

Full length article

## Decontamination of recycled LDPE using different washing methods

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## ABSTRACT

Post-consumer low density polyethylene samples were analysed for PAHs, PCDD/Fs and dioxin-like PCBs content. Subsequently, various treatments were applied to determine a process capable of decontaminating the plastic samples: extraction with polyethylene glycol at different temperatures with and without agitation; extraction using subcritical and hot water at different temperatures in a basic medium; compound degradation by ultraviolet radiation; and compound degradation by advanced oxidation processes using H<sub>2</sub>O<sub>2</sub>. The most effective treatment was extraction with polyethylene glycol (agitated) at 120 °C, reducing contamination by 89%, 85% and 95% of PAHs, PCDD/Fs, and dioxin-like PCBs, respectively. The least effective treatments (subcritical and hot water), maximum reductions of 47% and 19% of PAHs were obtained for the temperatures of 160 °C and 90 °C. UV oxidation increased the toxic equivalency of the samples (calculated using the toxicity equivalency factors) by up to 1400%, through the co-formation of the most toxic congeners, e.g., the non-ortho PCBs

## 1. Introduction

Plastics have become an essential material in our societies due to their many advantages. However, their negative environmental impact has become a major problem that needs to be urgently addressed. For instance, plastic waste in oceans and landfills has become a significant threat to wildlife and ecosystems. Therefore, innovative and sustainable solutions are needed to ensure that plastics are produced, used, and disposed of in a way that minimizes their impact on the environment. To achieve this goal, initiatives such as biodegradable plastics, plastic recycling programs, and reduced plastic usage campaigns should be promoted and developed. By adopting these measures, we can ensure that plastics have a positive impact on both people and the planet.

Currently, the lifespan of plastic-based products ranges from 1 year to 50 years, after which they become waste, with all the negative consequences that this entails. In 2020, 367 million tonnes of plastic were produced worldwide, of which 55 million tonnes in Europe (Plastics Europe, 2021). One of the problems is that of the 29 million tonnes of plastic waste collected for further treatment, only 34% was recycled (Plastics Europe, 2021). This amount, slightly above that of previous years (up by 4% compared to 2018), is still a far cry from the targets set by the European Union consisting of 50% of recycled plastic in packaging by 2025, and 55% by 2030 (European Council, 2019).

Of all the plastic produced annually around the world, the most sought-after plastics are Polypropylene (PP), Polyethylene (PE), Polystyrene (PS) and Polyethylene terephthalate (PET). PP (19.7%) are used for food packaging, sweet and snack wrappers, hinged caps, microwave containers, pipes, etc. For their part, LDPE (Low Density Polyethylene) and LLDPE (Lineal Low-Density Polyethylene) (17.4%) go into the composition of reusable bags, trays and containers, agricultural film, food packaging film, etc. HDPE (High Density Polyethylene) and MDPE (Medium Density Polyethylene) (12.9%) are used in toys, milk bottles, shampoo bottles, pipes, houseware, etc. PS (6.1%) are used for food packaging (dairy, fishery). Finally PET (8.4%) is used in bottles for water, soft drinks, juices, cleaners, etc. (Plastics Europe, 2021).

Despite their benefits for society, recovering plastics represents a major challenge. They are often contaminated after use with inks, dust, as well organic and inorganic substances which, at present, cannot be mitigated by conventional recycling processes (mechanical recycling without a specialised cleaning process, whereby the washing is done with hot water). For this reason, recycled plastic is used for lower quality products in construction, agriculture, or piping for example (Horodytska et al., 2020) (Núñez et al., 2022). It is difficult to use recycled plastics coming from post-consumer sources for more demanding applications, such as packaging. Indeed, these latter materials do not fulfil industry requirements regarding colour, odour, migration of unknown

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organic substances, etc. (García Ibarra et al., 2018). Furthermore, polyolefins are harder to clean than PET due to their greater permeability, which means that contaminants migrate faster from external sources to the inner polymer layers (Geueke, 2018). The migration of contaminants in a polymeric matrix is not only related to permeability, but also to the polarity of the material. PET is more polar and, therefore, creates a barrier against apolar contaminants, such as volatile organic compounds (VOCs), which have low solubility in PET due to their lack of polar interactions with the material (Feigenbaum et al., 2005). The hydroxyl groups and the polarity of the polyester chain of PET make it more resistant to the migration of apolar contaminants compared to less polar materials like LDPE. Besides all these issues related to polyolefin-recycling processes, the new EU directive on recycled plastic materials destined to come into contact with food has determined that polyolefins-type plastics can be recycled throughout novel technologies, with which a high degree of human health protection can be ensured, as is the case for PET (European Commission, 2022).

Despite the difficulties to recycle polyolefin, the plastics industry is striving to transform the traditional linear economy - in which plastics are discarded at the end of their useful life - into a circular economy. In a circular economy sustainable model, plastics remain in circulation for longer and are reused and recycled at the end of their useful life. The recycling industry is therefore targeting post-consumer plastic waste (Plastics Europe, 2022). To close the loop, i.e., to use the recycled plastic for the same application as the original material, we must be able to eliminate the contamination of post-consumer recycled plastics. Contaminants present in recycled plastic are classified as IAS (Intentionally Added Substances), or as NIAS (Non-Intentionally Added Substances).

IAS are additives incorporated into the plastics to improve their physicochemical properties, which can include flame retardants, (not allowed in EU in food contact materials) plasticisers, stabilisers and others (Wagner and Schlummer, 2020). Given their environmental impact, the capacity of IAS to migrate during the recycling process has been an object of study (Hahladakis et al., 2018). For their part, NIAS are highly diversified chemical compounds, which, if present in plastics in contact with food, could present toxicological risk. Their origin varies widely, from impurities in the substances used during manufacturing, to reaction products or contamination during the recycling stage, amongst others. Su et al. (2021), found more than 300 substances in a migration test using post-consumer plastic samples, of which 58 substances were classified as toxic. Moreover, Núñez et al. (2022) looked for PAHs (polycyclic aromatic hydrocarbons), PCDD/Fs (polychlorinated dibenzodioxins/polychlorinated dibenzofurans), and dioxin-like PCBs (polychlorinated biphenyls) in different LDPE samples of different origins (virgin, agricultural, post-commercial, post-industrial white, post-industrial black and post-consumer), and found the highest quantities of these contaminants in post-consumer recycled LDPE and proposed that one of their possible origins could be ambient air contamination, comparing the profiles obtained with others already studied in the available literature (Conesa et al., 2006). In fact, the contaminant concentration levels in samples subjected to a thorough washing process were found to be similar to that of the virgin plastic sample, or even lower. The thorough washing process was carried out by a recycling company (Cadel Deinking 2023) with the main objective of removing the ink printed on the plastic surface, not with the objective of decontaminating plastic (this is not a common process in recycling companies). This finding highlights the key role of washing processes in plastics recycling.

PAHs are type of organic compound that can persist in the environment. They are formed when biomass and fossil fuels are incompletely burnt, and they are considered hazardous pollutants due to their ability to cause cancer, mutations and birth defects. Various organizations, including the US Environmental Protection Agency (EPA) and the EU Scientific Committee for Food (SCF), have identified PAHs as dangerous substances. Similarly, there are other organic compounds that can persist in the environment and pose a threat to human health

and the ecosystem (JRC - European Commission, 2011). These include dioxins (PCDDs), furans (PCDFs), and dioxin-like PCBs, which are known to be harmful and can accumulate in the fatty tissue of living organisms. They are classified as “legacy” pollutants, which means they have been recognized as harmful for a long time (Stockholm Convention).

