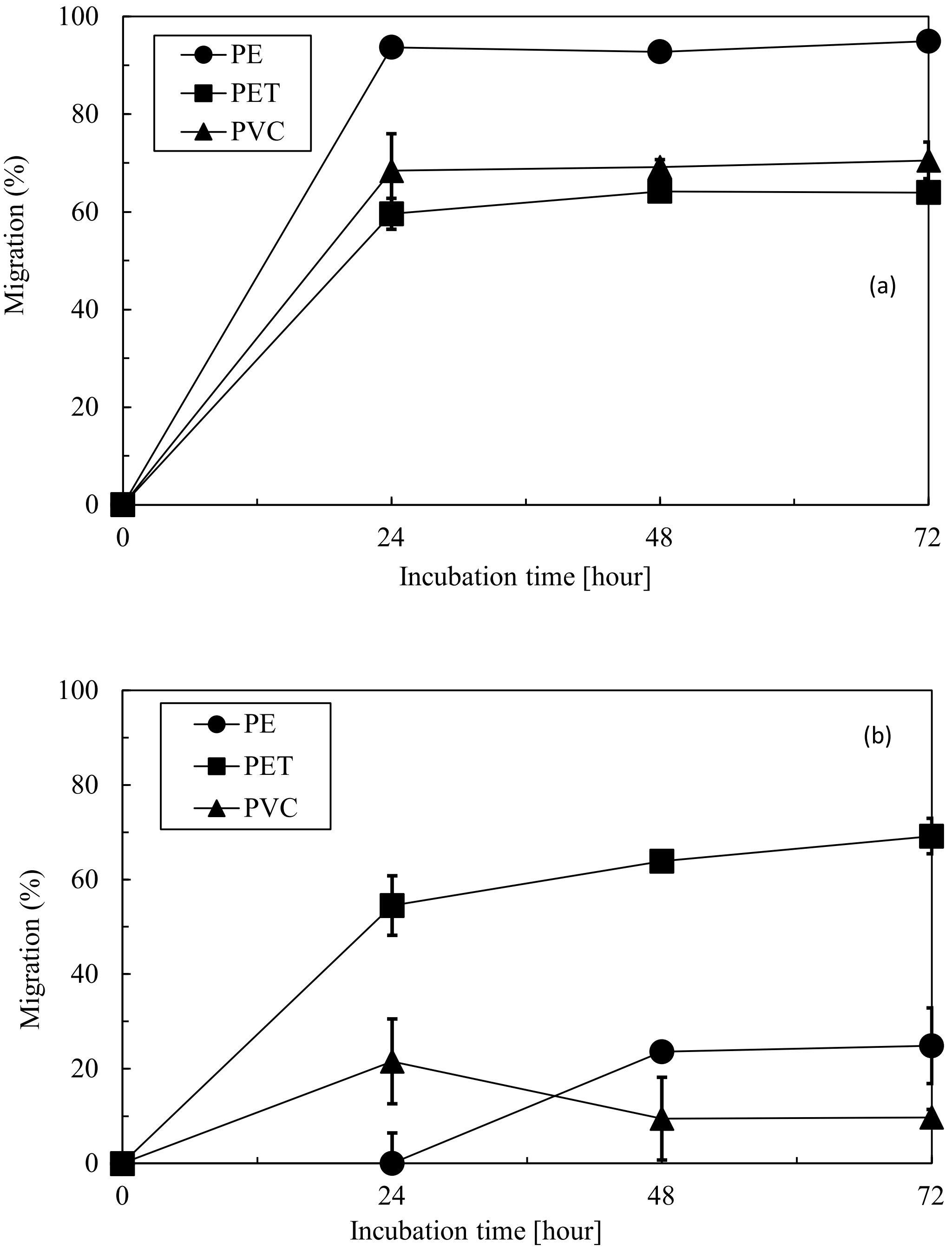

Figure 5.1 Migration of (a) TriCP and (b) ClOD from plastics to sterile sediment (at pH 7.9 and DOC 50.54 mg/L). Bars indicate standard deviation (n=3).