In this way, post-consumer recycled plastic material in which these contaminants were identified were subjected to different treatments designed to eliminate or reduce these contaminants. The ultimate objective of detect the best treatment amongst the following: extraction with polyethylene glycol; extraction with a sodium hydroxide solution in hot water and water under subcritical conditions; and finally, oxidation by ultraviolet radiation and advanced oxidation by ultraviolet radiation with H<sub>2</sub>O<sub>2</sub>.

Polyethylene glycol (PEG) was used to remove PAHs, PCDD/Fs, and dioxin-like PCBs, because polyethylene glycol is a low molecular weight polymer that serves as a non-volatile solvent, soluble in polar solvents such as water. Furthermore, PEG is biodegradable, biocompatible, non-toxic, non-corrosive, while being soluble in non-polar solvents and insoluble in aliphatic hydrocarbons (Vafaezadeh and Hashemi, 2015). Polyethylene glycol presents high miscibility with organic compounds compared to water. Moreover, a number of studies have shown its significant potential for the extraction of organic molecules (flavone and coumarin compounds from medicinal plants like Nevadensin, Aesculin and Aesculetin) (Zhou et al., 2011). In addition to its favourable properties, Cabanes et al. (2021) used polyethylene glycol to remove volatile organic compounds in post-consumer recycled HDPE samples at 100 °C and obtained 70% reductions in the volatile organic compounds they analysed.

With regard to the extraction treatment with subcritical water, it should be noted that subcritical water is generated when water is overheated, i.e., when its temperature is between boiling point (100 °C) and 300 °C (Curren and King, 2001) and remains in a liquid state due to the pressure effect. Under these conditions, water becomes less of a polar solvent and behaves like an organic solvent such as methanol. This significantly increases the solubility of organic compounds within it and decreases the solubility of polar compounds (Fernandez-Prini, 1991). Therefore, it can act as an organic cleaning solvent. For this reason, subcritical water seems to be a particularly suitable solvent to remove toxic compounds present in other materials (in this case, recycled plastic) that could be ingested by the human body. Carr et al. (2011) compiled information on some of the toxic organic compounds that could be dissolved by water under subcritical conditions. They included benzo[*a*]pyrene, anthracene, pyrene, and chrysene, which, according to the WHO (World Health Organization, 2021), are amongst the 16 most toxic PAHs to human health. They are the subject of the present study. Sodium hydroxide was also added to some runs, as it has been found that the addition of alkaline reagents in hydrothermal processes improves the degradation of dioxins and furans (Yamaguchi et al., 1996) (Qiu et al., 2019).

Finally, advanced oxidation (AOPs) is a physico-chemical process capable of changing the structure of chemical pollutants by increasing their degradability through the use of the hydroxyl radical (OH<sup>•</sup>). These processes can be non-photochemical or photochemical. In the present work, the UV/H<sub>2</sub>O<sub>2</sub> photolytic technology was used. This system has been used in other works, e.g., to eliminate organic compounds, such as antipyrone (Tan et al., 2013), and to eliminate PAHs in water (An and Carraway, 2002). More efficient results were obtained than when using ultraviolet light only.

It is worth noting that no other studies were found in the literature on the removal of PAHs, PCDD/Fs and dioxin-like PCBs from recycled plastic. If a method were found allowing to significantly reduce the presence of these contaminants and other NIAS in recycled plastics, the consumption of virgin plastic would decline and ever more recycled plastic would be added to the value chain, supporting the circular economy of plastics.

## 2. Materials and methods

### 2.1. Sample collection

The type of polymer used in the present study was recycled low density polyethylene (LDPE), that had been previously collected from the yellow bin (post-consumer recycled plastic) and treated by a local recycling company. The washing treatment was carried out with hot water (the treatment given to this type of plastic consists of grinding process followed by basic washings with hot or cold water before extrusion) (Horodytska et al., 2020).

The plastic sample collected was milled and homogenised using a Retsch model SM 200 (Haan, Germany) cutting mill with a 1.0 mm sieve. A 1 kg sample was obtained. Different fractions were taken and a total of 15 different treatments were applied in order to study their efficiency at eliminating contaminants. In addition, the results obtained were compared with the contamination present in a control sample (same untreated post-consumer plastic). Table 1 shows a list of the different treatments applied to the recycled LDPE sample, together with their nomenclature.

### 2.2. Treatments with polyethylene glycol

Polyethylene glycol 400 (PEG 400) purchased from Corquimia Industrial S.L, Barcelona, Spain, was used as a solvent to extract the contaminants under study. The polyethylene glycol extraction was performed in two different ways. Initially, 100 mL non-stirred recipients were used. To this end, Huanyu Hydrothermal Synthesis Autoclaves with teflon chamber were employed, shown in Fig. S1 in the supplementary material. The vessels were heated in a Memmert model UF30 universal oven (Schwabach, Germany). Moreover, a magnetic hotplate stirrer model VMS-C7 Advanced from VWR with a 1 L beaker was used for the PEG extraction experiments with stirring.

A total of 25 gs of recycled LDPE was treated in a total volume of 500 mL of PEG 400. In the non-stirred system 5 fractions of 100 mL with 5 gs of plastics each were made (due to the capacity of the autoclaves), and at the end of the extraction all fractions were pooled, the extraction was carried out for 2 h at a temperature of 120 °C (run NS-PEG 120). In the stirred system, the extraction took place for 2 h at 3 different temperatures: 120 °C, 90 °C and 70 °C (runs S-PEG 120, S-PEG 90 and S-PEG 70, respectively).

After extraction, the treated LDPE was separated from the PEG 400 using a sieve. Residues of the polyethylene glycol remaining on the surface of the plastic were removed by rinsing the plastic surface with 500 mL fresh cold water for 30 min and by stirring the plastic in a 1 L beaker using a magnetic stirrer. Finally, the water was drained, and the treated recycled plastic was left to dry for 48 h at room temperature.

**Table 1**

List of the different treatments applied.

ID	Treatment
S-PEG 120	Stirred with PEG-400 2 h at 120 °C
S-PEG 90	Stirred with PEG-400 2 h at 90 °C
S-PEG 70	Stirred with PEG-400 2 h at 70 °C
NS-PEG 120	Non-stirred with PEG-400 2 h at 120 °C
SB-WE 5–120	Subcritical water extraction (5% NaOH) 120 °C
SB-WE 20–120	Subcritical water extraction (20% NaOH) 120 °C
SB-WE 5–160	Subcritical water extraction (5% NaOH) 160 °C
ST-WE 5–70	Stirred water extraction (5%NaOH) 90 °C
ST-WE 5–90	Stirred water extraction (5%NaOH) 70 °C
UV 30 min	Stirred Ultraviolet 30 min
UV 120 min	Stirred Ultraviolet 120 min
UV 300 min	Stirred Ultraviolet 300 min
AOP 25mM	Advanced Ultraviolet with H <sub>2</sub> O <sub>2</sub> 25mM
AOP 50mM	Advanced Ultraviolet with H <sub>2</sub> O <sub>2</sub> 50mM
AOP 100mM	Advanced Ultraviolet with H <sub>2</sub> O <sub>2</sub> 100mM
CONTROL	Without treatment

### 2.3. Extraction in alkaline medium with subcritical water and with stirred water

Extractions under subcritical water conditions were performed in an autoclave reactor at temperatures between 100 and 150 °C. Different runs were performed changing the NaOH concentration in the extraction liquid. Specifically, two standardised NaOH solutions of 5% and 20% (by weight) were prepared. Solid NaOH from Sigma-Aldrich, Merck® was used. The extraction was conducted in two different ways: non-stirred and stirred. The non-stirring experiments (subcritical water extraction) were conducted using hydrothermal synthesis autoclaves in an oven at 120 °C and 160 °C to treat a total amount of 25 g of LDPE and using 500 mL of solution for each concentration at different temperatures (runs SB-WE 5–120, SB-WE 20–120, and SB-WE 5–160, as shown in Table 1). A 5% NaOH solution was used for the stirred water extraction runs. They were performed at two different temperatures, 90 °C and 70 °C (runs ST-WE 5–70 and ST-WE 5–90). In the case of these aqueous solutions, it is only possible to work at a higher temperature if a pressurized system is used. The working pressure for the maximum temperature (160 °C) was estimated to be 0.7 MPa, which is well below the maximum allowed safety pressure of the autoclaves used (3 MPa). In this procedure, 25 g of recycled LDPE was also treated at each temperature.

### 2.4. Advanced oxidation (UV/H<sub>2</sub>O<sub>2</sub> treatments)

In the advanced oxidation treatments, the recycled plastic pellets were subjected to a source of UV radiation in the presence of oxygen peroxide for different durations. The product obtained was analysed to determine the degree of contaminant removal.

Several runs were carried out using UV light treatment, some of which with two different concentrations of hydrogen peroxide. Three different solutions of hydrogen peroxide were prepared: 25mM, 50 mM, and 100 mM. The solutions were prepared using a 3% H<sub>2</sub>O<sub>2</sub> solution by weight from Sigma-Aldrich, Merck®.

For the UV treatment runs, a closed chamber with reflecting walls measuring 60 × 30 × 40 cm was designed (Fig. S2 in the supplementary material). The box was equipped with two UV lamps TUV PL-L 36 W/4P (UVC 250). These conditions provide a UV-intensity of around 400 W/m<sup>2</sup>. For all treatments, approximately 25 g of post-consumer recycled LDPE were used and loaded into a 1 L beaker with 500 mL water or H<sub>2</sub>O<sub>2</sub> solutions and stirred. Three experiments were performed with distilled water, varying the UV exposure time (0.5 h, 2 h, and 5 h) (runs UV 30 min, UV 120 min and UV 300 min), and three experiments were performed with different H<sub>2</sub>O<sub>2</sub> concentrations (25 mM, 50 mM and 100 mM) and 2-hour durations (runs AOP 25 mM, AOP 50 mM and AOP 100 mM).

### 2.5. PAHs extraction

The compounds to be analysed were separated from the plastic samples by solvent extraction using a method adapted to extract these compounds in recycled plastic (Núñez et al., 2022). To quantify PAHs, 10 µL of the internal standard Mix 33 with a concentration of 2000 µg/mL (1,4-dichlorobenzene-D<sub>4</sub>, naphthalene-D<sub>8</sub>, acenaphthene-D<sub>10</sub>, phenanthrene-D<sub>10</sub>, chrysene-D<sub>12</sub> and perylene-D<sub>12</sub>) was purchased from Dr. Ehrenstorfer-Schäfers and supplied by Wellington Laboratories. The internal standards used to quantify the analysed compounds were added to the samples before extraction.

To extract the PAHs, 2 g of recycled plastic (milled using a 1.0 mm sieve and homogenised) was introduced into a 50 mL vial with a 30 mL mixture of acetone and dichloromethane (1:1 by volume) and was spiked with the internal standard before mentioned. The vials were closed and the samples were stirred for 24 h at 1500 rpm using a MULTISTIRRER Digital 6 supplied by Velp Scientifica and at room temperature (25 °C). When the extraction process was completed, the

samples were filtered using glass wool as well as anhydrous sodium sulphate (to remove any possible moisture that may be present in the extract) and concentrated using a Super-Vap, from Fluid Management Systems (FMS), obtaining a final volume of approximately 1 mL.

To remove impurities and plastic dissolved during the extraction, all PAHs samples were cleaned following a procedure suggested by Li et al. (2017). The extracts were thus eluted in a C18 SPE cartridges purchased from Sigma-Aldrich, Merck, previously conditioned with 5 mL of dichloromethane and 5 mL of hexane. A total of 10 mL of hexane was used to elute the samples.

After the clean-up, all samples were concentrated again by means of a SuperVap, obtaining a final volume of approximately 1 mL, finally concentrated in vials using a Pasvial evaporator. Immediately prior to the analysis, a deuterated internal standard was added: 3 µL of Anthracene-d<sub>10</sub> with a concentration of 2000 µg/mL in dichloromethane, supplied by AccuStandard Inc., New Haven, CT, USA. This standard was spiked into the sample in order to calculate the recoveries obtained from the deuterated compounds added at the beginning.

The standards established by the U.S. EPA (EPA, 2018) were followed to identify and quantify the 16 priority PAHs. The PAHs analysis was performed via high-performance gas chromatography (Agilent 6890 N) with mass spectrometry (Agilent 5973 N) (HRGC-MS).

Calibration for quantification was done with MIX 63 with a concentration of 1000 µg/mL and was purchased from Dr. Ehrenstorfer-Schäfers and supplied by Wellington Laboratories. The calibration concentration was between 0.50–15 µg/mL for a total of 6 points. The native PAHs analysed in the samples can be found in Table S1 of the supplementary material.

## 2.6. PCDD/Fs and PCBs extraction

To extract the PCDD/Fs and PCBs, a similar procedure to the PAHs was followed, but the extraction solvent was substituted with 30 mL toluene, one of the solvents recommended by the environmental protection agency to extract these types of pollutants (EPA, 1994). Toluene is therefore one of the most commonly used solvents used for POP analysis (Conesa et al., 2021). To analyse the PCDD/Fs, 10 µL of internal standard EPA-1613LCS were added to the samples, and to analyse the dioxin-like PCBs, 10 µL diluted to 200 ppb of WP-LCS were added. Both were supplied by Wellington Laboratories.

To clean up the PCDD/Fs and PCBs extracts, the samples were purified using a Power-Prep™ automatic cleaning equipment from the FMS company, which is capable of automatically purifying the extract. The Power-Prep™ system was programmed to clean the extract using three different columns: a multilayer silica column, in which PAHs, phenols, acids and esters, as well as oils and lipids are retained; a basic alumina column, which allows separating PCDD/Fs and PCBs fractions from other organic compounds and also retains phenols and lipids; and finally, an activated carbon column that allows isolating PCDD/Fs from other organic compounds, as they are retained in the column head due to its planar configuration, being subsequently eluted in reverse flow. At the end of the purification, two fractions were obtained: the first one containing the PCDD/Fs in toluene and the second one containing the PCBs in a dichloromethane and hexane mixture (1:1 by volume).

After clean-up, all extracts were concentrated using SuperVap equipment to a final volume of approximately 1 mL and finally concentrated in vials using a Pasvial evaporator to a final volume of approximately 25 µL. Immediately before the analysis, the <sup>13</sup>C isotopically labelled standard was added: 10 µL of the EPA-1613ISS solution for the PCDD/Fs fraction, and the WP-ISS solution was diluted to obtain 10 µL with a concentration of 200 ppb for the analysis of dioxin-like PCBs. Both standards were supplied by Wellington Laboratories. PCDD/Fs and PCBs were identified and quantified by gas chromatography (Agilent 7890B) coupled with triple quadrupole mass spectrometry (Agilent 7010B) (GCMS-/QQQ) with an automatic injector (Agilent 7693A).