5.3.2 Effect of DOC on the migration of organochlorine

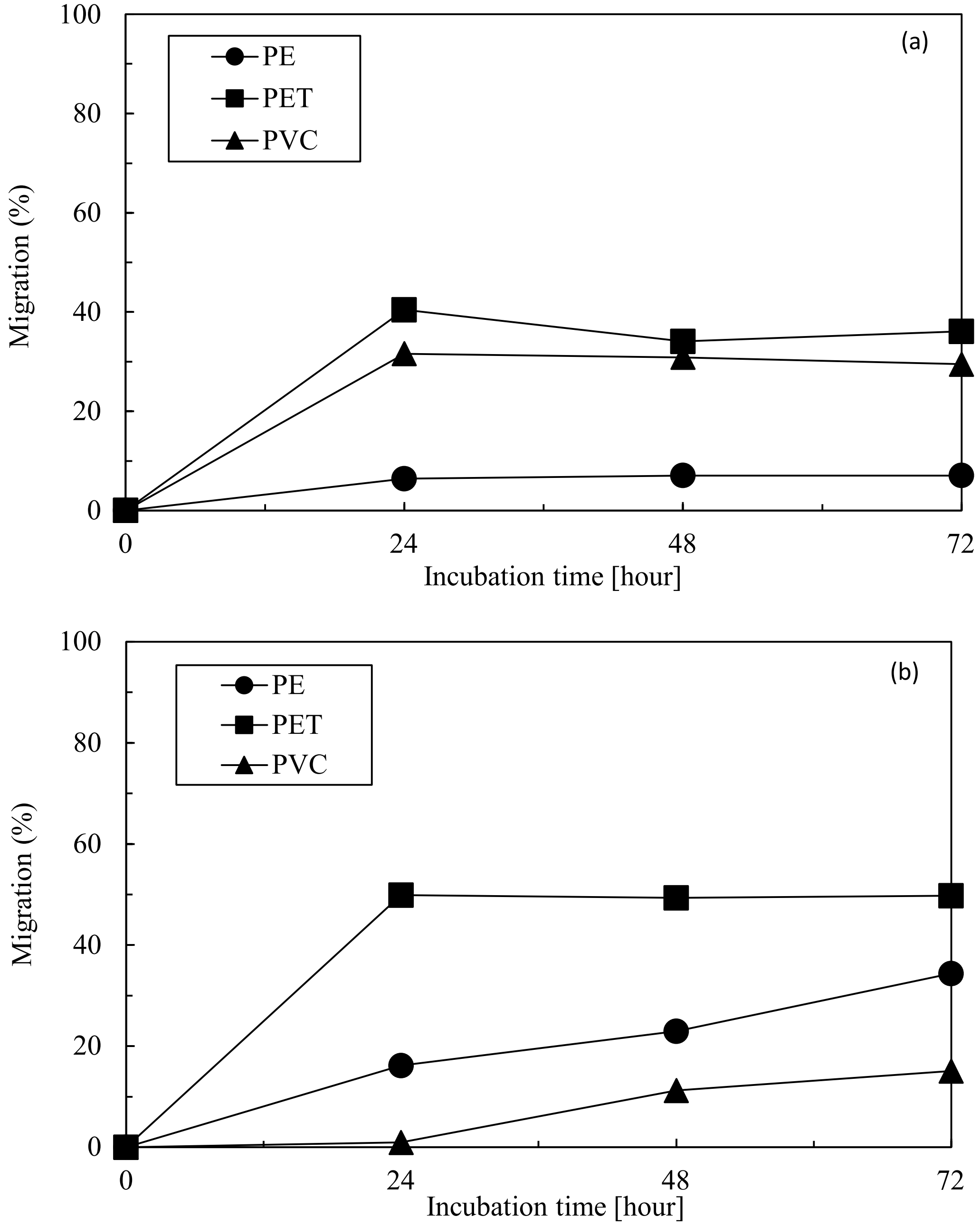

Figure 5.2 Migration as dissolution of (a) TriCP and (b) ClOD from plastics to artificial interstitial water (pH 8.0 and DOC 50 mg/L). The values were observed as the average (n=2).

As shown in **Figure 5.2 (a),** migration of TriCP and ClOD from all plastic sheets to the artificial interstitial water was confirmed. When Milli-Q water was used, no migration was observed.

However, the migration behaviors were different from that than sediment. PET showed a higher migration ratio for both TriCP and ClOD, to which the additives (**Figure 2.7**) might contribute. In contrast, PVC showed different trends for TriCP and ClOD, reasonably indicating that the migration of aromatic TriCP was greater than aliphatic ClOD from PVC. Although the dissolution trends could not be explained at this time, the results confirmed the dissolution of organochlorine from plastic surfaces.