The list of instrument injection conditions, the method used for data

acquisition, and the multiple reaction monitoring (MRM) for PCDD/Fs and dioxin-like PCBs are shown in Tables S4, S5 and S6 in the supplementary material.

Calibration for quantification PCDDs and PCDFs was done using EPA method 1613 standard solutions (EPA-1613LCS, EPA-1613CS0.5, EPA-1613CS1, EPA-1613CS2, EPA-1613CS3), that were supplied by Wellington Laboratories. The native PCDDs and PCDFs analysed in the samples can be found in Table S2 of the supplementary material. Finally, calibration for quantification dioxin-like PCBs was done WP-CVS standard solutions (WP-CS1, WP-CS2, WP-CS3 and WP-CS4), that were supplied by Wellington Laboratories. The native dioxin-like PCBs analysed in the samples can be found in Table S3 of the supplementary material.

## 3. Results and discussion

### 3.1. PAHs elimination

For this work, the 16 priority PAHs were tested based on toxicity, as stipulated by the World Health Organisation (World Health Organization, 2021). The recoveries of the PAHs deuterated congeners standards were used as a control measure. In all cases, the recoveries were within the permitted ranges of the EPA methods: 50–140% (EPA, 2018), and duplicates were made of the control sample and some of the intermediate samples (NS-PEG 120, SB-WE 5–120, and SB-WE 20–120).

Fig. 1 shows the results for the sum of PAH concentrations for the different treatments, which were calculated as ng of compound per g of analysed sample (ng/g). In addition, Figs. 2 and S3 in the supplementary material show PAHs profile concentrations after the different treatments and the percentages of PAHs reduction with respect to the control sample analysed, respectively.

#### 3.1.1. PAHs extraction with polyethylene glycol

As mentioned above, the 16 priority PAHs were analysed across a total of 4 post-consumer LDPE sample fractions with the different treatments. In addition, a control sample was analysed to determine the efficiency of the different treatments listed in Table 1. The concentrations of all residual congeners in the plastic after treatments obtained for the different samples are shown in Fig. 2.

As illustrated in Fig. S3 in the supplementary material, all the congeners concentrations obtained were lower than the control sample concentrations. This means that the treatments significantly reduced these pollutants. For example, pyrene, the most abundant compound in the control sample, was reduced by 54% and 95% following the NS-PEG 120 and S-PEG 120 treatments, respectively.

The sum of the PAHs concentrations found for each sample was considered in order to appreciate the overall efficiency of each treatment. These results are presented in Fig. 1. After applying the different treatments, as mentioned earlier, the sum of the concentrations of the 16 priority PAHs was lower than the contaminated control sample across all the treatments applied.

Comparing the effect of agitation on the extraction process, we found that the total concentration obtained was 169 ng total/g sample (S-PEG 120) for the agitated process, and 599 ng total/g sample (NS-PEG 120) for the non-stirred process. Worthy of note, at the same temperature (120 °C), the process improved by approximately 70% when agitation was included in the treatment. Another effect to compare in the pollutant removal process was temperature. Indeed, as temperature increases, the removal of polycyclic aromatic hydrocarbons also increases. An increase in temperature of 20 °C improved the removal process by 13%, from 313 ng total/g sample (S-PEG 70) to 272 ng total/g sample (S-PEG 90), while a more significant increase in temperature (50 °C) improved the process by 46%, from 313 ng total/g sample (S-PEG 70) to 169 ng total/g sample (S-PEG 120).

Therefore, the agitated polyethylene glycol extraction process at 120 °C (see Fig. 2) presented the highest removal value and a



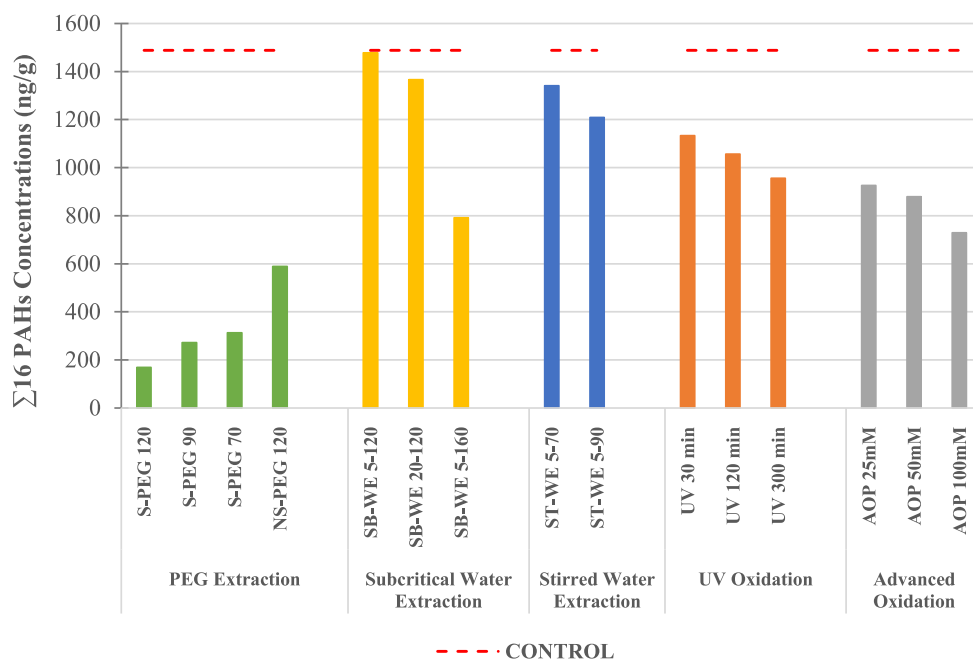


Fig. 1. Sum of PAHs concentrations (ng of compound per g of sample) for the applied treatments and for the control sample.

contamination reduction of 89% compared to the control sample. The concentration value obtained was compared with results in the literature and was determined to be lower than most of the food contact polystyrene samples analysed by Li et al. (2017). We also compared the values of PAHs concentrations reported by Núñez et al. (2022) in recycled LDPE samples and found that all treatments, except extraction without agitation, were even lower than the PAHs concentrations encountered in virgin LDPE (413 ng total/g sample). Cabanes et al. (2021) found a 74% reduction of VOCs by means of polyethylene glycol extraction, a value close to the 89% obtained in this work for the removal of PAHs.

### 3.1.2. PAHs extraction in alkaline medium with subcritical water and with stirred water

Regarding the extraction with subcritical water, a total of 3 runs were performed: two runs at 120 °C, varying the NaOH concentration used (5% and 20% by weight), and one experiment at 160 °C, with a NaOH concentration of 5% by weight.

All the results discussed below are presented in Figs. 1, 2 and S3 in the supplementary material. The sum of the concentrations obtained for the 120 °C treatments showed very little variation with respect to the control sample. In the case of the 5% NaOH concentration, a decrease in contamination of less than 1% was observed (SB-WE 5–120). However, increasing the NaOH concentration to 20% by weight at the same temperature (SB-WE 20–120) resulted in a 9% contamination reduction, thus showing that efficiency improved with increasing NaOH concentration levels. With respect to the subcritical extraction at 160 °C and 5% NaOH by weight (SB-WE 5–160), PAHs concentration dropped by about half (47%). This shows that subcritical extraction improves with increasing temperature, but the temperature should not be increased to above 160 °C to prevent the plastic from melting.

Comparing the reduction of PAHs in the literature using this technique, similar results to those of Islam et al. (2012) were obtained. The latter achieved pyrene reductions of 47% when applying the subcritical extraction technique to contaminated soil samples at 150 °C, which in this case was the most abundant polycyclic aromatic hydrocarbon in the samples analysed.

Finally, conventional washing with hot water (70 °C and 90 °C) was performed on the plastic samples, but this washing was carried out in an

alkaline medium, using a NaOH concentration of 5% by weight. The results obtained for the experiment at 70 °C (ST-WE 70) showed a 9% PAHs reduction, while a temperature increase of 20 °C (ST-WE 90) resulted in a 19% drop in PAHs concentration. This could be interesting regarding its possible application, because the process can be performed at atmospheric pressure. It should be noted that extraction with stirred water at 90 °C and 70 °C (ST-WE 90 and ST-WE 70) is more advantageous than extraction with subcritical water at 120 °C (SB-WE 5–120 and SB-WE 20–120). Indeed, the agitation of the 90 °C and 70 °C processes facilitates contaminant extraction, so it would be of interest to perform extractions with subcritical water using agitation.

### 3.1.3. PAHs advanced oxidation (UV/UV-H<sub>2</sub>O<sub>2</sub> treatments)

PAHs oxidation by ultraviolet radiation was performed for three sample fractions varying the exposure time (UV 30 min, UV 120 min, and UV 300 min). The advanced oxidation was also performed for three samples, in this case, for a fixed time of 120 min, and varying the hydrogen peroxide concentration, using 25 mM (AOP 25 mM), 50 mM (AOP 50 mM), and 100 mM (AOP 100 mM). The results of these experiments are shown in Figs. 1 and 2 (more information is given in Fig. S3 in the supplementary material).

The ultraviolet radiation method of PAHs oxidation was applied for 30 min, 120 min, and 300 min, resulting in PAH reductions of 24%, 29% and 36%, respectively, and demonstrating that the longer the plastic was exposed to ultraviolet radiation, the higher the percentage of contaminant removal. The presence of H<sub>2</sub>O<sub>2</sub> in the advanced oxidation process significantly increased the percentages of PAHs removal. The duration of the experiments corresponding to the concentrations above was 120 min. The achieved PAHs reduction percentages were 38% for a concentration of 25 mM, 41% for a concentration of 50 mM, and 51% for a concentration of 100 mM.

Comparing the 120-minute UV oxidation process with the advanced oxidation process at a concentration of 100 mM H<sub>2</sub>O<sub>2</sub>, the process efficiency was found to increase by 31%. The latter showed that PAH contamination was reduced by increasing the UV exposure time as well as by increasing the hydrogen peroxide concentration.

A number of authors have studied the effectiveness and degradation mechanisms of some PAHs. Examples include phenanthrene and pyrene for the UV/H<sub>2</sub>O<sub>2</sub> system (An and Carraway, 2002) and Tan et al. (2013),

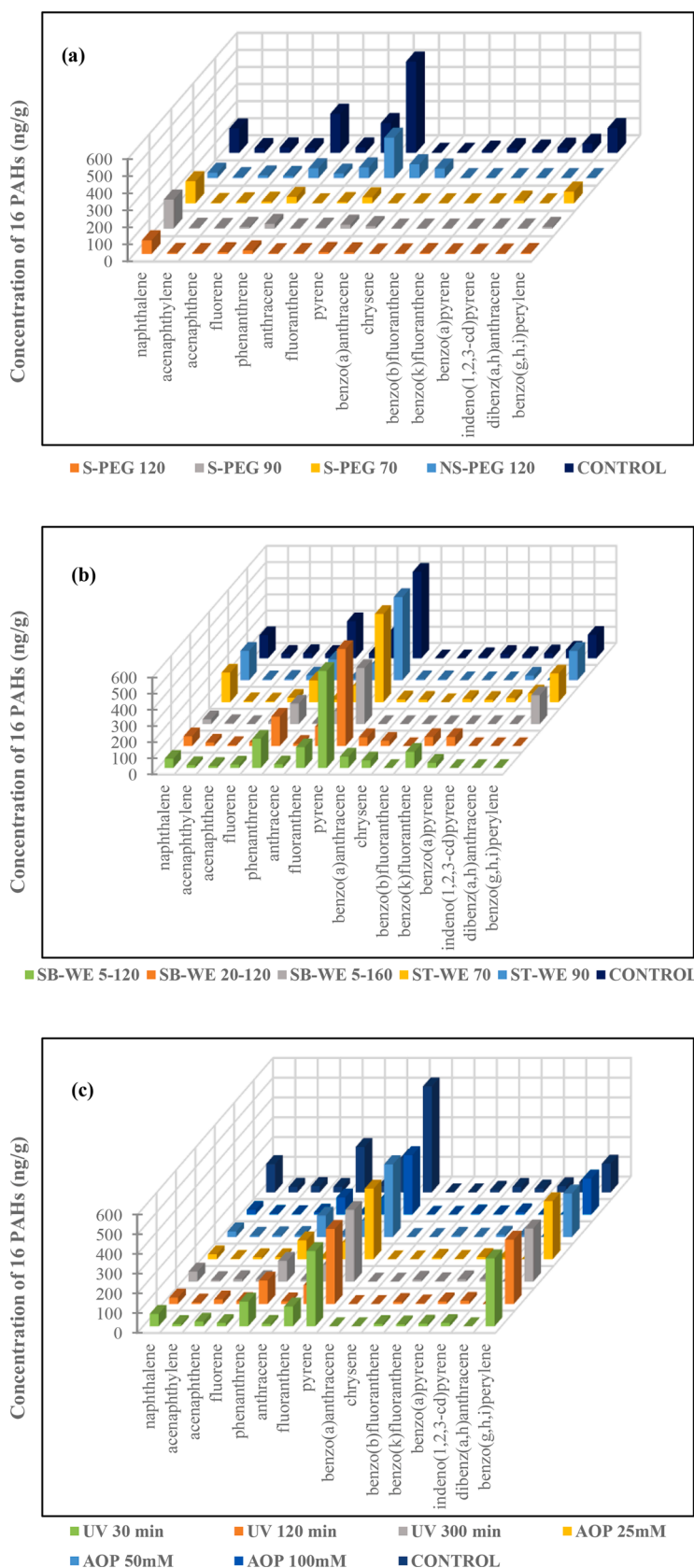


Fig. 2. PAHs reduction concentrations (ng of compound per g of sample) for the different treatments. (a) PEG extraction, (b) subcritical and stirred water extraction, and (c) UV/H<sub>2</sub>O<sub>2</sub> oxidation.

who demonstrated that the UV/H<sub>2</sub>O<sub>2</sub> system is more efficient for organic compound degradation than the UV system.

### 3.2. PCDD/Fs elimination

The same treatments included in Table 1 were applied to determine the concentrations of the different dioxin and furan congeners, based on which the toxicity of each sample was calculated through the toxic equivalency factors provided by the World Health Organisation (World Health Organization, 2010). A control sample was also analysed in order to determine the efficiency of the different treatments listed in Table 1.

As a quality control measure, the recoveries of the <sup>13</sup>C-labelled PCDD/Fs standards were used, all of which were found to be within the ranges allowed by the EPA 1613 method (1994). Further information can be found in Table S7 in the supplementary material. In addition, some of the aforementioned treatments were repeated (Control, NS-PEG 120, SB-WE 5–120, and SB-WE 20–120).

Fig. 3 shows the results for the toxic equivalents of dioxins and furans in the different samples obtained from the treatments applied, and Fig. S4 in the supplementary material shows the percentage reduction in calculated toxic equivalence compared to the control sample after the treatments were applied.