5.3.3 Migration pathways

In this experiment using sediment, PET showed 60% migration (**Figure 5.1**(**a**)). As for PE, more than 90% migration was observed for TriCP in the sediment (**Figure 5.1**(**a**)); however, in the artificial interstitial water, the migration ratio of PE was less than 10% (**Figure 5.2**(**a**)). This suggests that direct translocation by contacting with sediment particles may occur too. As for ClOD on PE and PVC, direct translation may be negligible because of the similar migration ratios in the sediment and artificial interstitial water (**Figure 5.2** (**a**) and (**b**)).

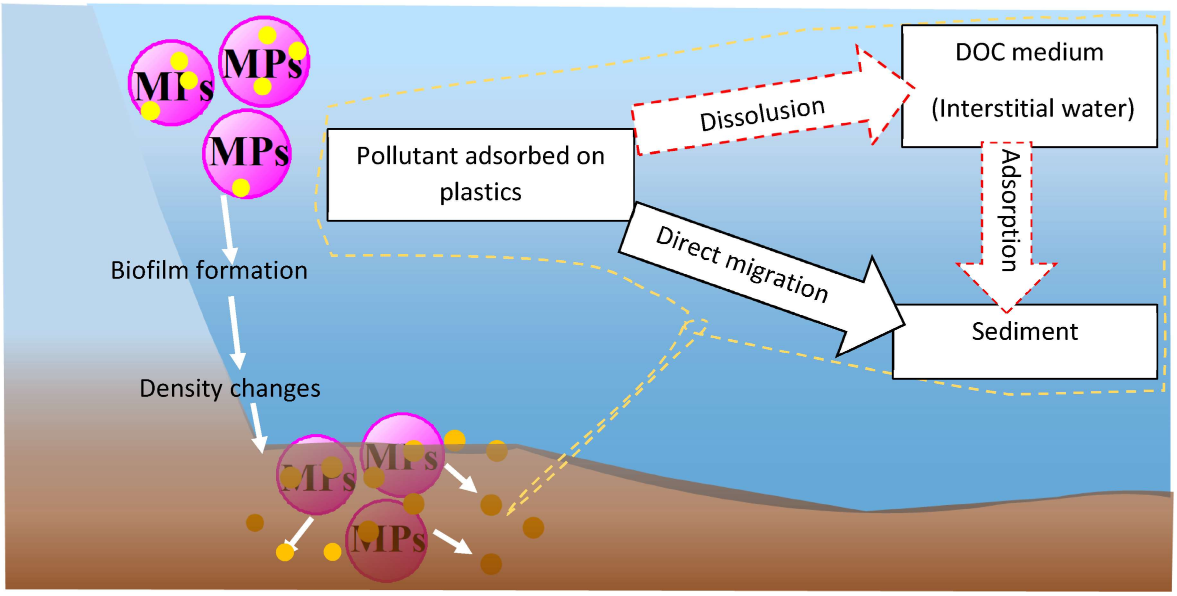

Figure 5.3 Plausible migration pathways of adsorbed organochlorines from plastics to sediment.

5.4 Conclusions

This study provided the first vital evidence that aliphatic and aromatic organochlorines, TriCP, and ClOD can migrate from plastics to sediment, indicating plastics' role in sediment contamination. As for migration mechanisms, dissolution followed by adsorption, direct translation, and direct translocation to sediment may be possible. However, the proof of migration of adsorbed HOCs from plastics to sediment via dissolution in interstitial water followed by adsorption on sediment and or direct migration of pollutants from plastics to sediment remains primitive. In the future, further focus is needed to elucidate the realistic migration of HOCs via plastic debris.

5.5 Literature cited

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Chapter 6

Conclusions

As a proof-of-concept, this study focused on the fate of HOCs adsorbed on plastic surfaces in the ocean, investigating possible effects on the photodegradation behaviors of HOCs during their floatation and migration from plastics to sediment after settlement. In the photodegradation experiments, virgin and artificially aged PE, PET, and PVC sheets were tested, according to their extensive use in the world, whereas PCP, TeCP, and TriCP CPs and NAP were used as model HOCs. In the migration experiment, TriCP, together with an aliphatic organochlorine, ClOD, were tested to find possible structure-specific effects. The highlights of this study are shown in **Figure 6.1** as follows.

1) The virgin PE accelerated the photodegradation of PCP and TeCP; the photodegradation rate constants on the PE surface were approximately 1.50 times higher than that on a glass surface. In contrast, the photodegradation of these CPs on PET was slower than on the glass surface. Furthermore, the photodegradation of PCP on the PVC surface was suspended after approximately 60 min of ultraviolet irradiation. These results confirmed that plastics affect the photodegradation behavior of HOCs adsorbed on their surfaces. FTIR analysis showed that C=C bonds were produced on PE after UV irradiation, suggesting that PE might act as a hydrogen donor to accelerate the photodegradation of PCP and TeCP. The findings suggest that the characteristics of plastics should be considered to understand the fate of HOCs adsorbed on plastics through phototransformation.

2) NAP was photodegraded on the glass and PE; however, PE accelerated photodegradation of NAP due to the possible hydrogen donation. As the photodegradation intermediates, oxy-PAHs, such as NAPQ, were found on both glass and PE; however, the abundance of NAPQ on the PE was much higher. As oxy-PAHs demonstrate higher toxicity than their precursors, these results

show that the remaining intermediates and precursor HOCs must be considered for risk assessment.

3) On the virgin PE sheet, the accelerated photodegradation of TriCP was also confirmed; however, on the aged PE, its photodegradation was suppressed rather than accelerated. In addition, the PET and PVC sheets also showed further suppression of TriCP photodegradation by aging, thereby confirming that plastic aging affects the photodegradation behaviors of the adsorbed TriCP. By aging, valley production and reduced plastic transparency to UV were confirmed, possibly contributing to the suppressed photodegradation on the aged plastic sheets. On the other hand, the possible release of additives was expected to be positive for the photodegradation of HOCs.

4) The migration of TriCP and ClOD to sediment was confirmed by burying the TriCP- and ClOD-adsorbed PE, PET, and PVC sheets. The degree of migration of the aromatic organochlorine, TriCP was in the order of the PE, PVC, and PET sheets, whereas the PET sheet released an aliphatic organochlorine, ClOD, at the most abundant level. These different trends of organochlorines in migration might be correlated with the plastic's properties and electrostatic interaction, such as π - π between plastics and pollutants. These results provided reasonable evidence that microplastics may act as HOC carriers from seawater to the benthic ecosystem to cause HOC sediment contamination.