#### 3.2.1. PCDD/Fs extraction with polyethylene glycol

The results of the concentrations of all congeners obtained for the different sample fractions are shown in Fig. S8 in the supplementary material. As expected, as in the case of the PAHs concentrations, the concentrations of all dioxin and furan congeners were lower than the concentrations obtained in the untreated control sample, that it was analysed just after collection.

When analysing dioxins and furans, it is usual practice to represent the toxic equivalents of the different samples in order to assess the risk when there is exposure. It is also useful to represent the concentration profiles to compare them with concentration profiles in different matrices thus allowing to intuit the possible origin of the contamination. The results are discussed on the basis of the calculated equivalent toxicity of each sample and are shown in Fig. 3.

The extraction process with polyethylene glycol without agitation (NS-PEG 120) provided a toxic equivalency reduction of 54%, resulting in 0.53 pg WHO<sub>2005</sub> TEQ/g sample, while the agitated process at the

same temperature (S-PEG 120) led to improving efficiency by 68%, resulting in a toxic equivalent of 0.17 pg WHO<sub>2005</sub> TEQ/g sample. This value is very close to zero and demonstrates the efficiency of the treatment applied.

With respect to the rest of the agitated extraction processes, at 90 °C (S-PEG 90) and 70 °C (S-PEG 70), temperature was observed to influence the pollutant removal process. Indeed, as the temperature decreased, the percentages of pollutant removal declined. No study on the concentration of recycled plastic in terms of dioxins and furans was found in the literature. Nevertheless, a comparison can be made with the limits established by EFSA that apply to certain types of food, such as milk and other dairy products. Their maximum toxicity value allowed is 3 pg WHO<sub>2005</sub>-TEQ/g (Commission Regulation (EC) No 1881/2006, 2006). This supports the technology used in this work. Indeed, the control sample was below this limit and the technology used achieved a toxic equivalency reduction of up to 85%.

Although there is legislation on recycled plastic for food contact that gives some requirements, these are not specific to the types of contaminants studied. Yet recently, in its efforts to ensure an increasing use of recycled plastic in contact with food, the European Union has emphasised the need to develop appropriate technologies to mitigate the presence of contaminants in plastic (European Commission, 2022). In this way, it is worth noting the important role of this study insisting on the presence of unwanted contaminants in recycled plastics and studying possible ways of eliminating these contaminants.

#### 3.2.2. PCDD/Fs extraction in alkaline medium with subcritical water and with stirred water

The dioxins and furans in this section were analysed based on a total of 5 post-consumer LDPE sample fractions subject to different treatments. The results of the concentrations of all congeners obtained for the different samples are shown in Fig. S6 in the supplementary material.

The contaminant removal process using subcritical water in alkaline medium failed to significantly reduce the concentration in the recycled plastic. As is visible in Fig. 3, the best results were obtained for the extraction process at 160 °C (SB-WE 5–160), which reduced the calculated toxic equivalence of the plastic by 26%, reaching a final value of 0.84 pg WHO<sub>2005</sub>-TEQ/g sample.

The processes conducted at 120 °C demonstrate the effect of the sodium hydroxide concentration used, as a 20% reduction difference

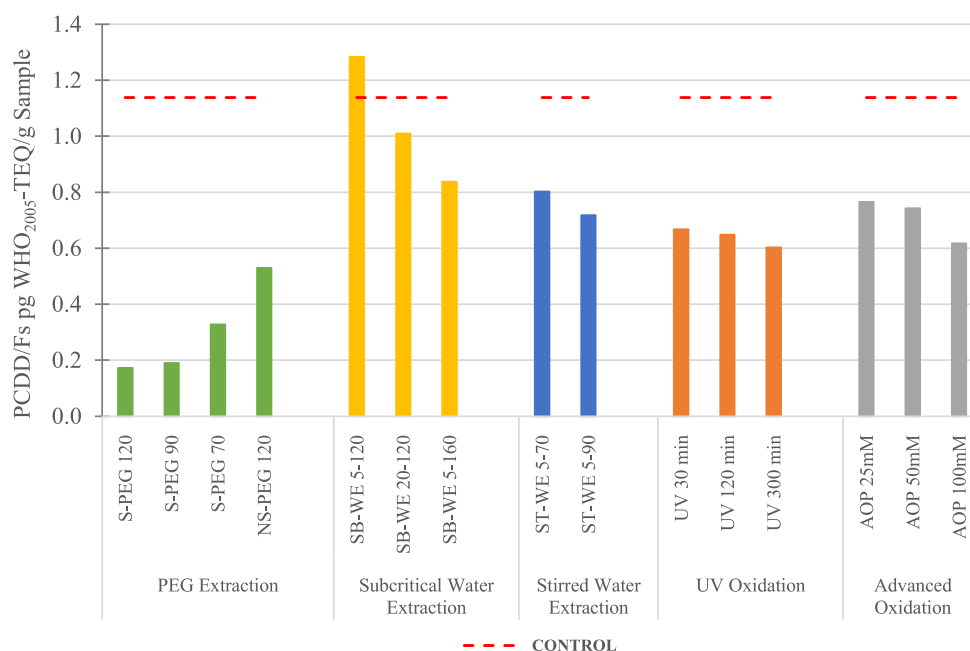


Fig. 3. PCDD/Fs toxic equivalent for the applied treatments and for the control sample.

was obtained after comparing the use of NaOH at 5% (SB-WE 5–120) with NaOH at 20% (SB-WE 20–120). Small differences in this type of analysis, where the analytes are in such a low concentration, may be due to experimental errors or the heterogeneity of the samples used. When the differences are larger, as in the other treatments presented in the present study, it is more likely to be due to the treatment itself and not to these factors.

A number of authors studied the mechanisms of dioxin dechlorination in soils by extraction with subcritical water in a basic medium using NaOH or KOH, obtaining reduction percentages of 66 to 99% depending on the conditions used (Hashimoto et al., 2004). In this case, one factor that may have reduced the treatment decontamination capacity could be temperature, since temperatures lower than 160 °C were applied. In addition, the agitation effect was found to be substantial. In the case of the extraction with agitation in basic medium at 90 °C (ST-WE 5–90), a toxic equivalency reduction of 36% was achieved, while at 70 °C (ST-WE 5–70), a 30% reduction was obtained, which also reveals the key role of temperature in these experiments.

### 3.2.3. PCDD/Fs advanced oxidation (UV/UV-H<sub>2</sub>O<sub>2</sub> treatments)

PCDD/Fs oxidation by ultraviolet was conducted over 3 runs, varying the exposure time (UV 30 min, UV 120 min and UV 300 min). Advanced oxidation was also performed over other 3 runs, in this case for a fixed duration of 120 min and varying the hydrogen peroxide concentration used: 25 mM (AOP 25 mM), 50 mM (AOP 50 mM), and 100 mM (AOP 100 mM). The results are given in Fig. 3 and further information on profile concentrations is presented in Fig. S7 in the supplementary material. Moreover, an additional test was performed in which only the PCDD/Fs labelled standards were subjected to UV radiation for 300 min. The objective was to verify the behaviour of the standards under UV radiation and thus determine the degree of degradation for each congener. To this end, 10 µL of labelled internal standards were placed in 100 µL of nonane, and their recoveries were calculated after 300 min. The recoveries obtained were between 0.4% (<sup>13</sup>C<sub>12</sub>-OCDD) and 70% (<sup>13</sup>C<sub>12</sub>-2,3,7,8-TCDD), leading to a degradation that ranged from 30% to 99.6%. These results are presented in Fig. S8 in the supplementary material.

Photodegradation varied little compared to the advanced oxidation process as in the case of polycyclic aromatic hydrocarbons. Indeed, a 33% toxicity reduction was found for the 120-minute UV exposure treatment with a concentration of 50 mM H<sub>2</sub>O<sub>2</sub> (AOP 50 mM), and 47% in the case of a 300-minute UV exposure process (UV 300 min). Visibly,

both the increase in exposure time and H<sub>2</sub>O<sub>2</sub> concentration in the process led to a larger drop in the concentration of contaminants in the sample.

Baron et al. (2005) succeeded at reducing the toxic equivalence in fishmeal from 2.80 ng WHO-TEQ/kg, to 0.80 ng WHO-TEQ/kg, but applying an ultraviolet exposure time of 10 days, which in the case of the target matrix in this study (post-consumer recycled LDPE) could entail matrix degradation.

### 3.3. Dioxin-like PCBs results

The treatments applied to determine the concentrations of the different dioxin-like PCBs are indicated in Table 1. The toxicity of each sample fraction was determined by applying the toxic equivalency factors provided by the World Health Organisation (World Health Organization, 2010).

As a quality control measure, the recoveries of the <sup>13</sup>C-labelled dioxin-like PCBs standards were used, all of which were found to be within the ranges allowed by the EPA 1668 method (EPA, 2008). Further information is given in Table S5 in the supplementary material. Duplicates of some samples were also made (Control, NS-PEG 120, SB-WE 5–120, and SB-WE 20–120).

The results obtained for the toxic equivalents of dioxin-like PCBs in the different treatments applied are presented in Fig. 4.

#### 3.3.1. Dioxin-like PCBs extraction with polyethylene glycol

As for other pollutants, the dioxin-like PCBs were analysed based on a total of 4 post-consumer LDPE sample fractions that were subjected to the different treatments and the control sample (treatments are listed in Table 1). The obtained concentrations of all congeners for the different samples are listed in Fig. S9 in the supplementary material. As in the case of PAHs and PCDD/Fs, and as expected, the concentrations of all dioxin-like PCBs congeners were lower than the concentrations obtained in the untreated control sample. The dioxin-like PCBs results are discussed in Fig. 4 as in the case of dioxins and furans.

The extraction process with polyethylene glycol without agitation (NS-PEG 120) led to a toxic equivalence reduction of 73%, resulting in 0.19 pg WHO<sub>2005</sub> TEQ/g sample, while the agitated process at the same temperature (S-PEG 120) resulted in a 92% reduction (0.06 pg WHO<sub>2005</sub> TEQ/g sample), representing 68% more efficiency. The intermediate processes led to a 94% reduction for S-PEG 90 (0.04 pg WHO<sub>2005</sub> TEQ/g sample) and 80% for S-PEG 70 (0.19 pg WHO<sub>2005</sub> TEQ/g sample).

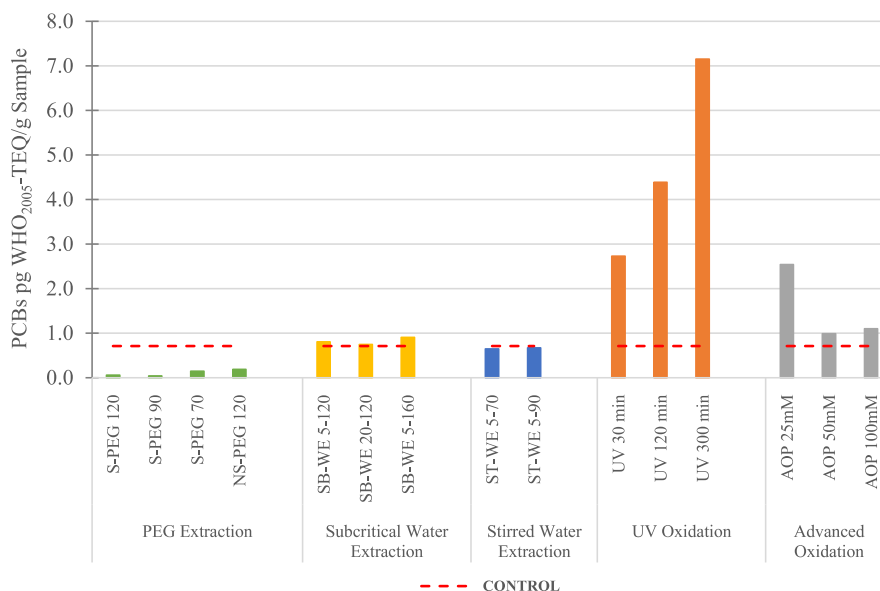


Fig. 4. Dioxin-like PCBs toxic equivalent for the applied treatments and for the control sample.



If two experiments are compared: S-PEG 120 and S-PEG 90 it is observed that the lower temperature resulted in a higher reduction in concentration, which may seem contradictory, since as mentioned above the higher the temperature applied the higher the percentage of removal. One possible explanation for this phenomenon has to do with diffusion, which depends on several factors and one of them is the concentration, since the lower the concentration, the more difficult it is for the contaminants to diffuse into the extractant solvent and this makes them more difficult to eliminate and small deviations may appear, as in this case.

Regarding PCDD/Fs, no study was found in the literature on the concentration of dioxin-like PCBs in recycled plastic. However, there are limits established by EFSA in food materials for certain types of food such as milk and other dairy products, whose maximum toxicity value allowed is 3 pg WHO<sub>2005</sub>-TEQ/g (Commission Regulation (EC) No 1881/2006, 2006) (which is the same limit set for the toxicity of PCDD/Fs). Although this value is not comparable with the values found in plastic, it could give an idea if the migration capacity of these compounds from plastic were known. Again, the concentration of contaminants was lower than in the control sample and the best treatment (S-PEG 90) achieved a 94% reduction in toxic equivalence.

### 3.3.2. Dioxin-like PCBs extraction in alkaline medium with subcritical water and with stirred water

The dioxin-like PCBs for this section were analysed based on a total of 5 post-consumer LDPE sample fractions subject to the different treatments listed in Table 1. The result of the concentrations obtained of all congeners for the different samples is shown in Fig. S10 in the supplementary material.

The contaminant removal process using subcritical water in alkaline medium failed to significantly reduce the concentration of contaminants in recycled plastic. As visible in Fig. 4, the best results were obtained for the extraction stirred process at 70 °C (ST-WE 5–70), which reduced the plastic toxic equivalence by only 8%, reaching a final value of 0.65 pg WHO<sub>2005</sub>-TEQ/g sample, and 6% for the stirred process at 90 °C (ST-WE 5–90) reaching a final value of 0.67 pg WHO<sub>2005</sub>-TEQ/g sample.

Liu et al. (2015) studied the thermal decomposition (300 °C - 600 °C) of dioxin-like PCBs in soils in alkaline media, using different NaOH concentrations (0.1% - 1%). Under these study conditions, Liu et al. achieved 40% dioxin-like PCBs reductions at 300 °C, and 98% reductions at 600 °C. These results illustrate the substantial effect of temperature on PCBs degradation in basic media. They also show that

clearly, the temperatures used in this study (due to plastic degradation issues) were not high enough to destroy dioxin-like PCBs.

### 3.3.3. Dioxin like-PCBs advanced oxidation (UV/UV-H<sub>2</sub>O<sub>2</sub> treatments)

As shown in Fig. 5, the results obtained for dioxin-like PCBs for UV oxidation and advanced oxidation treatments were unexpected because sample toxic equivalence increased in all cases for all treatments applied. This result was highly surprising, and even more so given the effective reduction in PCDD/Fs observed before. For this reason, an additional test was performed subjecting only the <sup>13</sup>C-labelled dioxin-like PCBs to ultraviolet radiation for 300 min. To this end, 10µL of labelled internal standards were placed in 100µL of nonane, and after 300 min of exposure, their recoveries were calculated and the degradation produced for each congener was determined. The results are presented in Fig. 5.