Recommendations

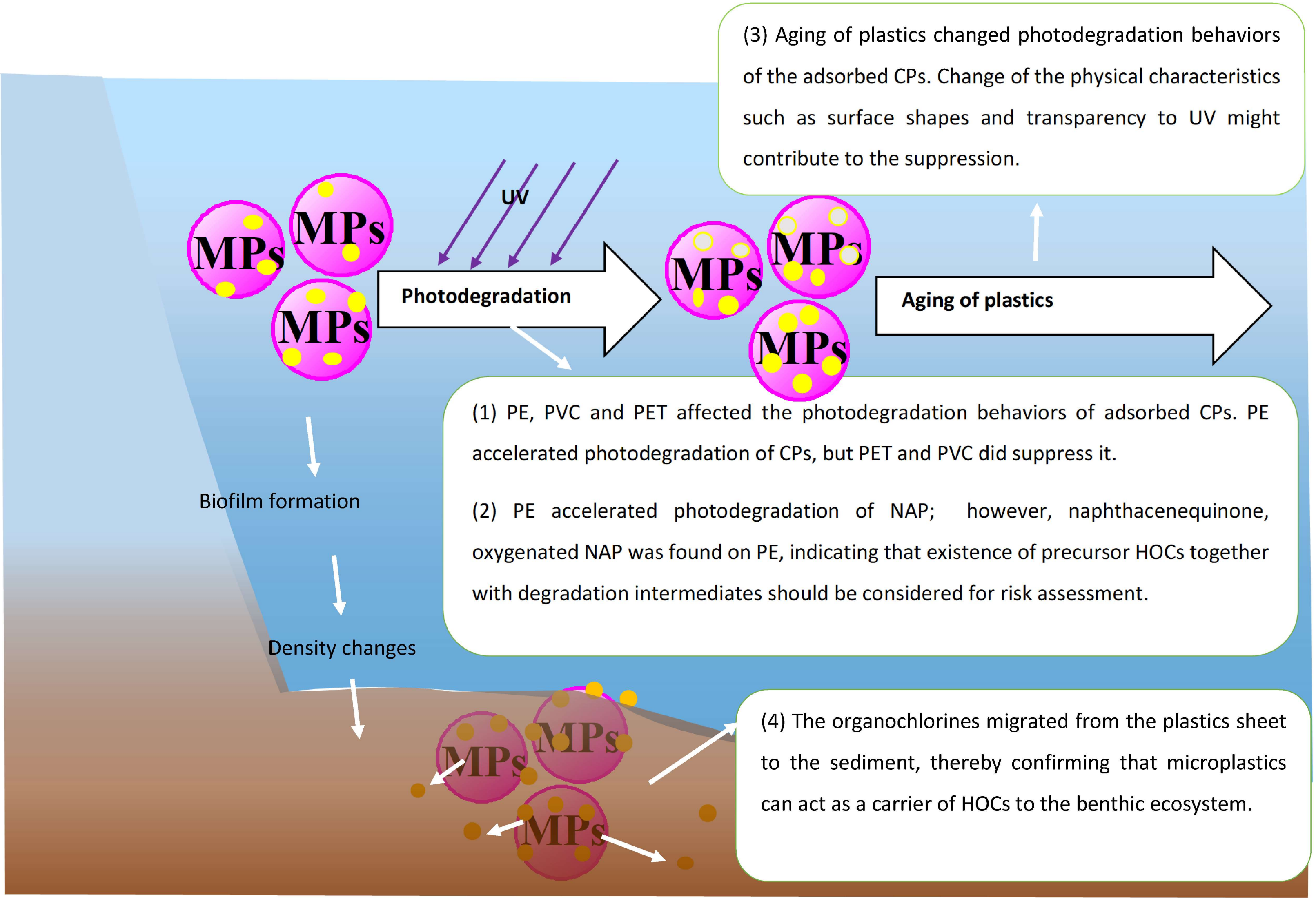
Although this study revealed that plastics affect the photodegradation behaviors of HOCs and act as HOC carriers, understanding the possible effects of plastics on the fate of adsorbed pollutants is still in a primitive stage. Comprehensive studies are needed to elucidate the fate of pollutants associated with plastics.

1) As the reported data are laboratory-based using UV, further studies should use actual sunlight to estimate photopollutant photodegradation.

2) The effect of plastics additives and inbound plasticizers, stabilizer effects on the photodegradation of adsorbed pollutants should be considered as these are not chemically bonded with plastics and may hinder the pollutant photodegradation process.

3) As plastics are sunken and reached in sediment, anaerobic degradation of plastics and adsorbed pollutants need to be understood.

4) Heavy metals are also adsorbed on plastics along with HOCs. Due to a possible action as a catalyst, studies should reveal the effects of heavy metals on the photodegradation of HOCs.



(3) Aging of plastics changed photodegradation behaviors of the adsorbed CPs. Change of the physical characteristics such as surface shapes and transparency to UV might contribute to the suppression.

(1) PE, PVC and PET affected the photodegradation behaviors of adsorbed CPs. PE accelerated photodegradation of CPs, but PET and PVC did suppress it.

(2) PE accelerated photodegradation of NAP; however, naphthacenequinone, oxygenated NAP was found on PE, indicating that existence of precursor HOCs together with degradation intermediates should be considered for risk assessment.

(4) The organochlorines migrated from the plastics sheet to the sediment, thereby confirming that microplastics can act as a carrier of HOCs to the benthic ecosystem.

Figure 6.1 Highlights of this study.

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List of publications

1) **Hassan M. N.,** Kuzukami A., Nakai S., Nishijima W., Gotoh T. “Effect of Plastics on the Photodegradation Behavior of Chlorophenols.” J. Chem. Eng. Japan. **2020**, *53* (10), 660–666. (Related to Chapter 2)
2) **Hassan M.N.**, Nakai S., Nishiima W., Gotoh T., Suenaga T. “Effects of the Aging of Plastics on the Photodegradation of Adsorbed Organic Pollutants.” 環境科学会誌, Japan, **2021**, 34 (6), 1–11. (Related to Chapter 4)

International Conference

1) **Hassan M. N.,** Nakai S., Nishijima W., Gotoh T., “Effects of aged plastics on photodegradation behavior of sorbed organic pollutants.” Society of Environmental Science, Japan, The 9th symposium, September 10th – 11th, 2021
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