As can be seen in Fig. 5, after an exposure time of 300 min under ultraviolet radiation, all the recoveries of the mono-ortho PCBs were practically nil, which implies that they were degraded under these conditions. However, for the non-ortho PCBs (PCB 81, PCB 77, PCB 126 and PCB 169) recoveries, a value above 100% was obtained. This implies that these compounds formed during UV exposure, especially PCB 126, the compound with the highest toxic equivalency factor, whose recovery was exactly 281%.

Based on these results, we consulted the literature on the exposure of PCBs to ultraviolet rays. We found that other authors had already explained this phenomenon and proposed pathways for the formation of these PCBs through the degradation of mono-ortho PCBs. For example, Baron et al. (2005) analysed PCBs in fishmeal samples and subsequently exposed them to ultraviolet radiation for 5 days. The result was that all mono-ortho PCB concentrations decreased by between 2% (PCB 189) and 12% (PCB 118), while for non-ortho PCBs, the concentrations increased by between 128% (PCB 169) and 713% (PCB 77). This resulted in an increase in the toxic equivalence of the sample from 3.63 ng TEQ/kg to 10.8 ng TEQ/kg.

A similar occurrence was found in the present work. When analysing the treated LDPE samples, the total TEQ for non-ortho PCBs increased after the exposure of the LDPE to UV radiation, varying between 3.8 pg WHO<sub>2005</sub>-TEQ/g (UV 30 min) and 10.1 pg WHO<sub>2005</sub>-TEQ/g (UV 300 min), leading to an increase of the most toxic congeners. The addition of H<sub>2</sub>O<sub>2</sub> in the UV oxidation process decreased this effect to a certain extent by more than halving the final toxic equivalence of the samples, 3.6 pg WHO<sub>2005</sub>-TEQ/g for a concentration of 25 mM H<sub>2</sub>O<sub>2</sub> (AOP 25 mM), 1.4

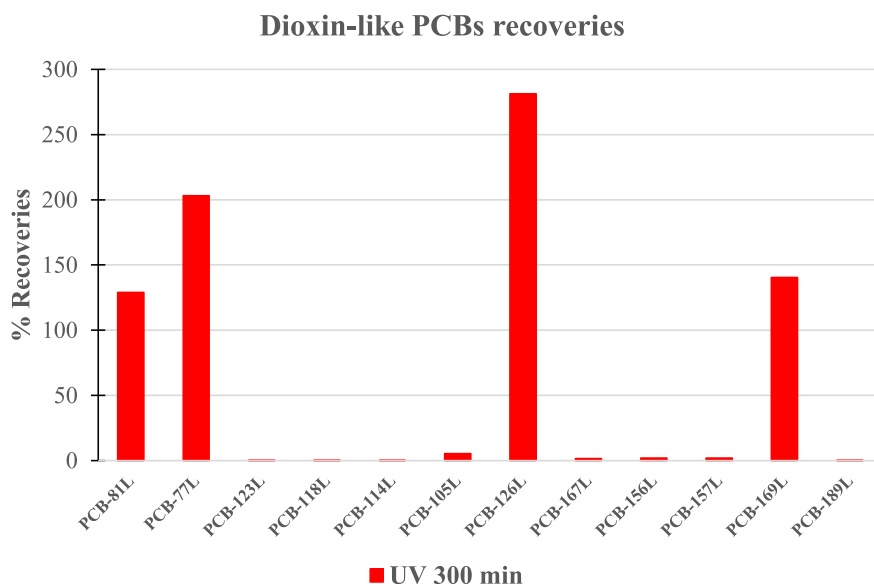


Fig. 5. Recoveries of dioxin-like PCBs after 300 min of UV exposure.

pg WHO<sub>2005</sub>-TEQ/g for a concentration of 50 mM H<sub>2</sub>O<sub>2</sub> (AOP 50 mM), and 1.5 pg WHO<sub>2005</sub>-TEQ/g for 100 mM H<sub>2</sub>O<sub>2</sub> (AOP 100 Mm). They were still higher, nevertheless, than in the control sample.

#### 4. Conclusions

The aim of this work was to determine a suitable treatment capable of eliminating hazardous contaminants (PAHs, PCDDs, PCDFs and dioxin-like PCBs) in recycled plastics (in this case for post-consumer LDPE). Various decontamination treatments were tested: stirred polyethylene glycol extraction at different temperatures (120 °C, 90 °C and 70 °C) and non-stirred polyethylene glycol extraction at 120 °C, subcritical water extraction in alkaline medium at 120 °C y 160 °C, stirred water extraction in alkaline medium at 90 °C and 70 °C, UV oxidation at different time (30 min, 120 min and 300 min), and finally, advanced UV oxidation (120 min) with different concentration of H<sub>2</sub>O<sub>2</sub> (25 mM, 50 mM, and 100 mM), and the reduction of contaminants as well as their potential to release them were quantified before and after each treatment.

It was demonstrated that some treatments are capable of reducing the levels of highly dangerous contaminants determined by the World Health Organisation, such as PAHs, PCDD/Fs and dioxin-like PCBs. The latter should not be present in recycled plastic, especially if destined to be in contact with food. In this study, a total of 15 treatments were studied under different conditions. The most effective treatment was extraction with polyethylene glycol stirred at 120 °C. It presented notable contamination reduction data for all the above-mentioned compounds: 89% reduction in the total amount of PAHs; 85% reduction in toxic equivalence by removing dioxins and furans; and 94% for removing dioxin-like PCBs from the plastic samples. These contamination values after application of the treatments were lower than some limits that have been established for products for human consumption. Therefore, even if they were able to migrate into food, they would still not be a danger to human health.

Another important finding was that not all treatments were equally effective. In the case of dioxins and furans, the treatments applied using ultraviolet radiation achieved a maximum decontamination reduction of 47%. The process would thus appear of interest, but when analysing the calculated toxic equivalency of dioxin-like PCBs under these same conditions, it was found that in the treated sample the value was 14 times higher than in the original control sample. This highlights the importance of performing a complete decontamination study, considering all types of contaminants and not only the most toxic, which in the case of this study were dioxins and furans.

Regarding subcritical water treatment, only treatment SB-WE 5–160 showed effectiveness in reducing PAHs and PCDD/Fs (46% and 26% respectively), but was unable to decrease the concentration of dioxin-like PCBs. Hot water treatment ST-WE 5–90 was effective in reducing the concentration of PAHs (19%) and PCDD/Fs (36%), but also ineffective in reducing PCBs. ST-WE 5–70 showed reductions, but to a lesser extent than ST-WE 5–90.

To conclude, to meet the European Union objective of increasing the amount of recycled plastic, it is important to create legislation establishing the maximum levels of permitted contamination in post-consumer recycled plastics such as LDPE. Indeed, it is clear that these types of plastics can be decontaminated.

#### CRedit authorship contribution statement

**Samuel S. Núñez:** Methodology, Writing – original draft, Data curation, Investigation, Formal analysis. **Juan A. Conesa:** Conceptualization, Funding acquisition, Project administration, Supervision, Writing – review & editing. **Julia Moltó:** Project administration, Supervision, Writing – review & editing, Formal analysis. **Andrés Fullana:** Funding acquisition, Project administration, Supervision.

#### Declaration of Competing Interest

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

#### Data availability

No data was used for the research described in the article.

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#### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.resconrec.2023.107017.

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